

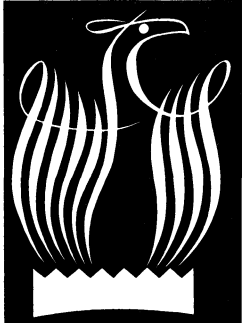
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**MICHIGAN MEMORIAL PHOENIX PROJECT
PHOENIX MEMORIAL LABORATORY
THE UNIVERSITY OF MICHIGAN**

**GASEOUS REACTIONS OF METHANE AND VARIOUS POLYHALOMETHANES
WITH BROMINE AND IODINE
ACTIVATED BY THE (n, γ) PROCESS**

A THESIS BY EDWARD P. RACK



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WITH BROMINE AND IODINE ACTIVATED BY THE (n,γ) PROCESS

by
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A dissertation submitted in partial fulfillment
of the requirements for the degree of
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Chapter I. INTRODUCTION

Definition of "Hot Atom" Chemistry

"Hot atom" chemistry is the study of chemical reactions activated by nuclear transformations. There are various types of nuclear transformations such as (p,n) , (γ,n) , (n,p) , and $(n,2n)$ which can be, and are, used to produce hot atoms.* A frequently used activation process is radiative neutron capture [(n,γ) process] employing a nuclear reactor or a portable neutron source. According to Willard,¹ the frequent use of this process "...is due to the relative availability of neutrons; the relative ease of using them under conditions where radiation damage and temperature effects are not serious; favorable capture cross sections for the (n,γ) process; and the fact that the (n,γ) process is capable of producing a number of radioactive species with chemical properties which are particularly suitable for studies of this type." The nuclear activation method employed in this thesis research is the (n,γ) process, and any discussion of nuclear transformations will specifically refer to this process.

As a consequence of its nucleus absorbing a thermal neutron an atom can acquire a high kinetic energy, a positive charge, and electronic excitation energy. Two requirements which must be met in order to study "hot atom" reactions are:

1. The activated atom must possess a radioactive tag (since the amount of activated atoms produced in a reaction system is smaller than that which can be detected chemically); and
2. There be no thermal exchange between stable molecules in the

* Even though a "hot atom" may be a positively charged ion, the term "hot atom" will refer to all activated atoms, irrespective of their nature.

system.²

Historical Background

In 1934, Szilard and Chalmers³ irradiated samples of liquid ethyl iodide, containing a trace of iodine, with thermal neutrons from a radium-beryllium source. They observed that a large fraction of the I^{128} atoms appeared in a form which could be extracted by aqueous solvent extraction, showing that, as a result of a special activation, the atoms acquired enough energy to break their chemical bonds.

Since 1934, there have been over 150 papers in "hot atom" chemistry. Two excellent review articles by Willard^{1,4} survey the field through 1955.

Because of the simple chemical properties of the hydrocarbons and alkyl halides and favorable nuclear properties of tritium and the halogens, their chemical reactions have been most extensively studied.

Although there have been various theories presented for explaining condensed state reactions -- such as the oversimplified "billiard-ball collision" hypothesis^{5,6,7} introduced by Libby, and the "random fragmentation"¹ hypothesis of Willard which treats the condensed states realistically, but unfortunately too qualitatively -- there is at the present time no good theory which explains the mechanisms of condensed state reactions. It is, therefore, unfortunate that most of the early work was with systems in the condensed states rather than with the simpler gaseous systems.

In 1952, Willard and his co-workers observed a unique reaction occurring between I^{128} , activated by radiative neutron capture,⁸ and CH_4 in the gaseous state. They found that about 50 percent of the I^{128} entered organic combination as CH_3I in what must be a one-step displacement reaction ($I + CH_4 \rightarrow CH_3I + H$) compared to the two-step abstraction reactions encountered in photochemical studies. These authors suggested that

the reaction proceeded directly or indirectly as a result of the positive charge on the iodine atom.

In order to determine the relative importance of charge and kinetic energy in the $I^{128} + CH_4$ reaction, Willard and Levey studied the moderation of the reaction by additives having ionization potentials higher and lower than that of the iodine atom. The authors suggest⁹ that the "...reaction of the I^{128} with CH_4 can only occur when the I^{128} is positively charged and has kinetic energy in excess of a minimum which appears to be in the range between 2 and 20 ev."

Gordus and Willard¹⁰ found that 18% of the Br^{80} activated by the (n,γ) process can undergo a displacement reaction with CH_4 in the gaseous state. These workers found that a trace of halogen, acting as a radical scavenger, must be present in the gaseous reaction systems in order to minimize radiation damage produced by the gamma radiation in a nuclear reactor.

If the positive charge is responsible for the reactivity of the Br, then different extents of reaction with CH_4 would be expected for (n,γ) activated Br^{80} , Br^{80m} , and Br^{82} since a minimum of 18, 12, and 25% respectively¹¹ of these isotopes are positively charged. In order to ascertain the relative importance of charge and kinetic energy on Br reactions, Willard and his co-workers¹² found that in gaseous mixtures of Br_2 and C_6H_5Br , C_6H_6 , or $n-C_3H_7Br$ the percent organic activity was the same for the three isotopes. The lack of an isotope effect in these experiments could be due to the fact that the ionization potential of the main component of each system is less than that of Br. However, a single experiment¹⁰ indicated that the extent of reactions (organic yields) of Br^{80} , Br^{80m} , and Br^{82} with CH_4 were identical, within experimental error.

Estrup and Wolfgang¹³ developed a mathematical model to describe the kinetics of hot atom reactions in the gas phase based partially on the mathematics of neutron cooling. They have applied it successfully to explain the inert gas moderation of the $H^3 + CH_4$ reaction.

Nuclear Activation

When a nucleus absorbs a thermal neutron, a compound nucleus is formed which possesses an excess energy equivalent to the neutron binding energy of the nucleus. This energy can be emitted by the nucleus in the form of one gamma ray or as a cascade of gamma rays. For example, when an I^{127} nucleus absorbs a neutron, the binding energy, 6.6 mev,¹⁴ if released in the form of a single gamma ray of 6.6 mev energy, would impart to the I^{128} nucleus an energy of $E = (537B^2)/128 = 182$ ev, where B is the energy in mev of the gamma ray and 128 is the mass in a.m.u. There is evidence which indicates that, on the average, more than one gamma ray is emitted by the nucleus. As a result of such multi-gamma emissions a single nucleus will acquire an amount of energy which will depend on the energies of the gamma rays and on the relative angles of emission.

The two isotopes whose chemical reactions are the subject of this thesis are I^{128} and Br^{80} . Unfortunately, because of the complex structure of the $I^{127}(n,\gamma)I^{128}$ spectrum, little information has been obtained regarding the neutron capture gamma ray decay scheme. A gross spectrum has been obtained for the bromine isotopes¹⁵ with peaks at 3.2, 5.3, 6.3, 7.3 and 8.0 mev. Measurements by Muehlhause¹⁶ show that an average of 3.4 gamma ray quanta are emitted per neutron absorbed. However, for this research, interest lay in the decay scheme of $Br^{79}(n,\gamma)Br^{80}$ reaction and not that of all the bromine isotopes. Studies of separated isotopes are rather beyond present techniques. Although there is a lack of ra-

diative neutron capture gamma ray decay scheme data for the halogens, there is no such lack of mathematical models which can be used to determine the recoil energy spectrum of the recoil atom when more than one gamma ray is involved.^{17,18,19} Because of the partial or total cancellation of recoil momentum when more than one gamma ray is emitted it would be expected that a certain fraction of the recoil atoms would acquire insufficient energy to break their chemical bond, i.e., Br⁸⁰ from CH₃-Br. Gordus²⁰ has measured the "failure to bond-rupture" for Cl³⁸, Br⁸⁰, and I¹²⁸ from various organic alkyl halides. For example, 0.33% of the Br⁸⁰ fail to break their bond in C₂H₅Br, while 1.05% of the I¹²⁸ fail to break their bond in CH₃I.

Positive Charge and Electronic Excitation Energy

A recoil atom can acquire a positive charge and electronic excitation energy as a result of internal conversion of the neutron capture gammas and the emission of Auger electrons. Wexler and Davies¹¹ have found that a minimum of 18% of the Br⁸⁰, 12% of the Br^{80m}, 25% of the Br⁸², and 50% of the I¹²⁸ become positively charged, resulting from internal conversion and Auger-electron emission. No evidence has been found concerning the extent of electronic excitation of the atoms. However, in view of the violent electronic rearrangements in the atom after internal conversion, it would be expected that some, if not all, of the atoms are born electronically excited.

Listed in Table I are the various nuclear activation properties of bromine and iodine isotopes.

Final Chemical Stabilization

After a hot atom is born with its high kinetic energy, positive

Table I. Nuclear Activation Properties of Bromine and Iodine Isotopes

Nuclear Activation Process	(n,γ) Thermal Neutron ²¹ Cross Section (Barns)	Neutron Binding Energy of Product Nucleus (mev) ^a	Half Life of Activated Nucleus	Positive Charge of Activated Atoms (Minimum values) ¹¹
Br ⁷⁹ (n,γ)Br ⁸⁰	8.5	7.3 ¹⁴	17.4 min. ²²	18%
Br ⁷⁹ (n,γ)Br ^{80m}	2.9	7.5 ^b	4.5 hr. ²³	12%
Br ⁸¹ (n,γ)Br ⁸²	3.5	7.0 ^b	35.87hr. ²⁴	25%
I ¹²⁷ (n,γ)I ¹²⁸	6.3	6.58 ¹⁴	25.0 min. ²⁵	50%

^a The maximum kinetic energy available to an unbound "hot atom" can be calculated from the relationship $E = \frac{537 B^2}{M}$, where B is the neutron binding energy, or the energy of the largest gamma ray emitted by the (n,γ) process, and M is the mass in a.m.u. of the activated atoms.

^b Calculated from nuclear masses and disintegration energies. For example the neutron binding energy of Br⁸² is equal to $\frac{\text{mass Br}^{81} + \text{mass neutron} - \text{mass Kr}^{82}}{931.16} - 3.092$ mev (disintegration energy of Br⁸²). The necessary data were found in reference 14.

charge, and electronic excitation energy it can undergo chemical reactions after losing most of its excess kinetic energy (chemical bond strengths are 2-6 ev, whereas hot atoms may have several hundred ev kinetic energy). Here interest is in the reactions of I^{128} and Br^{80} with the alkanes and various polyhaloalkanes. Two types of data which have proven valuable in recoil atom studies in organic media are (1) the organic yield and (2) the organic product distribution.

Organic Yield Concept.

The organic yield is a measure of the percent or fraction of the hot atoms created by the nuclear activation process which become stabilized in organic combination. The organic yield is used extensively as a research tool because of the ease with which it can be determined experimentally.

Organic Product Distribution.

Recoil atoms, by nature of their activation, can react with organic molecules forming both inorganic and organic products. Because of the presence of a halogen scavenger in the reaction system, rapid thermal exchange between the inorganic products, and the inability to detect the inorganic halogen products by gas chromatography, or by any other means, concern is with determining the organic products of the "hot atom" reactions, mostly.

Evans²⁶ was the first to demonstrate the applicability of gas chromatography in determining the organic product distribution of recoil-atom reactions.

Statement of Problem

Although the organic yield and the organic product distribution may show trends in reactions in a series of compounds, they do not, by themselves, suggest possible mechanisms for the reaction and the relative importance of kinetic energy, charge, and electronic excitation energy on recoil atom reactions.

Willard and Levey's attempt at determining the mechanism for the $I^{128} + CH_4$ reaction by employing the moderation technique (determining the influence of various additives on the reaction) did not suggest a reaction mechanism for the following reasons:

1. In many of the reaction systems no halogen scavenger (for radicals produced by radiation damage) was present, invalidating the results;
2. The error spread in the data was quite large; and
3. The technique of employing additives -- having an ionization potential lower than I compared to inert-gas additives having an ionization potential higher than I -- to ascertain the relative importance of kinetic energy and charge is not entirely valid for reasons discussed in Chapter III.

Previous attempts¹⁰ to determine the importance of charge on the $Br + CH_4$ reaction produced negative results.

The main purposes of this thesis research were to:

1. Determine the mechanism for the I^{128} and Br^{80} reactions with CH_4 activated by radiative neutron capture;
2. Ascertain the relative importance of kinetic energy, positive charge, and electronic excitation energy of the recoil atom in the reactions; and

3. Determine the relative importance of mass, reaction energy, ionization potential, and steric factors of the target molecule in the reactions with the recoil atom.

Chapter II. EXPERIMENTAL

Chemicals used in the Research

Listed below are all the chemicals which have been used throughout all phases of the research, with name of manufacturer, purification procedure, if employed, and mass spectroscopic analysis (if performed by the researcher).

Br ₂	Prepared by reaction between stoichiometric amounts of K ₂ Cr ₂ O ₇ , KBr and H ₂ SO ₄ in an all glass assembly, using standard tapered joints. The Br ₂ was dried over P ₂ O ₅ , employing vacuum line techniques and stored in a ground glass-stoppered bottle.
I ₂	A finely ground mixture of Baker reagent I ₂ , CaO and KI was placed in a porcelain dish and heated (subliming the I ₂); the I ₂ was collected on a cold surface placed above the porcelain dish, and stored in a ground glass-stoppered bottle.
H ₂ SO ₄	du Pont, reagent grade.
HNO ₃	Baker and Adamson, reagent grade.
CaCl ₂	Mallinckrodt, anhydrous, reagent grade.
CaO	Baker and Adamson, reagent grade.
NaOH	Merck, reagent grade.
Na ₂ CO ₃	Baker and Adamson, anhydrous, reagent grade.
Na ₂ SO ₃	Mallinckrodt, anhydrous, reagent grade.
NaNO ₂	Mallinckrodt, reagent grade.
MgSO ₄	Mallinckrodt, anhydrous, reagent grade.
KBr	Baker and Adamson, reagent grade.
KI	Baker and Adamson, reagent grade.

$K_2Cr_2O_7$	Merck, reagent grade.
P_2O_5	Baker and Adamson, anhydrous, reagent grade.
CH_4	Phillips, research grade. 99.65 mole percent purity, small amounts of N_2 and C_2H_6 are usual impurities.
C_2H_6	Phillips, research grade. 99.9 mole percent purity, an extremely small amount of ethylene is usually present.
$n-C_4H_{10}$	Phillips, research grade. 99.99 mole percent purity.
$n-C_5H_{12}$, $n-C_6H_{14}$	Phillips, pure grade. 99 mole percent minimum purity.
C_3H_8	Matheson, instrument grade. 99.5 mole percent minimum purity.
CD_4	Volk, degassed on vacuum line prior to use. Mass spectrometric analysis indicated 0.25% N_2 , 0.29% O_2 , 0.39% CH_4 , and 0.02% Ar impurities.
CF_4	Matheson, analyzed by mass spectrometer, indicating 0.1% O_2 , and 0.2% N_2 impurities.
C_2F_6	du Pont research sample, analysis by mass spectrometer indicated 0.1% N_2 impurity.
CHF_3	Matheson "Genetron 23," analysis by mass spectrometer indicated 0.3% N_2 impurity.
CH_2F_2	du Pont research sample, analysis by mass spectrometer indicated 0.1% N_2 and 1.7% CHF_3 or CF_4 impurities.
CCl_4	Merck, reagent CCl_4 purified by photobrominating, extracting with aqueous sulfite, washing with water, refluxing with 10% NaOH solution, washing with distilled water, drying over $CaCl_2$, and fractionating taking center cut.

CHCl_3	Merck, reagent CHCl_3 purified by stirring with concentrated H_2SO_4 until colorless, washing with Na_2CO_3 solution, washing with water, drying over CaCl_2 , and fractionating taking center cut.
CH_2Cl_2	Eastman Kodak, red label CH_2Cl_2 purified by stirring with concentrated H_2SO_4 until colorless, washing with Na_2CO_3 solution, washing with water, drying over CaCl_2 , and fractionating taking center cut.
CH_3Cl	Matheson. 99.5 mole percent minimum purity.
$\text{C}_2\text{H}_5\text{Br}$	Eastman Kodak, white label, purified by stirring with concentrated H_2SO_4 until colorless, washing with Na_2CO_3 solution, washing with distilled H_2O , drying over CaCl_2 , fractionating taking center cut.
CH_3Br	Matheson. 99.5 mole percent minimum purity.
$\text{C}_3\text{H}_7\text{I}$, $\text{C}_3\text{H}_7\text{I}$	Eastman Kodak, white label, purified by extracting with aqueous sulfite solution, washing with distilled water, drying over CaCl_2 , fractionating taking center cut.
N_2	Airco, Assayed reagent. No reported impurities.
O_2	Matheson, extra dry grade. 99.6 mole percent minimum purity.
NO	Matheson. 99.0 mole percent minimum purity.
NO	Matheson. 99.0 mole percent minimum purity.
He, Ar, Kr	Airco, Assayed reagent. No reported impurities.
Ne	Airco, Assayed reagent. 0.007 mole percent He impurity.
Xe	Airco, Assayed reagent. Mass spectrometer indicates 0.04 mole percent Kr impurity.

Preparation of Reaction Systems

Neutron activated gaseous reactions of I^{128} and Br^{80} with CH_4 and various organic molecules were studied in the presence or absence of molecular and atomic moderators (additives). Vacuum line techniques were used to prepare these systems.

Gaseous Systems

Quartz bulblets, varying in size from 1 to 7 ml., were first washed in distilled water and then heated. They were then attached to the vacuum line by means of pyrex-quartz graded seals. The necks of the quartz bulblets were tapered down by heating in order to facilitate in sealing off the samples after preparing the reaction mixture. After testing for leaks using a tesla coil, the quartz bulblets were evacuated on the vacuum line and gently flamed in order to volatilize any adsorbed substances inside the bulblets. Quartz was used rather than pyrex for several reasons: (1) The neutron induced activity level in quartz is much less than that in glass; and (2) Na^{23} activated in glass could be leached out in the chemical extraction procedure, described later, and affect the radioactivity counting values.

Duplicate samples were prepared on the vacuum line. All samples contained either 0.1 mm I_2 or 2 mm Br_2 , except where noted, in order to serve as a radical scavenger in the system. The I_2 was metered into the bulbs at its vapor pressure at $15^\circ C$ and Br_2 at its vapor pressure at about $-40^\circ C$. In addition to I_2 , these samples contained 0.5 to 2 mm CH_3I , whose pressure was read by a manometer, in order to give a high enough I^{128} count. It was noted that there was a smaller error spread in samples containing the CH_3I . The target compound and the additive were then added to the reaction systems (not necessarily in that order) from tanks connected to

the vacuum line by tygon tubing or from a metering flask present on the vacuum line (pressure was noted by reading the manometer). The actual compound pressure in the system is equal to the difference between the pressure read on the manometer and the previous pressure existing in the quartz bulblet. The quartz bulblets were frozen down with liquid N₂ and sealed off by heating at the thin neck constriction. With additives having appreciable vapor pressures at liquid N₂ temperature, a pressure correction must be made for the amount of gas between the neck of the bulblet and the stopcock leading to the vacuum system. Knowing the compound vapor pressure at liquid N₂ temperature, the volume of the bulblet, and the volume between the neck and stopcock the pressure correction can easily be made. For example, CH₄ has about a 15 mm pressure at liquid N₂ temperature. For a 4 ml quartz bulblet and a 1 ml volume between the neck and the stopcock a pressure of $1/5 \times 15 = 3$ mm must be subtracted from the measured CH₄ pressure. In samples containing gases such as O₂ or Ne, having appreciable vapor pressures at liquid N₂ temperature, larger bulblets were used to minimize the correction.

Samples Containing I₂¹³¹ Tracer

Preparation of I₂¹³¹. I¹³¹, procured from Oak Ridge, is in the iodide state. The technique used to produce I₂¹³¹ from the Oak Ridge activity was oxidation of the iodide ion. 6N HNO₃ and 0.1N NaNO₂ were added to a small separatory funnel containing 2-3 millicuries of Iodide-131 with carrier iodide in distilled water and freshly purified methylene chloride. The tagged I₂ was extracted by the methylene chloride and then passed through a funnel containing anhydrous MgSO₄ over glass wool in order to remove any water. Using vacuum line techniques the methylene chloride was separated from the tagged I₂. Two quartz bulblets were filled with about

0.1 mm I_2^{131} in order to test its purity and activity. From one quartz bulblet, using the extraction and counting techniques discussed later, it was found that less than 0.1% of the I^{131} remained in the $CHCl_3$ phase. The other gas bulblet containing I_2^{131} was irradiated in the reactor, extracted, and counted. It was found, after correcting for the I^{131} activity present, that the I^{128} decayed with its characteristic half life.

Sample preparation. Quartz bulblets of methane with methyl iodide (0.1 mm I_2^{131} + 0.5 mm CH_3I or 17 mm CH_3I) were prepared with no extraordinary precautions. After storing the samples for several days at room temperature and with no particular exclusion of light, it was found that there was an organic pickup of about 1-6% (0.5 mm CH_3I) and 15% (17 mm CH_3I).

Harris and Willard²⁷ studied the photochemical gaseous exchange of CH_3I and I_2 . They found, using I^{131} tracer techniques, an exchange reaction produced by light, whose rate increased with increasing methyl iodide concentration and was not significantly affected by the iodine concentration.

In order to control any possible thermal and photochemical exchange all the samples were prepared in a minimum of light and, if neutron irradiation was not immediately feasible, stored at about $0^\circ C$ in the dark. This technique resulted in a reduction of the pre-irradiation I^{131} organic pickup to 0-1.5%.

I^{131} present in neutron irradiated samples indicates the fraction of the molecular iodine, present as a scavenger, which reacts with radicals produced in the system. Because the amount of I_2 present in a gaseous sample is limited by its small vapor pressure, the possibility exists that in some of the reaction systems radiation damage occurs. The I^{128} organic yield equals the experimentally determined value corrected for

I^{131} organic pickup (I^{128} O.Y. - I^{131} O.Y. = True I^{128} O.Y.). For quantitative results of I^{131} organic pickup as a function of additive pressure or mole fraction, it is necessary to control the iodine pressure in all the samples. In the work reported here it was estimated that there was less than 10% variation in the I_2^{131} pressure.

For the purpose of correcting for radiation damage all the samples were exposed to comparable neutron irradiations.

Neutron Irradiation of Samples

Quartz bulblets containing the reaction systems were packed singularly with Kleenex-type tissues in Lusteroid "rabbits," which consist of two Lusteroid tubes scotch-taped together. The rabbits contained a layer of paraffin melted into the tube ends in order to give weight to the rabbit and to protect the fragile bulblet during its ride in the pneumatic tubes. Because the pneumatic tube system is operated on a vacuum principle in order to prevent radioactive gases escaping from the reactor, rabbits have to weigh at least 20 grams in order that they break the vacuum seal at the exit door.²⁸

The Ford Nuclear Reactor, which is a modified "swimming pool" reactor, was used for all the neutron irradiations when it was operating at a power level of one megawatt (thermal neutron flux within the core about 1×10^{13} neutrons-cm²-sec⁻¹). Pneumatic tube stations PL-1 and PL-4 were used for all the irradiations. The thermal neutron flux was 1.76×10^{12} for station PL-1²⁹ and 2×10^{12} for PL-4*. The gamma-ray flux** was approximately 8000 r/min for both stations.

* Estimated, based on known flux at 100 kv.

** V. Serment, private communication.

The durations of the neutron irradiations were from 2 to 40 seconds (most irradiations being less than 15 seconds). In most of the reaction systems (for this irradiation time range) the organic yields were independent of the duration of the neutron irradiations. However, in some systems, notably I + CH₄ (inert gas and fluorocarbon moderators) reaction mixtures, it was necessary to make an organic-yield correction (see Ch. 5) for radiation-induced reactions produced by the reactor gamma-ray flux. It was necessary to have comparable neutron exposures. Although the neutron flux variation is of the order of 10%, and the possibility exists that the samples will not position themselves identically at the core, these sources of error are not too serious as the magnitude of the radiation damage correction is not very large in general.

After the sample left the reactor it was monitored for beta and gamma radiation. The gamma level at the surface of the rabbit was about 30 mr/hr for a 7 second irradiation. The Lusteroid rabbit was cut open using a small razor-knife. It usually took no longer than 30 seconds for monitoring, opening the Lusteroid rabbit, and removing the quartz bulblet.

Extraction of Organic and Inorganic Activities

Quartz bulblets (gaseous systems) were placed in a wide mouthed, 125 ml separatory funnel, with ungreased stopcock, containing 50 ml of CHCl₃ + trace I₂ and 50 ml 0.5 M Na₂SO₃ solution. The quartz bulblets were broken beneath the chloroform layer by means of a pyrex breaking rod inserted through a glass tube. The separatory funnel was immediately shaken for 30 seconds in order to extract all the inorganic halogen species into the aqueous phase. All of the organically-bound halogens were retained in the chloroform phase. Depending on whether the organic yield was determined using the G-M tube and scaler (when only one halogen activity was present)

or the 100 channel analyzer (when more than one halogen isotope was present) the following techniques were employed.

Samples Prepared for G-M Counting.

After waiting for the two layers to separate, the bottom organic fraction was passed through a small cylindrical funnel, containing anhydrous MgSO_4 over glass wool, into a solution counting jacket, which can be fitted over an Amperex counting tube. The volume of the counting jackets varied from 20 to 35 ml. After pouring out the excess organic phase into a radioactive waste disposal bottle, the aqueous phase was poured, using a funnel containing glass wool, into a similar solution counting jacket. The solutions were now ready for counting.

Samples Prepared for 100 Channel Analysis.

Rather than transfer the organic and aqueous solutions for counting into jackets, the solutions were poured into small beakers or bottles from which 10 ml aliquots were taken and placed into 150 x 13 mm lipless test tubes which were used for counting on the 100 channel analyzer.

Counting Techniques

Mono-isotope Counting.

Equipment used. An Atomic Instrument Company scaler, Model 1020A, scale of 256, and a Nuclear Instrument Chemical Corporation Scaler, Model 165, were used. Two Amperex Model AB-90, thin walled, metal G-M tubes were used for counting the halogen activity. The G-M tubes were mounted inside cylindrical lead pigs, in order to reduce the background counting level. The radioactive solutions were contained in pyrex counting jackets which could be placed over the Amperex tubes.

Counting coincidence losses. In using G-M tubes the total counting rate must be corrected for the counts lost as a result of the dead time of the tube. The technique used to measure the counting loss at the various counting rates was to count simultaneously (on both the "organic" and "inorganic" counters) aqueous sulfite solutions of I^{128} activity which had an initial counting rate of about 50,000 counts per minute. One minute counts were taken every two minutes until the I^{128} decayed to about 2000 counts per minute. Each individual count was corrected for background activity, and for radioactive decay (relative to the first count). The corrected counts between 2000 and 6000 c/m were averaged to indicate the true counting rate. The percent counting loss and the counts which must be added for the various counting rates were determined. It was found that there was a negligible counting correction for counting rates below 7000-9000 counts per minute. In almost all of the samples studied in this research, the counting rates were below 15,000 counts per minute.

"Density" corrections. In determining the organic yield for a reaction mixture it is necessary to count halogen activities in two different media, 0.5M aqueous sulfite solution and $CHCl_3$. Since Br^{80} and I^{128} are strong beta emitters, their counting rates are effected by the density of the medium.³⁰ Since the counting geometry may not be identical, the densities of the two media are different, and the response of the two scalers may not be equal, a "density" correction must be made in order to correlate the activity in the two solution jackets.

The following procedure was employed for determining the "density" corrections for the halogen isotopes studied. A small quartz bulblet containing I_2 at its vapor pressure or a few mm of Br_2 was irradiated for a period of time sufficient to result in about 20,000 counts per minute.

The quartz bulblet was broken beneath 105 ml. of $\text{CHCl}_3 + \text{I}_2$ in a separatory funnel, which was then shaken for about 30 seconds in order to insure that all of the halogen activity was in solution. The solution was passed through a funnel containing anhydrous MgSO_4 over glass wool into a ground glass-stoppered bottle. One fraction of this solution was poured into the organic solution counting jacket. 50 ml., as measured by a volumetric flask, was added to a separatory funnel containing 50 ml. of 0.5M Na_2SO_3 solution. After shaking the funnel, extracting the halogen activity into the aqueous phase, and waiting for the two layers to settle, the organic phase was poured off into a separate flask, while the aqueous phase was poured through a funnel containing glass wool into the aqueous solution counting jacket. Negligible activity remained in this organic phase. The organic and aqueous phases were counted simultaneously on their respective Amperex tubes. The ratio by which the organic or aqueous phase must be multiplied in order to make the counts comparable was thus determined. For example, in Jacket Set III the I^{128} activity in the organic phase is multiplied by the factor 1.246; while Br^{80} activity in the organic phase is multiplied by 1.248, in order to correct for geometry, "density", and the scalers employed.

Counting of activity in solution jackets (determining the organic yield).

In all of the samples employing the Amperex tubes, the aqueous and organic solution jackets were counted simultaneously for one minute counts every two minutes, for a total of 6 to 20 minutes. The counting data, after being corrected for background activity, was plotted on semi-log paper. The best straight line corresponding to the half life of the activity was drawn through the points, noting any marked deviation from this line which would suggest the presence of a contaminating activity. The intercepts at

time zero were used as the counting rates for the respective solution jackets. After introducing the density correction, the organic yield, equal to the fraction (100 x organic activity)/total activity, was easily calculated.

In calculating the organic yield of Br^{80} an additional correction was necessary because of the presence of $\text{Br}^{80\text{m}}$ in the system. Br^{82} is also formed, but in short irradiations (several seconds) the amount is negligible compared to the Br^{80} activity. The emanations from $\text{Br}^{80\text{m}}$ can not be detected by the counting arrangement used. However, it decays to Br^{80} which is a strong beta emitter. In order to obtain the true Br^{80} count, it is necessary to multiply the counts at each time interval by a factor correcting for the growth of Br^{80} from $\text{Br}^{80\text{m}}$. In these measurements it is necessary to know the time the sample left the reactor with respect to the time of each count.

Samples containing inert gases. In the study of the moderation of the I^{128} and Br^{80} reactions with CH_4 by the inert gases, it is necessary to know whether the inert gases contributed anything to the measured counting rates. Quartz bulblets containing about 150 mm of argon, krypton, and xenon (all of which have radioactive isotopes formed by radiative neutron capture) were prepared, irradiated for about 30 seconds, extracted (using the procedures described previously), and counted. Negligible activities were found in the aqueous and organic phases from the argon and krypton samples. However, the organic phase of the xenon sample contained an activity which decayed with a 4.0 minute half life, which corresponds to the Xe^{137} (3.9 minutes) activity. Negligible xenon activity was found in the aqueous phase. About 30 minutes was allowed to elapse before reaction system samples containing xenon were counted. During the counting a rough

half life plot was made of the organic fraction to insure the absence of the xenon activity.

Multi-isotope Counting.

Because of similarities in decay properties, it is not possible to separate the individual activities in samples containing mixtures of various halogen isotopes using the counting arrangement previously described. In order to determine the I^{128} organic yield in reaction systems also containing Cl^{38} activity (37.5 min.), the 100-channel, pulse height analyzer with a three inch NaI(Tl) scintillation crystal detector of the Nuclear Chemistry Group under the direction of Professor W. W. Meinke was used.

Since the subject of gamma scintillation spectroscopy is well reviewed in the literature^{31,32,33} and the description and operation of the equipment is thoroughly covered in progress reports^{28,29,34} and theses³⁵ of the Nuclear Chemistry Group, the theory and counting will be only briefly discussed here.

Radioactive isotopes have characteristic decay properties by which they can be identified. Gamma rays emitted by an isotope can interact with the NaI(Tl) scintillation detector by means of three processes:³⁶

1. Photoelectric effect, resulting in a pulse having the energy of the incident gamma ray;
2. Compton absorption which yields a spectrum of pulses having a maximum energy less than that of the gamma ray; and
3. Pair production absorption which results in pulses having an energy of 1.02 mev less than the energy of the incident gamma ray rays.

The crystal is viewed by a photomultiplier tube which converts visible light emitted by the crystal (produced by the electrons) into

voltage pulses which are first amplified and then fed into the 100-channel pulse height analyzer which prints out the gamma ray spectrum for the activity analyzed. Figure 1a illustrates an energy spectrum for I^{128} activity obtained from the 100-channel analyzer (the actual height of the peaks is a function of the amount of activity present). The peaks at 0.45, 0.54, 0.75, and 0.98 mev indicate the various photopeaks corresponding to the energy of the gammas emitted by I^{128} . Knowing these peaks and the half life of the activity measured by the rate of decay of the photopeaks the isotope can be easily identified. The area under the photopeaks (counts per unit time) can be used as a quantitative measure of the amount of activity present in the sample.

When a sample containing both I and Cl is counted by the 100-channel analyzer, the I^{128} and Cl^{38} activities can be separated since their photopeaks do not overlap (lowest Cl^{38} photopeak is at 1.64 mev). Figure 1b shows a spectrum for a mixture of I^{128} and Cl^{38} activities. The areas under the peaks, of course, are proportional to the amounts of I and Cl present in the sample. It is noted that the 0.45 mev I^{128} peak is resting on the 1.67 mev Cl^{38} Compton edge, and the total counts under the I^{128} peak must be corrected for this effect. Since this research was concerned only with determinations of organic yields, it was sufficiently accurate to correct for the Compton edge by subtracting the counts in the area below the dotted line (see figure 1b) in the I^{128} photopeak.

Determination of I^{128} organic yields. The preparation of the sample for counting has been described previously. The stoppered glass tube containing the organic phase was placed on a lucite sample holder which places the sample at a reproducible position (at least for the accuracy desired) from the scintillation crystal detector. The instrument dead time was

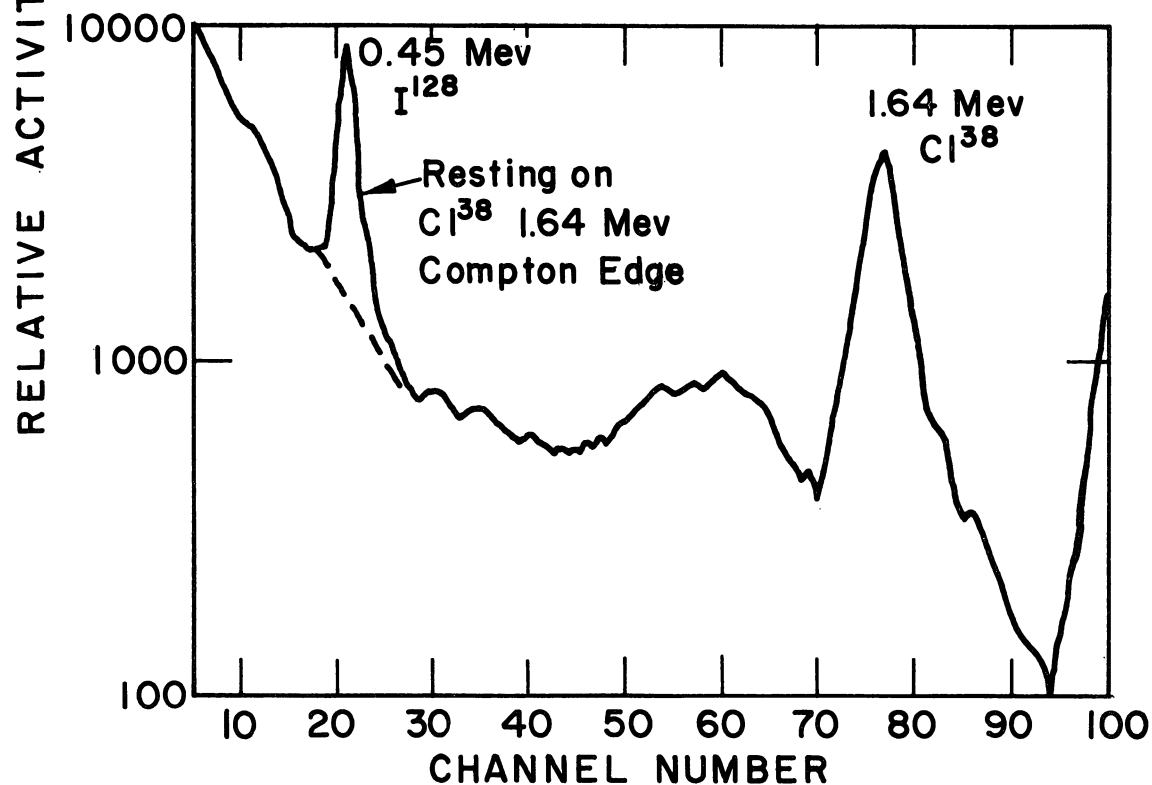
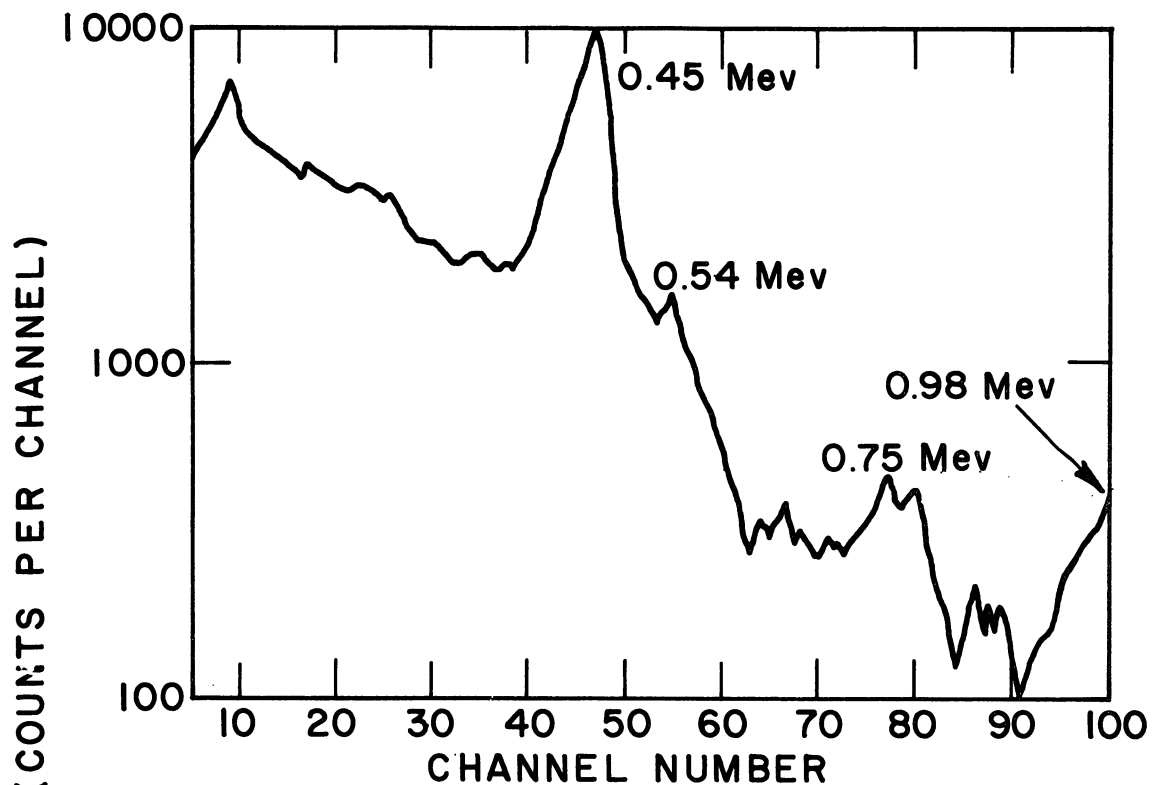


Fig. 1. (a) I^{128} gamma spectra, (b) Combined spectra of I^{128} and Cl^{38} .

read from the dead-time meter and the time at the beginning of the 100-channel analyzer operation was noted. The spectrum was printed out by the machine. The above operation was repeated for the aqueous sample.

After correcting the 0.45 mev photopeak for the Cl^{38} Compton edge and for decay (aqueous sample), the organic and aqueous counts were corrected for dead time. The true count is expressed by the following relationship:³⁵

$$C = C_{\text{obs}} \times \frac{100}{100 - T}$$

where C = total counts under photopeak corrected for dead time, C_{obs} = total counts observed by 100-channel analyzer, and T = observed dead time in percent.

No density correction was necessary since the geometries were comparable and only the gamma activity was counted.³⁰ The organic yield was then equal to 100 x organic counts/total counts.

Although main interest lay in the I^{128} organic yields those for Cl^{38} could easily be determined simply by considering the total area under the 1.64 mev Cl^{38} photopeak. (No Compton edge correction is necessary).

Chapter III. THE MODERATION TECHNIQUE

Studying the effects of atomic and molecular additives on the organic yield in order to determine the reaction mechanism can be called the moderation technique.

Levey and Willard,⁹ first to employ the moderation technique, did not consider the possibility of electronically excited states in their study of the $I^{128} + CH_4$ reaction. It is felt by the author that there is no justification in using only the ionization potential as a criterion in determining the reaction mechanism. Effective moderation (decreasing the organic yield) by an additive having an ionization potential lower than that of the iodine atom may be due to quenching of excited electronic states. In this research the moderation technique has been used in determining the mechanisms for the Br^{80} and I^{128} reactions with CH_4 . In the interpretation of the data all the possible interactions between the "hot atom" and the moderator were considered. In the last few years there have been rapid advances in the study of ion-molecule reactions (excited or ground state ions), charge transfer reactions, kinetic energy moderation, and in measurements of various internal molecular parameters (bond strength, ionization potentials, etc.) which have helped make the moderation technique a valuable tool in "hot atom" chemistry.

Although halogen recoil atoms (by virtue of their activation) can react to form inorganic as well as organic products, only the organic reactions are of interest here, since the true inorganic yield and product distribution can not be determined experimentally.

There are at least four different ways in which the halogen + CH_4 organic reaction can be moderated* depending upon the nature of the

* The word moderate shall mean, in this thesis, to decrease the organic yield of the reaction.

halogen "hot atom" and the additive:

1. Removal of the "hot atom" kinetic energy;
2. Neutralization of halogen ions;
3. Inelastic collisions resulting in physical quenching of excited ions or atoms; and
4. Reaction of the "hot atom" with the additive.

Removal of "Hot Atom" Kinetic Energy

If kinetic energy is a requirement for reaction, the moderator can decrease the organic yield of the reaction through elastic collisions with the recoil atom by removing the necessary energy for reaction. Considering the various masses of the "hot atom" (A) and the target compound (B) the recoil atom must possess a kinetic energy $\frac{\text{Mass A} + \text{Mass B}}{\text{Mass B}}$ times as great as the endothermicity of the reaction in order to have sufficient internal energy for the reaction.

Qualitatively it would be expected that the efficiency of the moderator would increase with the collision-energy decrement and the gas-kinetic cross-section of the moderator. The energy decrement for a head-on collision is given by the relationship:

$$\frac{\Delta E}{E} = \frac{4M_A M_B}{(M_A + M_B)^2}$$

where $\Delta E/E$ is the energy decrement and M_A and M_B are the masses of the colliding particles.⁴

Estrup-Wolfgang Model

In their study of the moderation of the $H^3 + CH_4$ reaction by inert gases, Estrup and Wolfgang^{13,37} developed a mathematical model for "hot

atom" reactions based partially on the mathematics of neutron cooling processes. Although their model does not predict whether a reaction will take place by virtue of kinetic energy, positive charge, or electronic excitation energy, it can quantitatively predict the effects of inert moderators on "hot" reactions (activated by kinetic energy). Since the Estrup-Wolfgang equations for hot reactions have been used in these studies of the I^{128} and Br^{80} reactions, a discussion of the pertinent features, relating specifically to the moderation of the I^{128} or Br^{80} reaction with CH_4 by a single moderator, follows.

Assumptions of the Estrup-Wolfgang Theory. In order to utilize the Estrup-Wolfgang theory for the I^{128} and Br^{80} reactions with CH_4 certain assumptions must be made:

1. The kinetic-energy loss of the hot atom occurs as a result of elastic-sphere collisions; this is generally valid for inert-gas moderation.
2. The minimum energy required for reaction is large compared with thermal energies. The reaction of Br^{80} with CH_4 , for example, could not occur via the usual photochemical mechanism: $Br^{80} + CH_4 \rightarrow CH_3 + HBr^{80}$ followed by $CH_3 + Br_2 \rightarrow CH_3Br + Br$ since the Br^{80} content of Br_2 is extremely small. It would appear that the reaction must be a one-step process: $Br^{80} + CH_4 \rightarrow CH_3Br^{80} + H$. This reaction is endothermic by 1.51 ev for ground-state Br atoms. However, if this energy is to be supplied by the Br^{80} , then only a fraction of the kinetic energy of the Br^{80} could be available for the internal energy of the activated complex. The Br^{80} must possess at least $(1.51) \times (96/16) = 9.0$ ev of recoil energy for reaction to occur. If the reaction is a result of ground-state

Br ions, then the process could be: $\text{Br}^+ + \text{CH}_4 \rightarrow \text{CH}_3\text{Br}^+ + \text{H}$ (0.20 ev endothermic) or $\text{Br}^+ + \text{CH}_4 \rightarrow \text{CH}_2\text{Br} + \text{H}^+$ (2.35 ev endothermic). For these reactions to occur the Br^+ must possess at least 1.2 ev and 14.1 ev of recoil energy, respectively. Similar results occur for comparable I^{128} reactions.

3. The initial energy of the atoms is high enough so that the atoms undergo a number of collisions and assume a statistically well-defined distribution of energies prior to reaction. This assumption is justified for the $\text{He}^3(n,p)\text{H}^3$ process which produces hot atoms of 0.2 mev energy. It will be assumed to be justified for Br^{80} and I^{128} reactions which have a maximum of about 357 ev and 182 ev of recoil energy, respectively.

The kinetic-energy moderation equation. In order to correct for unequal collision cross sections between the "hot atom" and CH_4 or the moderator, a function f was used instead of the mole fraction of CH_4 or the moderator. The quantity, f , was calculated from the expression:

$$f_{\text{CH}_4} = \frac{X_{\text{CH}_4} S_{\text{CH}_4}^2}{X_{\text{CH}_4} S_{\text{CH}_4}^2 + X_{\text{Mod}} S_{\text{Mod}}^2}, \text{ and}$$

$$f_{\text{Mod}} = 1 - f_{\text{CH}_4};$$

where X denotes the mole fraction and S^2 denotes the cross section for an I^{128} or Br^{80} collision with either CH_4 or the moderator.

The values for S^2 were calculated from gas-kinetic cross-sections³⁸ for the halogen atom, CH_4 , and the moderators used. The cross-section was

estimated where no value was given. S^2 is equal to the sum of the two diameters (collision partners) divided by 2, the quantity squared.

The quantity α is the average logarithmic energy loss per collision in the system:

$$\alpha = f_{\text{CH}_4} \alpha_{\text{CH}_4} + f_{\text{mod}} \alpha_{\text{mod}}$$

$$\alpha_{\text{CH}_4} \text{ or } \alpha_{\text{mod}} = 1 - \frac{(M_j - m)^2}{2M_j m} \ln \left| \frac{M_j + m}{M_j - m} \right|$$

where m is the mass of the hot atom and M_j is the mass of the molecule struck -- either CH_4 or the moderator.

The moderation equation derived by the Estrup-Wolfgang model for a system composed of a single reactant can be written as:

$$\frac{\alpha}{f_{\text{CH}_4}} \text{ (fraction of the activity in a given form)} = I - \frac{f_{\text{CH}_4}}{\alpha} \times K$$

where the constants, I and K , can be determined in a manner indicated below.

The "fraction of the activity in a given form" can be chosen as the organic yields of Br^{80} and I^{128} with CH_4 since the organic products are mainly in the methyl halide form.

According to the above equation, a plot of (α/f_{CH_4}) (fraction "hot atom" as organic) versus f_{CH_4}/α -- regardless of the moderator used -- should approximate a straight line with intercept I and slope K .

Neutralization of the Halogen Ions

Massey and Burhop³⁹ give an excellent review of the experimental re-

sults and theoretical views of charge transfer reactions through 1952.

Dibeler,⁴⁰ and Dibeler and Reese^{41,42} review some of the more recent work, especially in relationship to mass spectrometry.

Massey and Burhop stated that the charge-transfer cross-section between two atoms with initial relative velocity, v , in which a change, ΔE , (energy defect) of internal energy occurs will be small compared with the gas-kinetic cross-section if:

$$\frac{a|\Delta E|}{hv} > 1$$

where a is the interaction distance, being of the order of the gas-kinetic radius, ΔE is the difference in ionization potential of the colliding atoms, and h is Planck's constant.

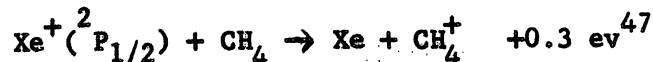
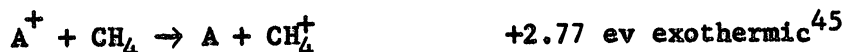
For a fixed ΔE the charge-transfer cross-section should increase rapidly with relative velocity until $a|\Delta E|/hv$ is 1, after which it decreases slowly. When ΔE is equal to zero (exact resonance) the cross-section should decrease slowly as v increases from zero. As $|\Delta E|$ increases the cross-section should fall off rapidly, exhibiting a maximum at exact energy resonance ($|\Delta E| = 0$).

Ghosh and Sheridan⁴³ attempted to test the adiabatic hypothesis in various unsymmetric charge-transfer reactions. It is known that the (CO^+, CO) and (O_2^+, O_2) reactions, for example, have true symmetric characteristics ($\Delta E = 0$) -- the cross-section is large at low ion energy and then decreases with increasing energy. However, they observed that the unsymmetric reactions (A^+, CO) , (A^+, CO_2) , and (A^+, NO) having positive energy defects seem to possess the symmetric characteristics even though they have large positive energy defects. According to the adiabatic hypothesis the cross-sections should be negligible at the energies studied,

becoming maximum at an energy of several kev. Since these reactions are symmetrical in character either the newly created ions or the atoms are excited to proper energy levels, or dissociated so that the energy defect approaches zero. Reactions having negative energy defects such as $(\text{CO}_2^+, \text{A})$ and (CO^+, A) show a steady rise of cross-section with increasing energy as expected by the adiabatic hypothesis.

Gurnee and Magee⁴⁴ have treated the near-resonant case theoretically for atomic and molecular charge-transfer processes, which are of most interest here. In charge-transfer processes having favorable free energy changes (positive ΔE) and a sufficient number of vibrational degrees of freedom, the excess energy can go into these degrees of freedom and result in a small energy defect. This would explain why various unsymmetric charge-transfer reactions have large cross-sections, which, according to the adiabatic hypothesis, should be negligible.

Unsymmetric charge-transfer reactions involving excited and ground state ions such as:



have been verified using the mass spectrometer.

If positive ions are involved in the chemical reaction they can be removed from organic combination by charge transfer-reactions with the moderator if the energy defect approaches zero. It is obvious to the author that the relative importance of kinetic energy and positive charge cannot be determined by merely considering the ionization potentials of

the atom and the moderator. If the chemical reaction occurs by virtue of an electronically excited halogen ion, its organic yield can be decreased (via a charge-transfer process) by moderators having an ionization potential higher (by the amount of the electronic excitation energy of the atom) than that of the halogen atom.

Inelastic Collisions Resulting in Physical Quenching
of Excited Ions or Atoms

Physical quenching is deactivation of an electronically excited atom, or ion, by collisions with a moderator, with the excitation energy going into translational and internal degrees of freedom of the moderator.

It is unfortunate that there is no information on the physical quenching of electronically excited halogen atoms and ions. Laidler⁴⁸ has summarized physical quenching cross-sections of Na(²P), Hg(³P₁), and Cd(³P₁) atoms by various moderators.

Although the quenching cross-sections were specifically for excited Na, Cd, and Hg atoms, one observation which relates to quenching of excited halogen atoms and ions is that inert gases are extremely poor quenchers of excited electronic states, regardless of the excited atom or ion.

It may be possible to determine the relative importance of electronic energy on "hot atom" reactions by employing inert gases. If a reaction proceeds via an electronically excited halogen mechanism, then there should be no moderation (decrease in organic yield) of the reaction by inert-gas additives. Unless there is some other experimental or theoretical information available it may not be possible to distinguish excited state reactions from other possible thermal reactions.

Reaction with Additive

Unless one is studying inert-gas moderation, the additive can moderate the organic reaction by reactions with the "hot atom" leading to inorganic formation. Since a fraction of the "hot atoms" are born positively charged, there is a possibility that the reaction can be moderated by ion-molecule reactions with the additive. The subject of ion-molecule reactions has been well reviewed by Dibeler,⁴⁰ and Dibeler and Reese.^{41,42} Rosenstock and co-workers⁴⁹ have published a monograph containing all the available theoretical and experimental information on ion-molecule reactions as of 1959. This topic will be discussed in more detail in Chapter V.

Discussed in Chapters IV and V are the problems of determining the Br⁸⁰ and I¹²⁸ reaction mechanisms based on the moderation technique.

Chapter IV. REACTION OF (n, γ) ACTIVATED Br^{80} WITH CH_4

Results

The percent of the Br^{80} present as organic activity (organic yield) for the CH_4 -moderator systems is given in Table II.

Corrections of Observed Br^{80} Organic Yields.

In samples containing $\text{C}_2\text{H}_5\text{Br}$ as the main source of Br^{80} activity, the organic yields must be corrected for the small fraction of the Br^{80} which will not split from the $\text{C}_2\text{H}_5\text{Br}^{80}$ molecule. This failure to bond-rupture which amounts to 0.33%²⁰ for $\text{C}_2\text{H}_5\text{Br}$, must be subtracted from the organic yields of Table II. In addition, the Br^{80} could react with the molecular additives and contribute to the observed organic activity. Thus, it is necessary to correct further these data of Table II for the fractional reactivity with the molecular additives. To do this, one subtracts from the observed values the product of the mole fraction of the additive multiplied by the extent of reaction with essentially pure additives to produce organically bound Br^{80} . These maximum extents of reaction (listed in Table III) to produce organic Br^{80} , are, correcting for any failure to bond-rupture: CF_4 - 0.7%, C_2F_6 - 3.0%, and $\text{C}_2\text{H}_5\text{Br}$ - 2.2%.

Since the samples were irradiated for only 2 seconds and contained about 2 mm Br_2 radical scavenger, except where noted, no correction for radiation damage was necessary (see Chapter V).

These corrected data of Table II are depicted graphically in Figs. 2 and 3. The solid curves were calculated according to the Estrup-Wolfgang theory (method described below). In order to avoid confusion the uncertainties have been omitted from these figures.

Table II

Percent Br⁸⁰ Stabilized in Organic
Combination in Various Gaseous Mixtures^a

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Percent Br ⁸⁰ as Organic ^b
He	654	27	0.040 ± .007	13.5 ± .2 13.6 ± .4
	549	83	0.131 ± .002	12.6 ± .1 12.6 ± .2
	440	87	0.165 ± .005	12.0 ± .2 12.0 ± .2
	127	300	0.703 ± .123	8.5 ± .4 9.2 ± .4
Ne	416	52	0.111 ± .012	11.2 ± .4 12.5 ± .3
	454	129	0.221 ± .017	10.8 ± .3
	239	217	0.476 ± .052	9.6 ± .2
	239	219	0.478 ± .052	8.6 ± .4
Ar	501	127	0.202 ± .026	12.1 ± .5 12.2 ± .5
	238	177	0.427 ± .035	5.5 ± .6 6.7 ± .4
	148	279	0.653 ± .040	4.8 ± .6
Kr	649	41	0.059 ± .001	11.5 ± .3 11.5 ± .4
	589	97	0.141 ± .002	8.7 ± .4 8.9 ± .3
	283	147	0.342 ± .003	5.3 ± .2 5.6 ± .2
	106	91	0.462 ± .007	3.6 ± .3 3.6 ± .1

Table II (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Percent Br ⁸⁰ as Organic ^b
Xe ^c	663	20	0.029 ± .002	11.8 ± .3 14.2 ± .2
	662	43	0.061 ± .001	11.3 ± .4 13.8 ± .4
	568	60	0.096 ± .001	9.8 ± .3 10.0 ± .4
	335	62	0.156 ± .002	6.9 ± .3 8.0 ± .4
	150	65	0.302 ± .003	5.1 ± .5 4.7 ± .5
CF ₄	557	90	0.139 ± .002	8.0 ± .2 8.4 ± .3
	437	241	0.356 ± .003	4.7 ± .2 5.0 ± .3
	262	438	0.626 ± .005	2.8 ± .1 3.4 ± .1
C ₂ F ₆	498	143	0.223 ± .002	6.3 ± .3
	368	275	0.428 ± .003	5.2 ± .2 6.6 ± .2
Br ₂	714	2	0.003 ± .001	13.1 ± .7 14.3 ± .6
	658	3	0.005 ± .001	13.4 ± .4
	656	23	0.034 ± .007	11.3 ± .3 13.0 ± .2
	629	65	0.096 ± .007	10.4 ± .1 10.9 ± .2
	268	65	0.195 ± .015	6.6 ± .1 7.2 ± .1
	112	63	0.360 ± .029	3.2 ± .1 4.4 ± .1

Table II (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Percent Br ⁸⁰ as Organic ^b
C ₂ H ₅ Br ^d	699	11	0.015 ± .004	12.8 ± .4 13.1 ± .4
	657	20	0.029 ± .001	12.4 ± .4 13.4 ± .3
	467	22	0.045 ± .002	11.1 ± .3 11.6 ± .3
	323	23	0.067 ± .003	10.5 ± .2 12.1 ± .3
	213	26	0.109 ± .004	9.0 ± .7 9.1 ± .2
	360	93	0.205 ± .002	7.2 ± .1 7.5 ± .1
	183	101	0.356 ± .005	5.8 ± .1
	179	149	0.454 ± .005	5.4 ± .1 5.5 ± .1

- a. All samples, except where noted, contained 2 mm Br₂.
- b. Uncertainties based on estimates of uncertainty in positioning 17.4 min. slope through decay data for inorganic and organic fractions for each run.
- c. Samples contained 2 mm. C₂H₅Br and 0.2 mm Br₂.
- d. 0.2 mm. Br₂ scavenger present.

Table III

Percent Br⁸⁰ Stabilized in Organic Combination
in Various Gaseous Mixtures of
a Bromine and Additive

Additive	Pressure Br ₂ (mm)	Mole Fraction Additive	Percent Br ⁸⁰ As Organic
CF ₄	28	0.972	0.5 ± .3
			0.9 ± .2
C ₂ F ₆	1	0.998	2.4 ± .1
			3.7 ± .2
C ₂ H ₅ Br	0.2	0.999	2.6 ± .1
			2.5 ± .1
			2.5 ± .1

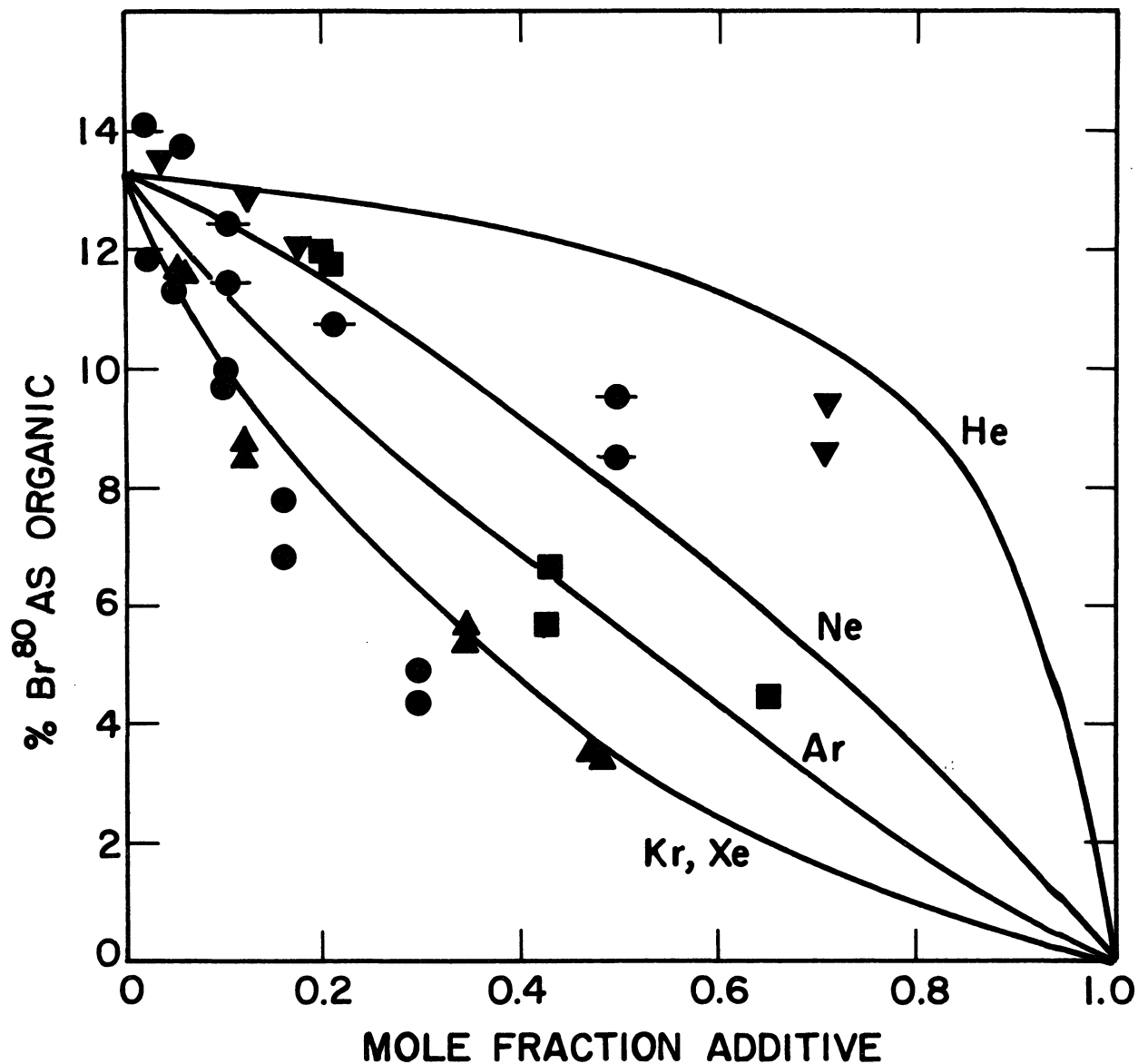


Fig. 2. Effect of inert-gas moderators on the reaction of gaseous CH_4 with Br^{80} activated by the (n,γ) process. Moderators: helium, \blacktriangledown ; neon, \bullet ; argon, \blacksquare ; krypton, \blacktriangle ; xenon, \bullet .

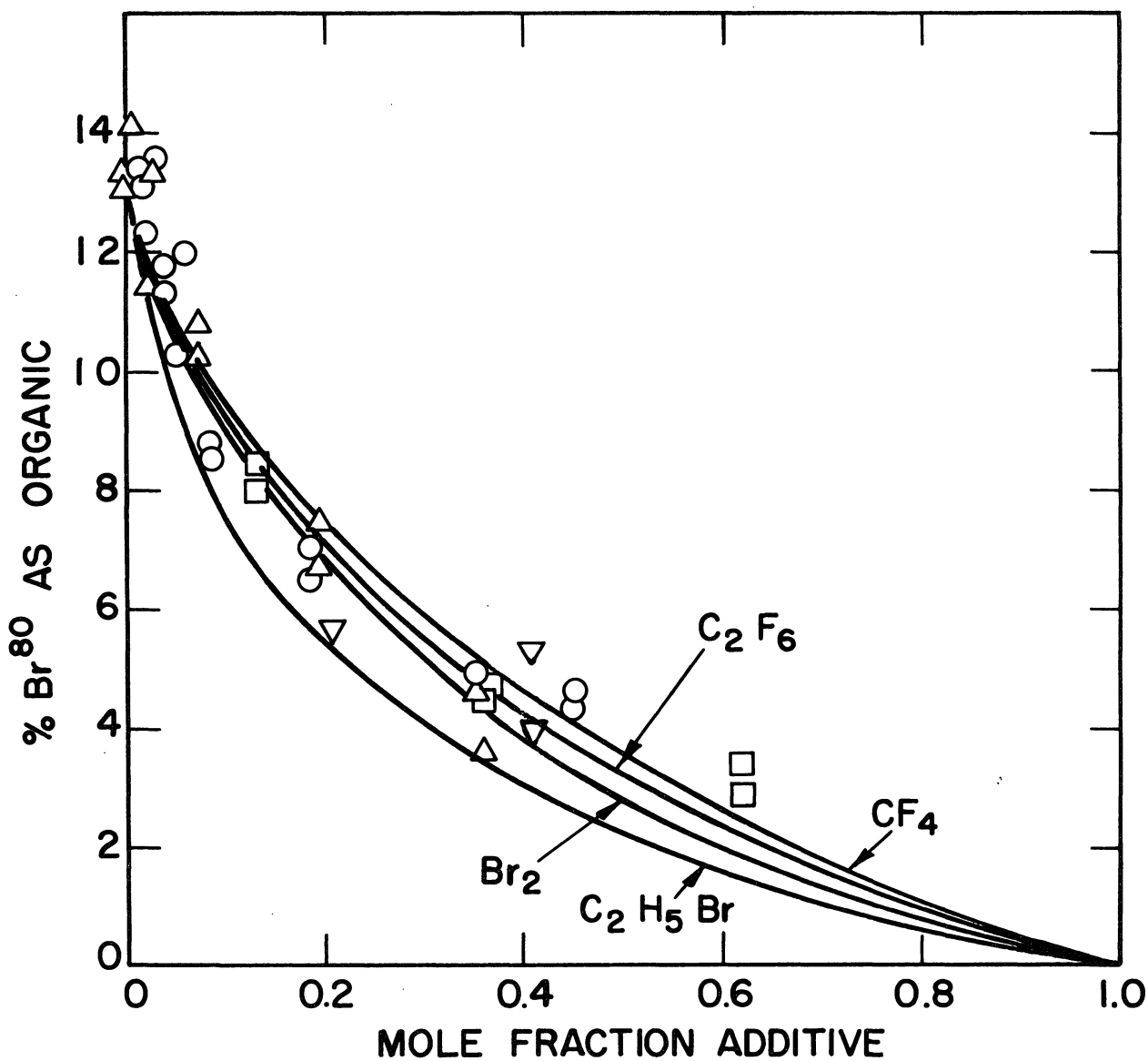


Fig. 3. Effect of molecular moderators on the reaction of gaseous CH_4 with Br^{80} activated by the (n,γ) process. Moderators: CF_4 , \square ; C_2F_6 , ∇ ; Br_2 , \triangle ; $\text{C}_2\text{H}_5\text{Br}$, \circ .

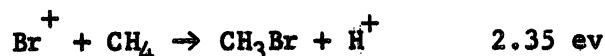
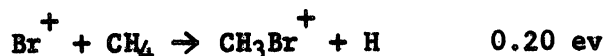
Limiting Organic Yield of Br⁸⁰ in CH₄.

It was found that at zero mole-fraction additive, $13.3 \pm 0.5\%$ of the Br⁸⁰ reacts with CH₄ to become stabilized in organic combination. This was found by extrapolating the data on a log-log plot of Br⁸⁰ organic yield versus mole fraction of CH₄ where the mole-fraction additive was less than 0.1. The only other determination of this quantity was made by Gordus and Willard¹⁰ and indicated 18% Br⁸⁰ as organic. The reason for this difference was probably due to the presence of radiation-induced reactions in their experiments. The gamma dose received by the samples of Gordus and Willard was almost 100 times that received by these samples.

From chromatographic analysis¹⁰ it is known that at least 95% of the organic yield corresponds to CH₃Br⁸⁰, with the remaining 5% fraction as CH₂Br₂. Since the percent error in each Br⁸⁰ organic yield measurement in a reaction system of CH₄ and moderator is at best 5%, the presence of CH₂Br₂ can be neglected, and the organic yield can be considered as corresponding to that of the CH₃Br⁸⁰ only.

Discussion

Various single step endothermic displacement reactions of Br atoms and ions with CH₄ which lead to organic Br⁸⁰ formation are:



In order to have available, as internal energy of the activated complex, the energies listed above, the Br atom or ion must possess a minimum

kinetic energy, that is $(80 + 16)/16 = 6$ times as great as the endothermicity of the reaction. This energy for reaction can be supplied by the kinetic energy of the recoil Br.

In addition to the above reactions, the organic Br⁸⁰ could be produced by electronically excited Br atoms or ions possessing enough internal energy to make the above reactions thermal (kinetic energy independent). Using the moderation technique it may be possible to resolve the problem of the relative importance of the above reactions on the extent of the Br⁸⁰ organic reaction.

As discussed in Chapter III, there are various ways in which the Br⁸⁰ + CH₄ reaction can be moderated, depending upon the nature of the Br⁸⁰ and the moderator: (1) removal of the Br⁸⁰ kinetic-energy; (2) neutralization of Br⁸⁰ ions; (3) inelastic collisions resulting in the quenching of excited Br⁸⁰ ions or atoms; (4) reaction of Br⁸⁰ with the additive, the Br⁸⁰ becoming stabilized in chemical combination.

Inert-Gas Moderation.

Inert-gas moderation of the Br⁸⁰ + CH₄ reaction is depicted in Fig. 2. Inert gases cannot moderate via process 4. In addition, inert gases are found to be inefficient in quenching excited species⁴⁸ and because of their high ionization potentials are very inefficient in undergoing charge-transfer with Br⁺ ions. Therefore, if moderation of the reaction by the inert gases occurs it must be due mainly to process 1.

One may next examine the experimental data for the samples containing inert gases. Referring to Fig. 2 and ignoring the solid curves, it is seen that each inert gas is capable of suppressing the extent of formation of organic Br⁸⁰. If the inert gases moderate the reaction principally via

process 1, then the relative effectiveness of the additives would depend on the size of the inert-gas atoms and on the fractional energy transfer per Br^{80} -inert-gas collision. Thus, a plot such as Fig. 2 should indicate that the moderating efficiencies increase in the order: He, Ne, Ar, Kr, Xe. As seen, the data of Fig. 2 are in accord with that expected for kinetic-energy moderation.

One may also attempt to determine qualitatively whether the formation of organic Br^{80} is due totally to hot processes. This may be accomplished by extrapolating the data of Fig. 2 to zero mole fraction CH_4 . If, for example, the data extrapolated to 6%, such data would suggest that 6% of the organic Br^{80} is formed via thermal processes (for example, processes involving electronically excited Br atoms or ions), and $13.3 - 6 = 7.3\%$ via hot processes. The data for Ar, Kr, and Xe, however, extrapolate to about $0 \pm 2\%$ and there is no reason to expect the He and Ne data to extrapolate to a value which differs from that of the other inert-gases. Therefore, it would appear that the organic Br^{80} is formed principally via hot reactions.

Molecular Additive Moderation.

Molecular additive moderation of the $\text{Br}^{80} + \text{CH}_4$ reaction is depicted in Fig. 3. The molecular additives are capable of moderating according to all four processes. However, as with the inert-gases, we may eliminate certain processes from consideration.

Molecular Br_2 and $\text{C}_2\text{H}_5\text{Br}$ should be able to moderate efficiently via all four processes.

For CF_4 we would expect charge-transfer to be a very inefficient process⁴⁴ since the ionization potential⁴⁴ of CF_4 (probably about 13 ev) is greater than that of Br. This compound has been found to be highly inefficient in quenching excited I^{128} ions (see Chapter V). Therefore, it

might also be expected that CF_4 should be inefficient in quenching excited Br^{80} atoms or ions. Reactions of Br^{80} atoms or ions with CF_4 to yield inorganic or organic Br^{80} are more endothermic than similar reactions of Br^{80} with CH_4 . Therefore, it is possible that the Br^{80} would react preferentially with CH_4 . This conclusion is substantiated by the fact that the reaction of Br^{80} with excess CF_4 results in only 0.7% Br^{80} as organic, whereas 13.3% Br^{80} as organic is found in the $\text{Br}^{80} + \text{CH}_4$ reaction. In addition, the endothermicities for the reaction with CF_4 to form inorganic and organic Br^{80} are of the same order of magnitude (80-90 kcal). As an approximation, it is possible that only about 0.7% Br^{80} as inorganic would result in the reaction with CF_4 . Since processes 2, 3, and 4 are probably of minor importance, we would expect CF_4 to moderate principally via process 1.

Similar arguments may be presented for C_2F_6 moderation. On the basis of experiments with I^{128} , (see Chapter V) quenching should be unimportant. Because of the high endothermicities and the low extent of production of organic Br^{80} (3%), reaction of Br^{80} with C_2F_6 to yield inorganic Br^{80} may also be of minor importance. Although the ionization potential of C_2F_6 is not available in the literature it is probably equal to or greater than 11.65 ev since the ionization potential of C_2H_6 is 11.65 ev. Since the ionization potential of Br is 11.84 ev, charge-exchange could be possible. Removal of kinetic-energy, process 1, could also occur.

Mechanism of $\text{Br}^{80} + \text{CH}_4$ reaction.

Experimentally, it is observed that the moderation exhibited by all the molecular additives is quite similar to that exhibited by krypton and xenon. It was seen from the inert-gas data that thermal processes are of little importance. The ionization potentials, quenching abilities, etc.,

and the chemical reactivities toward bromine atoms or ions vary greatly among the molecular additives. Since similar moderation efficiencies result from substances of similar molecular or atomic weights (xenon, krypton, and the molecular additives), these data would suggest that, for the molecular additives, processes 2, 3, and 4 are not as important as kinetic-energy transfer. Thus, it would appear that the reaction of Br^{80} with CH_4 proceeds mainly via a mechanism involving hot Br^{80} atoms, rather than positively charged and electronically excited Br .

Evaluation of Estrup-Wolfgang Theory

Since the $\text{Br}^{80} + \text{CH}_4$ reaction proceeds by virtue of its kinetic energy, it is of interest to determine if these data can be described by the Estrup-Wolfgang theory (see Chapter III).

In order to calculate S^2 for the various moderators, the diameters³⁸ used were: He, 2.2; Ne, 2.6; Ar, 3.6; Kr, 4.3; Xe, 4.9; Br_2 , 8.4; CF_4 , 5.5; C_2F_6 , 6.8; $\text{C}_2\text{H}_5\text{Br}$, 9.0; Br , 4.2; CH_4 , 4.2 Å. The diameters for Br_2 , CF_4 , C_2F_6 , and $\text{C}_2\text{H}_5\text{Br}$ were estimated.

Figure 4 is a plot of the experimental data corresponding to the equation $\alpha/f_{\text{CH}_4} (\text{Br}^{80} \text{ organic yield}) = I - (f_{\text{CH}_4}/\alpha)K$. For essentially pure methane, $f/\alpha = 2.84$ and $(\alpha/f)(\text{fraction of } \text{Br}^{80} \text{ as organic}) = 0.0470$. The best straight line drawn through the data and ending at the point (2.84, 0.0470) has an intercept $I = 0.057 \pm 0.005$ and a slope $-K = -(0.0035 \pm 0.0020)$. It should be emphasized that the points for all moderators, with the possible exception of $\text{C}_2\text{H}_5\text{Br}$, appear to approximate the same line. The upward trend exhibited by the $\text{C}_2\text{H}_5\text{Br}$ data could be due, in part, to an incorrect choice of the value of the apparent diameter of the compound.

The solid curves of Figs. 2 and 3 were calculated using the above

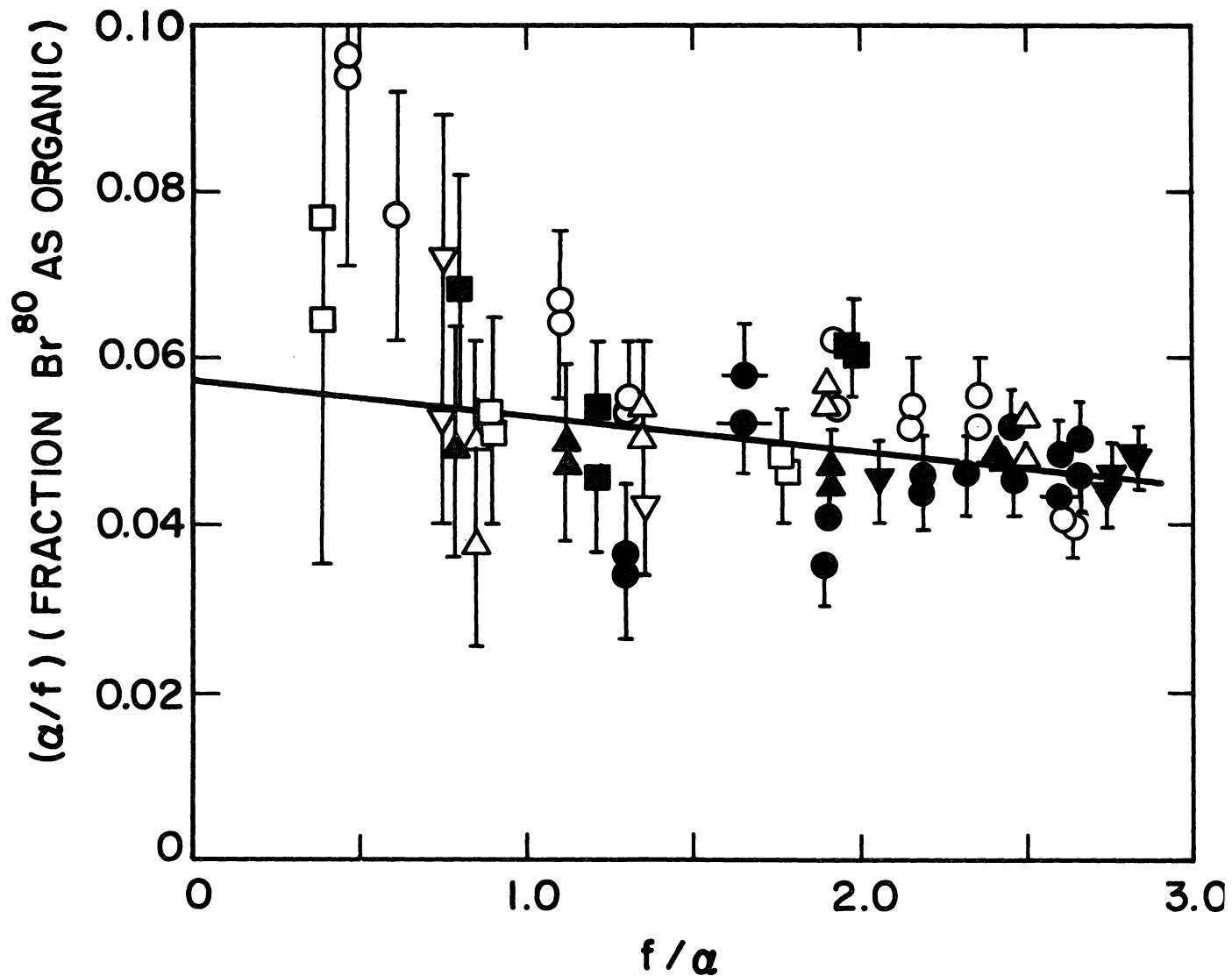


Fig. 4. Plot corresponding to the Estrup-Wolfgang moderation equation for the Br^{80} in organic combination. Moderator symbols are listed in captions for Figs. 2 and 3.

equation and the above values of K and I. It is seen that the curves for Xe and Kr moderation are identical. This is due to the fact that, whereas the Xe-Br cross-section is larger than that of the Kr-Br, per collision, because of the similarity in atomic weights, krypton is capable of removing, on the average, more energy from Br^{80} than is xenon. It should also be noted that this kinetic theory results in curves for the molecular additives (Fig. 3) which are in reasonable agreement with the data. This suggests, as do the data of Fig. 4, that the molecular additives serve mainly to remove Br^{80} excess kinetic energy. If moderation by the molecular additives were via a process other than kinetic-energy removal, it would only be under the most fortuitous circumstances that their moderation data would be described by the kinetic-theory curves.

In summary, the data of Fig. 4 would tend to support the conclusion stated earlier that the reaction of Br^{80} with methane occurs principally, if not completely, as a result of the gamma-recoil kinetic energy acquired by Br^{80} .

Effect of Inert-Gas Moderators on the Reaction

Results

Listed in Table IV are the observed I¹²⁸ organic yields and I¹³¹ organic pickup for the various CH₄-inert-gas reaction systems. In order to interpret correctly the relative effects of the additives, it is necessary to correct the observed I¹²⁸ organic yields for (a) the 1.1% failure to bond-rupture²⁰ of CH₃I, used as the main source of I¹²⁸ and (b) any radiation induced reactions.

Radiation induced reactions. In order to determine whether the observed I¹²⁸ organic yield is due in part to radiation induced reactions activated by the reactor gamma flux, reaction systems containing I₂ tagged with I¹³¹ were also irradiated. It was found that there was negligible I¹³¹ organic pickup in samples containing only CH₃I(I₂) and CH₄. As depicted in figure 5, it can be seen that the extent of I¹³¹ pickup is a function of both the inert gas and its mole fraction. If a sample contained I¹³¹ the observed I¹³¹ organic pickup was subtracted from the I¹²⁸ organic yield. For those samples not containing I¹³¹ the correction for radiation-induced reactions was determined in terms of the straight-line plots of figure 5. This was plausible since the lengths of the irradiations and the I₂¹³¹ vapor pressures were comparable in all the samples. The data could have been corrected using a pressure plot rather than a mole fraction plot, but it made little difference since the total pressure of the reaction systems varied by less than 10%.

Levey and Willard, in their work on the neutron activated I¹²⁸ + CH₄ reaction,⁹ found low or negligible I¹³¹ organic pickup in their neutron

Table IV.

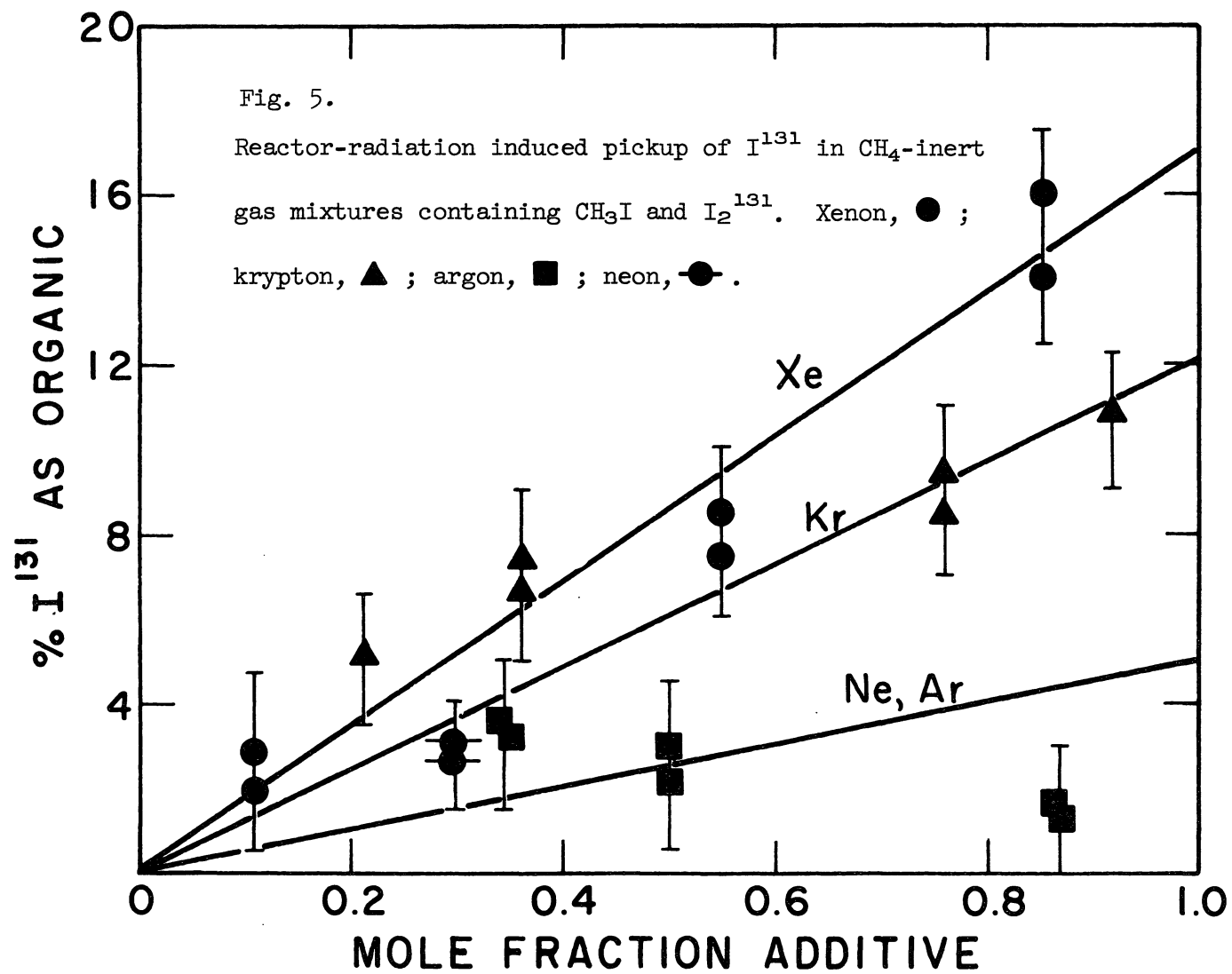
Percent I¹²⁸ (and I¹³¹) Stabilized in Organic
Combination in Various Gaseous Mixtures^a

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive ^b	% I ¹²⁸ as Organic ^c	% I ¹³¹ as Organic ^d
Ne	594	76	0.113 ± .011	52.9	
	489	159	0.245 ± .008	53.1 52.2	
	308	128	0.294 ± .024	53.3 52.8	2.6 2.2
	362	231	0.390 ± .045	50.0 54.0	
	205	133	0.394 ± .032	50.1	
	205	129	0.386 ± .032	50.1	
Ar	400	189	0.321 ± .027	54.3 54.5	3.8 3.9
	295	235	0.443 ± .031	52.2 52.0	3.0 2.0
	109	410	0.765 ± .059	45.4 47.4	
	50	341	0.872 ± .067		1.0 1.5
Kr	595	80	0.119 ± .002	53.8 53.5	
	483	106	0.180 ± .003	52.4	5.1
	320	120	0.273 ± .003	49.5 48.5	
	432	236	0.353 ± .003	50.5 51.8	6.2 7.3

Table IV (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive ^b	% I ¹²⁸ as Organic ^c	% I ¹³¹ as Organic ^d
Kr	194	141	0.421 ± .001	45.6 45.0	
	143	412	0.742 ± .004	49.3 49.0	8.8 9.1
	43	456	0.914 ± .003	48.0	10.8
Xe	615	40	0.061 ± .002	50.8 50.5	
	563	61	0.098 ± .004	48.3 47.3	2.3 2.5
	554	101	0.154 ± .002	45.2 46.5	
	489	179	0.268 ± .002	39.6 39.8	
	251	307	0.552 ± .004	31.6 29.4	7.7 8.0
	179	331	0.649 ± .004	30.5 29.2	
	72	447	0.865 ± .005	31.0 30.4	16.0 14.0
	60	454	0.883 ± .005	29.2 29.3	
	23	515	0.957 ± .005	24.1 24.5	

- a. All samples contained 0.1 ± 0.01 mm I₂ and 0.5 ± 0.1 mm CH₃I and were irradiated for 7 sec.
- b. Calculated assuming additive pressures. Uncertainty in last figure or figures is based on estimates of determining individual pressures.
- c. An uncertainty of ± 0.5 was associated with the positioning of the 25.0 min. slope through the decay data.
- d. An uncertainty of ± 1.5 was associated with the decay data and possible pre-irradiation I₂-CH₃I exchange.



irradiated I_2-CH_4 samples which received a dose of about 1.6×10^4 roentgens. However, samples containing high ratios of Xe to CH_4 gave unexpectedly high and variable I^{128} organic yields. These workers suggested that their results were caused by a radiation-induced reaction of CH_4 and I^{128} sensitized by the Xe. In order to test their supposition they exposed samples containing Xe, CH_4 , and I_2 tagged with I^{131} , to the gamma radiation of a Co^{60} source for a total exposure of about 10^5 roentgens. In the Xe- CH_4 (I_2) samples the I^{131} organic pickup was as high as 46% and increased with increasing radiation dosage. Tagged samples of Ar- CH_4 (I_2) gave high I^{131} organic pickup which was lower than that of the Xe samples. From these preliminary experiments Levey and Willard supposed that the I^{131} organic pickup in the I- CH_4 system would increase with the pressure of the inert-gas additive and with the number of electrons per molecule of inert gas.

The relative extents of radiation-induced reactions for Xe, Kr, and Ar and Ne are 17, 12, and 5, respectively, which is in the same ratio, approximately, as the number of electrons in the inert gas. The number of radicals produced by the interaction of gamma rays in the medium should be a function of both the primary interaction of the gamma rays, and the secondary effects of the electrons produced in the initial gamma ray interaction. Since the average energy of the gamma rays in a nuclear reactor is of the order of 2 mev^{50,51} the main interaction of these gamma rays with matter proceeds mainly via Compton scattering,⁵² whose interaction probability is related directly to the first power of the atomic number of the material. The I^{131} pickup results may be fortuitous, but they seem to indicate, to a first approximation, that the primary interaction of the gamma rays with the matter is an important factor in the number of

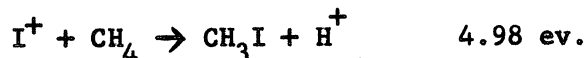
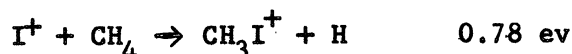
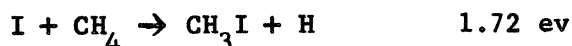
radicals produced in the system.

The data of Table III, corrected for failure to bond-rupture and radiation-induced reactions, are depicted graphically in figure 5. The method for calculating the solid curves is described in the discussion.

Maximum extent of reaction. Extrapolation of the molecular moderation data (CH_3I , $n\text{-C}_3\text{H}_7\text{I}$, and C_6H_6 of Table V) to zero mole-fraction additive, where the mole fraction of the additive was less than 0.1, indicates that $54.4 \pm 0.5\%$ of the I^{128} reacts with CH_4 to become stabilized in organic combination. On the basis of previous gas chromatographic analysis it is known that $\text{CH}_3\text{I}^{128}$ is the major organic product; the only other observable organic product was $\text{CH}_2\text{II}^{128}$ present to the extent of only about 1%. Therefore, the observed organic yields may be considered to correspond to the organic yield of $\text{CH}_3\text{I}^{128}$ only.

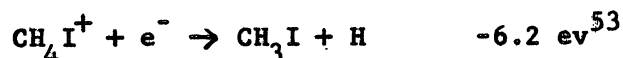
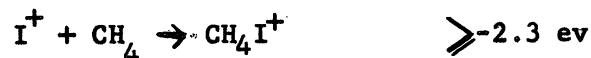
Discussion

Single step endothermic displacement reactions of I atoms or ions with methane which could lead to organic I^{128} formation are:



The reaction energy can be supplied by the "hot atom" kinetic energy. In addition to the above "hot" reactions, I^{128} could go into organic formation by thermal, electronically excited atom or ion reactions where the reaction energy is supplied by the electronic excitation energy. It is also possible that a positively charged I^{128} atom reacts with CH_4 by means

of an ion-molecule mechanism. For example, the following thermal reactions could occur:



Inert gases can only moderate the $I^{128} + CH_4$ reaction by kinetic energy cooling and by charge-transfer reactions. It is known that inert gases are extremely poor quenchers of excited states⁴⁸ and cannot undergo chemical reactions with the I^{128} recoil atom. Therefore, if the CH_3I^{128} is formed only as a result of a hot reaction, then a large excess of an inert gas should be capable of suppressing completely the formation of CH_3I^{128} . As seen in Fig. 6, the inert gases only partially suppress the reaction. Apparently, then, only a fraction of the CH_3I^{128} is formed by a hot reaction, the remainder being formed by thermal processes. It should be noted that Xe reduces the CH_3I^{128} yield to $11 \pm 2\%$, whereas other inert gases reduce this yield to only about $36 \pm 2\%$. The assumption that the reduction to 36% is a result mainly of a hot reaction is justified by the mathematical analysis given in the next section.

The fact that Xe reduces the extent of formation of CH_3I^{128} by an additional $25 \pm 3\%$ must be due to a unique ability of Xe to neutralize or quench excited I^{128} ions or atoms. Therefore, this additional moderation by Xe must be due to a charge-transfer process. For Xe alone to exhibit moderation by charge transfer requires that the energy defect of the reaction approaches zero more closely than that for charge transfer with the other inert gases.

The first four excited states of I^+ and their excitation energies are as follows:⁵⁴ (3P_0), 0.800; (3P_1), 0.879; (1D_2), 1.702; (1S_2), 4.044

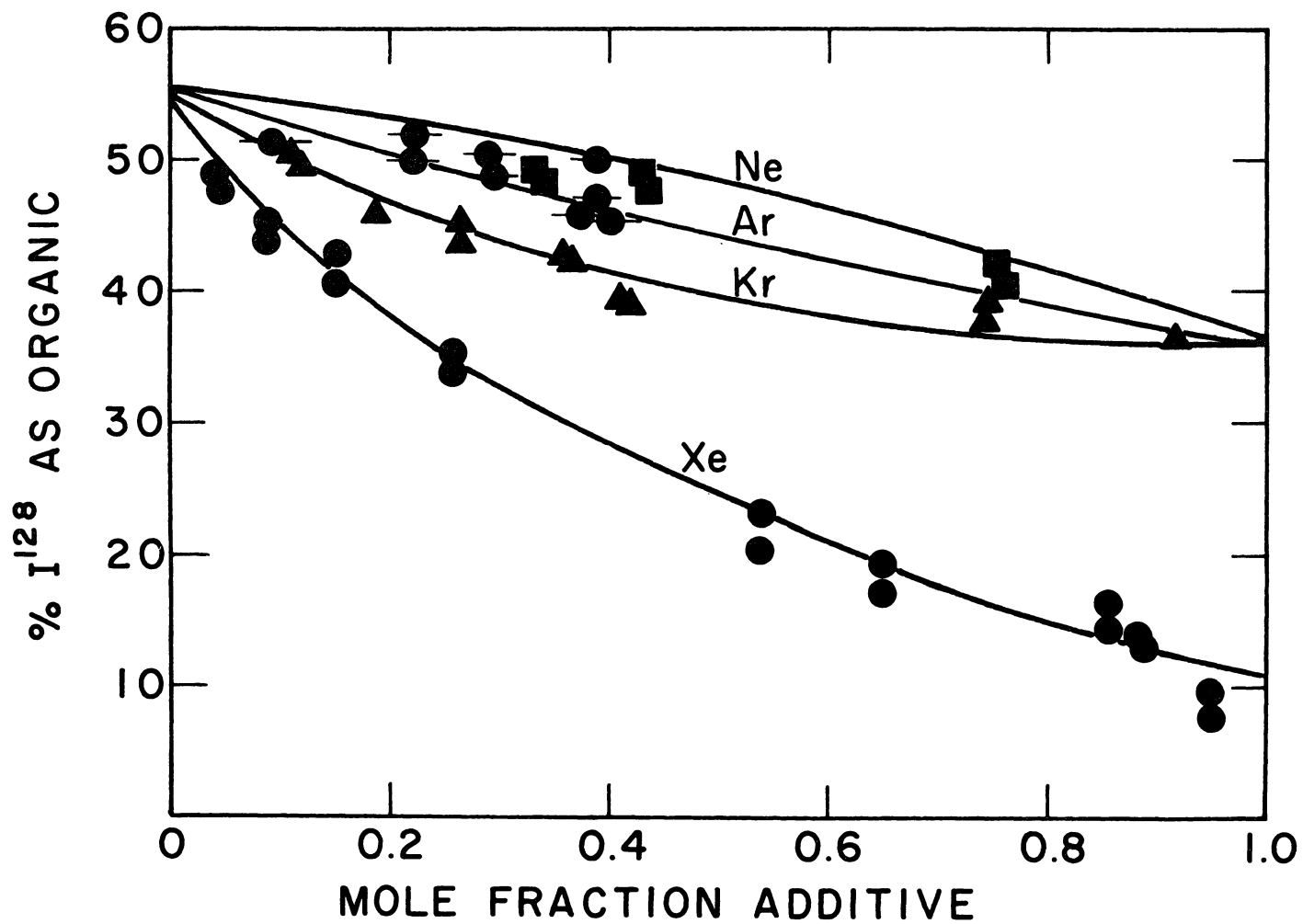


Fig. 6. Percent I^{128} formed as organic activity in CH_4 -inert gas mixtures containing CH_3I and I_2 . Moderator symbols are listed in caption for Fig. 5. The solid curves are calculated.

ev. It is unlikely that excited ionic states higher than the 1D_2 will exist in the CH_4 environment. The ionization potential of CH_4 is 12.99 ev.⁵⁵ For the process $I^+(^1D_2) + CH_4 \rightarrow I + CH_4^+$ to occur, the relative energies of the reacting species must be much greater than that supplied by the (n,δ) activation.⁴⁴ However, charge transfer between CH_4 and I^+ in the 1S_2 or higher states are exothermic and very probable since the excess energy (the energy defect) is assimilated by the various internal degrees of freedom of the CH_4 ion.

The ionization potential of an I atom is 10.454 ev and that of Xe is 12.127 ev.⁵⁴ Thus, the process $I^+(^1D_2) + Xe \rightarrow I + Xe^+$ is exothermic by 0.029 ev. For this near-resonance charge-transfer process, the cross-section will be maximum for relative energies of about 2 ev and slowly decrease for energies greater than 2 ev.⁴⁴ The smallest energy defect for the possible charge-transfer processes involving the other inert gases is 1.840 ev endothermic for the $I^+(^1D_2) + Kr$ reaction. Hence, these processes involving Kr, Ar, or Ne charge-transfer with I^+ ions in energy states of 1D_2 or less have an extremely small probability of occurrence.

Kinetic energy moderation. All attempts to fit the data of figure 6 to the Estrup-Wolfgang theory were unsuccessful. However, if it is assumed that the maximum inert-gas kinetic energy moderation is $54.4 - 36 = 18.4\%$ then the Estrup-Wolfgang moderation equations (Chapter III) serve to describe the observed effects.

In order to calculate S^2 for the inert-gas moderators, the following diameters³⁸ were used: I, 4.8; Xe, 4.9; Kr, 4.3; Ar, 3.6; Ne, 2.6; and CH_4 , 4.2 Å.

Neon, argon, krypton. Thirty-six percent was subtracted from the in-

dividual values for the Ne, Ar, and Kr samples. For essentially pure CH₄, $f/\alpha = 4.29$; thus, $(\alpha/\bar{f})(\text{fraction of } I^{128} \text{ as organic}) = 0.0428$. Figure 7 is a plot of the experimental data corresponding to $\alpha/f_{\text{CH}_4} \times (I^{128} \text{ Organic Yield} - 36) = I - f_{\text{CH}_4} / \alpha \times K$. A straight line representation indicates agreement with theory. The best visual straight line drawn through the data and ending at the point (0.0428, 4.29) has a slope $K = -0.004 \pm 0.003$ and an intercept $I = 0.06 \pm 0.01$. It is interesting to note that, within the limits of uncertainty, these values correspond to those found for the Br⁸⁰ + CH₄ reaction (Chapter IV). The solid curves of Fig. 6 for Ne, Ar, and Kr were calculated using these values of K and I and the above equation.

Xenon. As stated earlier, the Xe data are not described by the kinetic theory. A lack of agreement still exists even after subtracting 11% from each experimental result. It was suggested in the previous section that Xe could be a more effective moderator since it could easily undergo charge transfer with I⁺(¹D₂). To determine the moderation via the charge-transfer process, the following were subtracted from the original data: (1) the 1.1% CH₃I failure to bond-rupture, (2) the 11% organic I¹²⁸ which is not effected by Xe, and (3) the expected kinetic-energy moderation by Xe. This last factor varied from zero to 18.4% and was calculated in terms of the moderation equation using the slope and intercept determined from Fig. 7 above. Depicted in Fig. 8 is the percent organic I¹²⁸ remaining after correcting for these three effects.

Let the assumption be made that this remaining extent of reaction of I¹²⁸ with CH₄ to produce organically bound I¹²⁸, R, depends on the probability, P, that the I¹²⁸ "collides" with CH₄. Thus, $R = 25P$. The probability will depend on (1) the mole fraction of CH₄, (1 - N), where N is the mole fraction of additive and (2) the relative cross-sections, C, for

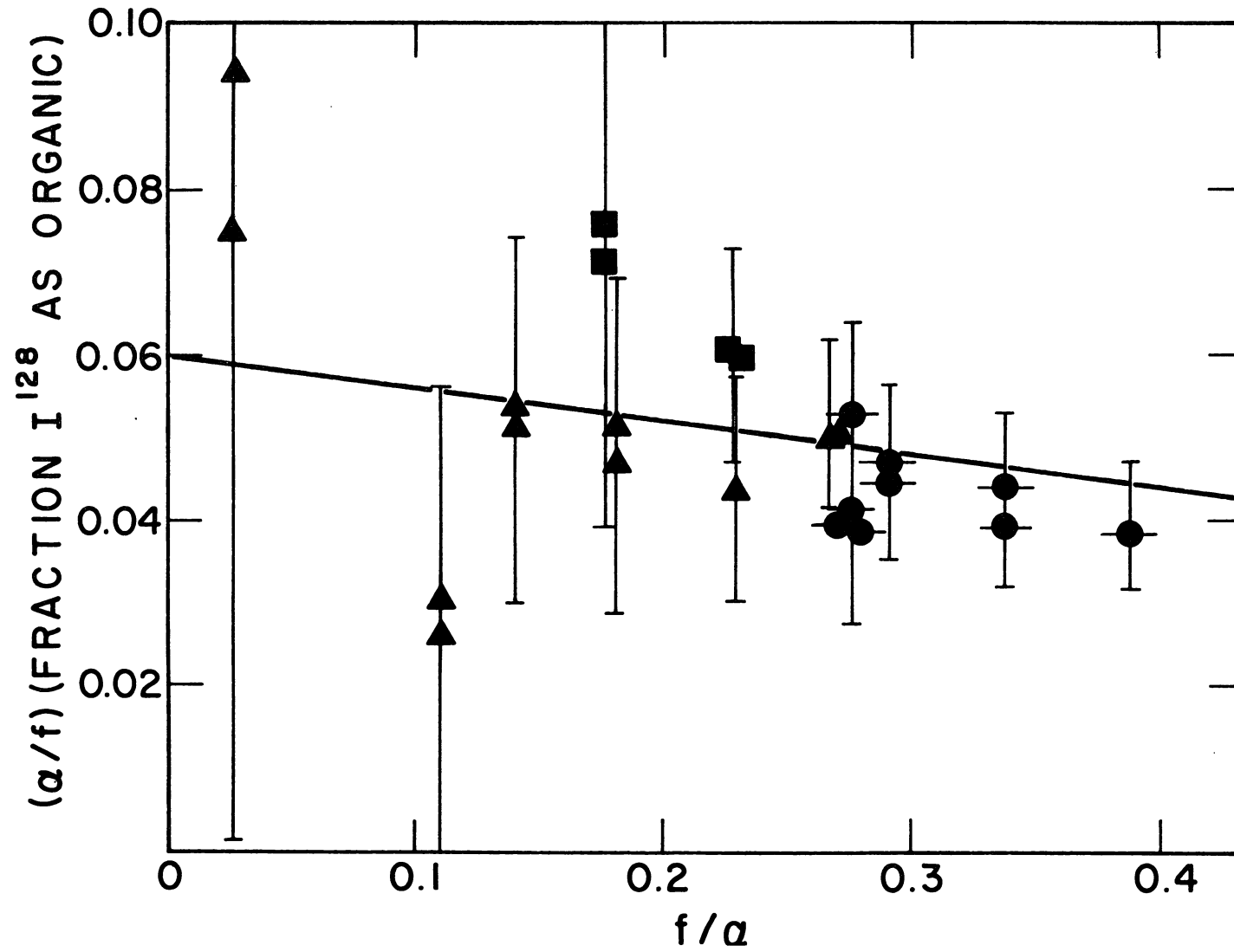
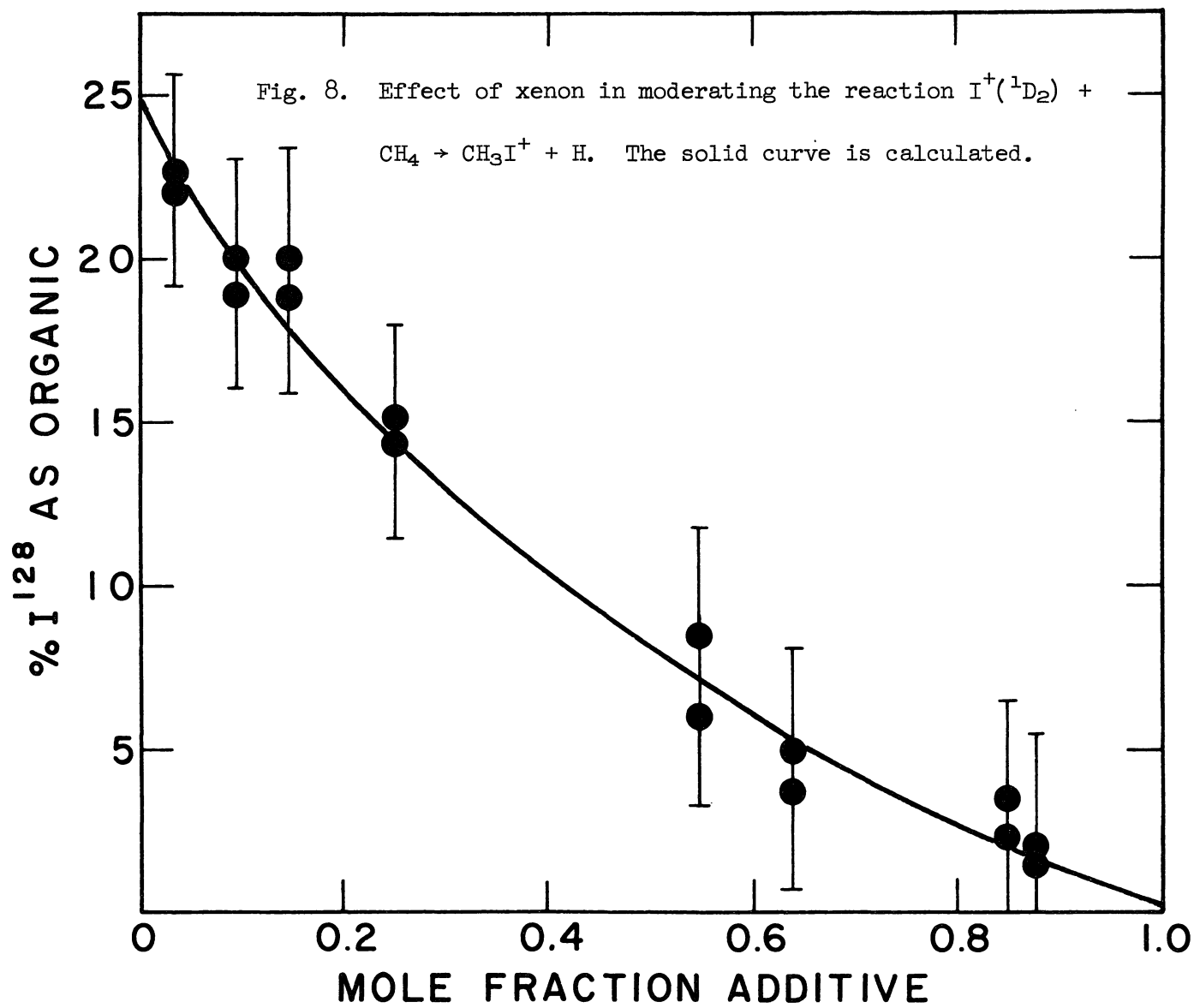


Fig. 7. Plot corresponding to the Estrup-Wolfgang equation. Moderator symbols are listed in captions for Fig. 5.



the two-types of interactions; $C = \sigma[I^+(^1D_2) + \text{Xe charge exchange}] / \sigma[I^+(^1D_2) + \text{CH}_4 \text{ to yield } \text{CH}_3\text{I}^{128}]$. Using these definitions, $C = [(25 - R)(1 - N)]/RN$.

The value of C calculated from the data of Fig. 8 is 2.2 ± 0.6 . Considering the various subtractions and uncertainties, it is somewhat fortuitous that the calculated C values for the various experimental points are in reasonable agreement. The solid curve of Fig. 8 was calculated using this value of C .

It is reasonable to expect the excited I ions to react prior to becoming deactivated by fluorescence. The I ions would have undergone of the order of 100 collisions in the 10^{-8} to 10^{-7} sec. associated with fluorescent deactivation. Only in systems containing a large excess of inert gas would there be a possibility of fluorescent deactivation. This could be the reason that the last Xe data of Fig. 6 are somewhat low.

$\text{I}^{128} + \text{CH}_4(n, \delta)$ Activated Reaction Mechanisms

On the basis of the previous discussions it is concluded that of the $54.4 \pm 0.5\%$ I^{128} found as organic:

$18.4 \pm 2\%$ is formed by a hot reaction or reactions. The experimental evidence, however, is insufficient to conclude whether the hot I^{128} species is an ion or an atom.

$25 \pm 3\%$ is formed as a result of the $\text{I}^+(^1D_2) + \text{CH}_4$ reaction. Considering the energy requirements, if the reaction is a simple H displacement, then the reaction must be $\text{I}^+(^1D_2) + \text{CH}_4 \rightarrow \text{CH}_3\text{I}^+ + \text{H}$.

$11 \pm 2\%$ is formed as a result of the reaction of I^{128} ions (or excited atoms). Either 3P_2 , 3P_1 , or 3P_0 I^+ ions are involved since, as stated above, ions in energy states greater than the 1D_2 would not exist in the

CH₄ environment. If the ionic reaction taking place involves H displacement then, considering the energy available, the reaction must also be

$$I^+ + CH_4 \rightarrow CH_3I^+ + H.$$

The manner in which the CH₃I⁺ gains an electron is not known. It is difficult to accept electron capture as the process. The 9.54 ev exothermicity⁵⁵ would, most probably, be partially dissipated in the form of the internal energy of the molecule and thus probably result in C-I bond rupture.^{56,57} If, instead, C-H bond rupture occurred, then because of the presence of I₂ in the reaction system, CH₂I₂ should be a major product. Gas chromatographic analysis indicated that only a small amount of CH₂I₂ was formed. However, because of the presence of CH₃I and I₂ in the reaction mixture, neutralization of the CH₃I⁺ probably takes place by charge-transfer.

Effect of Molecular Moderators on the Reaction

Results

Listed in Table V are the observed I¹²⁸ organic yields and the values corrected for (a) failure to bond-rupture, (b) I¹²⁸ organic reaction with additive (whose limiting extents of reaction are listed in Table VI), (c) any radiation induced reactions and (d) the fact that the additive removes some I¹²⁸ from organic combination with CH₄.

Failure to bond-rupture. The main source of I¹²⁸ in all the systems is either CH₃I or n-C₃H₇I. The failure to bond-rupture values for I¹²⁸ from CH₃I and C₃H₇I, which must be subtracted for all observed organic yields, are 1.1 and 0.78%, respectively.²⁰

Reaction with additive. Listed in Table VI are the limiting I¹²⁸ organic

Table V.

Organic Yields of I¹²⁸ with CH₄ at Various Mole
Fractions of the Molecular Additives^a

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic Yield (% ± 2.0) ^f
O ₂ ^b	574	80	0.122 ± 0.011	53.5	51.8
	574	87	0.132 ± 0.006	53.5	51.7
	459	180	0.282 ± 0.019	53.0	50.5
	459	192	0.295 ± 0.013	50.8	48.2
	35	482	0.932 ± 0.070	40.5	34.7
				43.0	37.2
N ₂ ^b	608	59	0.089 ± 0.009	49.6	48.4
	608	65	0.097 ± 0.006	53.6	52.0
	529	132	0.200 ± 0.016	51.1	49.0
	529	148	0.219 ± 0.009	54.9	52.7
	411	207	0.335 ± 0.026	54.5	51.7
	35	329	0.890 ± 0.120	48.2	42.6
			46.8	41.2	
CF ₄ ^b	577	93	0.139 ± 0.002	52.7	51.1
				52.7	51.1
	445	249	0.359 ± 0.002	50.0	47.4
				50.1	47.5
	247	429	0.635 ± 0.003	47.3	43.5
			47.6	43.8	
	67	640	0.905 ± 0.004	42.6	37.4
			42.8	37.6	
	35	653	0.950 ± 0.003	42.2	36.8
			42.7	37.3	
CH ₂ F ₂ ^b	545	146	0.211 ± 0.002	45.3	43.4
				46.6	44.7
	282.	168	0.373 ± 0.003	42.7	40.2
				44.1	41.6

Table V (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic (% ± 2.0) ^f
CH ₂ F ₂ ^b	284	283	0.499 ± 0.003	37.1	34.5
	229	450	0.663 ± 0.003	31.0	27.4
				31.5	27.7
CHF ₃ ^b	587	88	0.130 ± 0.002	52.9	51.1
				54.1	52.3
	233	143	0.300 ± 0.003	49.4	46.8
				50.0	47.4
	254	334	0.568 ± 0.003	49.1	45.2
				51.1	47.2
192	526	0.733 ± 0.003	39.2	33.8	
			42.2	37.0	
83	536	0.866 ± 0.003	42.9	36.8	
			43.2	37.1	
C ₂ F ₆ ^b	590	92	0.135 ± 0.002	48.8	44.8
				49.2	45.2
	367	188	0.339 ± 0.002	39.7	31.1
				44.0	35.5
	389	311	0.444 ± 0.004	42.0	31.1
	399	331	0.453 ± 0.002	42.0	30.8
				44.3	33.2
	171	287	0.627 ± 0.004	39.5	24.2
150	520	0.776 ± 0.003	40.2	21.4	
			41.4	22.7	
14	649	0.979 ± 0.004	37.2	13.2	
			37.3	13.3	
NO ^c	679	9	0.013 ± 0.001	52.9	51.8
				51.8	50.7
674	13	0.019 ± 0.001	49.4	48.3	
			51.0	49.9	

Table V (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic (% ± 2.0) ^f
NO ^c	652	16	0.024 ± 0.001	47.2	46.1
				51.6	50.5
	454	38	0.077 ± 0.002	42.6	41.5
				43.0	41.9
	373	44	0.106 ± 0.002	39.6	38.5
				39.3	38.2
	562	112	0.166 ± 0.001	35.5	34.4
				36.8	35.7
457	132	0.224 ± 0.002	34.1	33.0	
			31.1	30.0	
289	161	0.337 ± 0.002	26.2	25.1	
			25.1	24.0	
149	561	0.790 ± 0.001	9.2	8.1	
			9.9	8.8	
CH ₃ I ^d	721	1	0.001 ± 0.001	54.8	53.7
	710	2	0.003 ± 0.001	55.0	53.9
				53.4	52.3
	665	3	0.005 ± 0.001	54.2	53.1
				53.9	52.8
	659	7	0.011 ± 0.001	47.1	46.0
				47.8	46.7
	558	10	0.018 ± 0.001	42.2	41.1
				42.3	41.2
	532	12	0.022 ± 0.001	39.2	38.1
40.6				39.5	
460	11	0.023 ± 0.002	38.5	37.4	
			37.9	36.8	
342	12	0.034 ± 0.002	33.5	32.4	
			33.1	32.6	

Table V (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic Yield (% ± 2.0) ^f
CH ₃ I ^d	186	12	0.061 ± 0.004	24.5	23.4
	233	22	0.086 ± 0.003	17.6 17.6	16.5 16.5
	131	22	0.144 ± 0.005	11.7	10.6
	111	34	0.234 ± 0.006	7.4 5.9	6.3 4.8
	197	128	0.417 ± 0.005	4.2 3.9	3.1 2.8
	132	163	0.553 ± 0.005	2.9 2.5	1.8 1.4
n-C ₃ H ₇ I ^d	684	7	0.010 ± 0.001	44.7 44.8	43.6 43.7
	678	15	0.022 ± 0.001	37.4 35.2	36.3 34.1
	482	28	0.055 ± 0.001	28.9 27.3	27.8 26.2
	288	21	0.068 ± 0.002	20.1 18.6	19.0 17.5
	187	22	0.105 ± 0.001	15.9 11.4	14.8 10.3
	181	25	0.121 ± 0.004	14.9 11.8	13.8 10.7
CF ₃ I ^d	620	16	0.025 ± 0.001	35.4 33.7	34.3 32.6
	178	42	0.191 ± 0.004	6.6 5.9	5.5 4.8
C ₆ H ₆ ^c	646	10	0.015 ± 0.001	46.4 48.4	45.3 47.3
	659	15	0.022 ± 0.001	37.7 37.6	36.6 36.5

Table V (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic (% ± 2.0) ^f
C ₆ H ₆ ^c	675	27	0.039 ± 0.001	31.4	30.3
				32.4	31.3
	155	27	0.148 ± 0.002	9.7	8.6
				9.2	8.1
C ₂ H ₆ ^c	470	53	0.101 ± 0.002	31.2	29.9
				32.3	31.0
				293	171
15.4	13.6				
	142	478	0.771 ± 0.003	7.6	4.9
				7.6	4.9
C ₃ H ₈ ^c	630	71	0.101 ± 0.002	22.0	20.6
				24.6	23.2
	500	179	0.264 ± 0.002	15.0	13.1
				17.0	15.1
n-C ₄ H ₁₀ ^c	584	112	0.161 ± 0.002	11.0	9.4
				12.8	11.2
	412	214	0.342 ± 0.002	7.5	5.0
				8.3	5.8
n-C ₅ H ₁₂ ^c	658	37	0.053 ± 0.001	20.1	18.8
				21.3	20.0
	555	92	0.142 ± 0.002	12.5	11.0
				13.6	12.1
n-C ₆ H ₁₄ ^c	648	32	0.047 ± 0.002	18.7	17.5
				22.1	20.9
	358	74	0.171 ± 0.002	8.4	7.0
				11.0	10.6
CH ₃ Cl ^e	585	107	0.155 ± 0.002	29.5	27.7 ^g
				30.0	28.2 ^g
CH ₂ Cl ₂ ^e	589	108	0.155 ± 0.002	22.1	20.7 ^g
				25.2	23.8 ^g

Table V (Con't.)

Additive	Pressure CH ₄ (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % Organic Yield I ¹²⁸	Corrected Organic (% ± 2.0) ^f
CHCl ₃ ^e	561	103	0.155 ± 0.002	23.7 24.8	21.8 ^g 22.9 ^g
CCl ₄ ^e	272	51	0.158 ± 0.001	16.3 19.8	14.8 ^g 18.3 ^g

- a. All samples, except when an iodide was the main source of I¹²⁸, contained 0.5-2 mm CH₃I and 0.1 mm I₂.
- b. Except for a few samples which were irradiated for about 15 seconds, samples were irradiated for 7 seconds.
- c. Samples were irradiated for 15-20 seconds.
- d. Samples were irradiated for 2-30 seconds.
- e. Samples were irradiated for 30 seconds.
- f. Uncertainties based on estimates of uncertainty in positioning 25.0 min. slope through decay data for inorganic and organic fractions for each run and for the uncertainties in applying the various corrections to the data.
- g. Data not corrected for any possible radiation-induced reactions. Since the mole fraction additive was relatively small, it would not be expected that the correction, if any, was larger than 2% at the mole fraction studied.

Table VI

Limiting Organic Yields of I^{128} with the
Additives used in Table V.^a

Additive	Pressure Additive (mm)	Pressure CH_3I (mm)	Mole Fraction Additive	Organic Yield % I^{128}
CH_3I	18		0.995	1.2 ± 0.1
				1.3 ± 0.1
	28			1.4 ± 0.2
CF_3I	44		0.998	1.1 ± 0.2
				1.2 ± 0.1
$n-C_3H_7I$	19			1.3 ± 0.1
C_6H_6	31	(0.1 I_2)	0.997	1.2 ± 0.1
				1.5 ± 0.1
	30	1		1.4 ± 0.1
				1.3 ± 0.1
CH_3Cl	646	5	0.992	7.3 ± 0.5^b
				7.9 ± 0.5
CH_2Cl_2	209	2	0.991	3.9 ± 0.5^b
				4.4 ± 0.5
$CHCl_3$	99	2	0.980	8.7 ± 0.5^b
				7.4 ± 0.5
CCl_4	52	1	0.981	5.2 ± 0.5^b
				2.8 ± 0.5
CH_2F_2	650	10	0.985	3.5 ± 0.1
				3.0 ± 0.1
	693	17	0.976	3.4 ± 0.1
				2.9 ± 0.1
CHF_3	691	1	0.999	5.7 ± 0.4
				7.0 ± 0.4
	630	(0.1 I_2)	0.999	6.7 ± 0.2
				4.7 ± 0.2

Table VI (Con't.)

Additive	Pressure Additive (mm)	Pressure CH ₃ I (mm)	Mole Fraction Additive	Organic Yield % I ¹²⁸
CF ₄	618	4	0.994	4.4 ± 0.4
				4.6 ± 0.4
C ₂ F ₆	621	2	0.997	8.9 ± 0.2
				8.8 ± 0.7
nC ₅ H ₁₂ ^c	113	1	0.991	3.2 ± 1.2
				4.5 ± 0.4
nC ₆ H ₁₄	93	1	0.989	3.1 ± 0.3
				3.2 ± 0.7

- a. All samples containing CH₃I were irradiated 2-25 seconds; I₂ samples were irradiated about 5 minutes.
- b. Isotopes resolved by 100 channel analysis.
- c. Limiting I¹²⁸ organic yields for C₂H₆, C₃H₈, and n-C₄H₁₀ were 2.0, 2.6, and 3.9%, respectively.¹⁰

yields of the molecular additives which were used to moderate the $I^{128} + CH_4$ reaction. A subtractive correction corresponding to the product of the average value of the I^{128} limiting organic yield in the additive multiplied by the additive mole fraction in CH_4 was employed.

Radiation-induced reactions. It was determined that corresponding to a unit mole-fraction of additive there was an organic I^{131} pickup of 3.0%, and 17.0% for CH_4 systems containing CF_4 and C_2F_6 respectively.

Since Ne or Ar + CH_4 systems had an I^{131} pickup of 5% at unit mole fraction additive it was assumed that O_2 and N_2 had the same value (based on electron number of the additive molecule). Relative to CF_4 a value of 2.0% was assumed for CHF_3 and CH_2F_2 . In all the above cases the radiation-induced reaction contributions at a given mole fraction additive were assumed to correspond to the product of the mole fraction additive and the limiting I^{131} organic pickup values quoted above.

No radiation damage was observed in CH_4 systems containing the alkanes and CH_3I . Since the NO moderation curve extrapolates to zero mole fraction NO, it is assumed that no radiation damage occurs in the system under the irradiation conditions.

Removal of I^{128} from CH_4 reaction. In the molecular additive study of the $Br^{80} + CH_4$ reaction, since the limiting organic yields of Br^{80} in the additive and the Br^{80} organic yield with CH_4 were low, no correction was necessary for the Br^{80} removed from possible reactions with CH_4 by additive reaction. However, in the $I^{128} + CH_4$ reaction the organic yields are relatively high and in some cases the limiting organic yields are relatively high (CHF_3 , 5.9%). The maximum correction may amount to a few percent in some cases. This correction corresponds to multiplying the individual I^{128} organic yields, as corrected above, by the factor $100/(1 - x)$ (where

x is the product of the limiting organic yield of I^{128} in the additive and the additive mole fraction in CH_4).

Undoubtedly some of the I^{128} undergoes inorganic reactions (by virtue of its nuclear activation) with the additive. Since the extent of this inorganic I^{128} reaction is not known (probably of the same order of magnitude as the limiting I^{128} organic yield in the additive) only a correction for the organic I^{128} additive reaction is made.

Discussion.

Compared to the inert gases, which can moderate the $I^{128} + CH_4$ reaction only by removal of kinetic energy and charge-transfer processes, molecular additives can moderate the reaction by the four processes discussed in Chapter III. Since it was determined from the inert-gas moderation that a large fraction of the I^{128} organic yield is the result of electronically excited ion reactions, it may be possible to observe charge transfer and ion-molecule reactions involving the molecular additives. In addition, it may be possible to determine relative quenching efficiencies of excited I species by the molecular moderators.

All molecular additives, regardless of their nature, should be able to moderate the "hot" reaction to 36% (at unit mole-fraction additive) I^{128} organic yield, which corresponds to kinetic energy removal of the 18.4% "hot" reaction.

In addition to moderation of the 18.4% hot reaction, if the additive can undergo charge transfer or ion-molecule reactions with $I^+(^1D_2)$ it can inhibit the formation of organic I^{128} (an additional 25%) to 11% I^{128} organic yield (at unit mole fraction additive).

If the additive can undergo charge transfer, chemical reactions, or physically quench the excited species, it can inhibit the formation of

organic I^{128} to 0% at unit mole fraction additive.

Unless thermal ion-molecule reactions involving the excited I^+ can be ruled out on the basis of energy requirements, it is impossible to distinguish between ion-molecule and charge-transfer reactions using the moderation technique. Another complicating factor is that the observed moderation of the thermal reactions may be a result of quenching of excited I species.

N_2 , O_2 , and CF_4 moderation. The data for the moderation of the $I^{128} + CH_4$ reaction by N_2 , O_2 , and CF_4 are depicted in figure 9. The solid curves were calculated according to the Estrup-Wolfgang moderation equation using the values for I and K determined by the inert-gas moderation. The molecular diameters used to calculate S^2 for O_2 and N_2 are ³⁸ 3.6 and 3.7 Å, respectively, and the diameter for CF_4 , 5.5 Å, was estimated. The data tends to extrapolate to 36%, indicating that these additives are only effective in cooling the 18.4% "hot" reaction. Although the O_2 data are fairly well described by the solid curve, the experimental values for N_2 and CF_4 tended to be slightly higher than their respective solid curves. A possible reason for this difference is that in a high velocity collision between I^{128} and the molecular additive, because of the presence of more than one atom in the molecule, the effective collision may not be with the whole molecule but with an atom in the molecule, resulting in a smaller energy decrement. Since the molecular diameter for CF_4 was estimated and the solid curves were based on values of I and K determined by inert-gas moderation, uncertainties in these values could result in some change in the shape of the solid curves.

Since the moderation data extrapolates to about 36%, cross-sections for charge transfer, physical quenching of excited I atoms, and I reaction

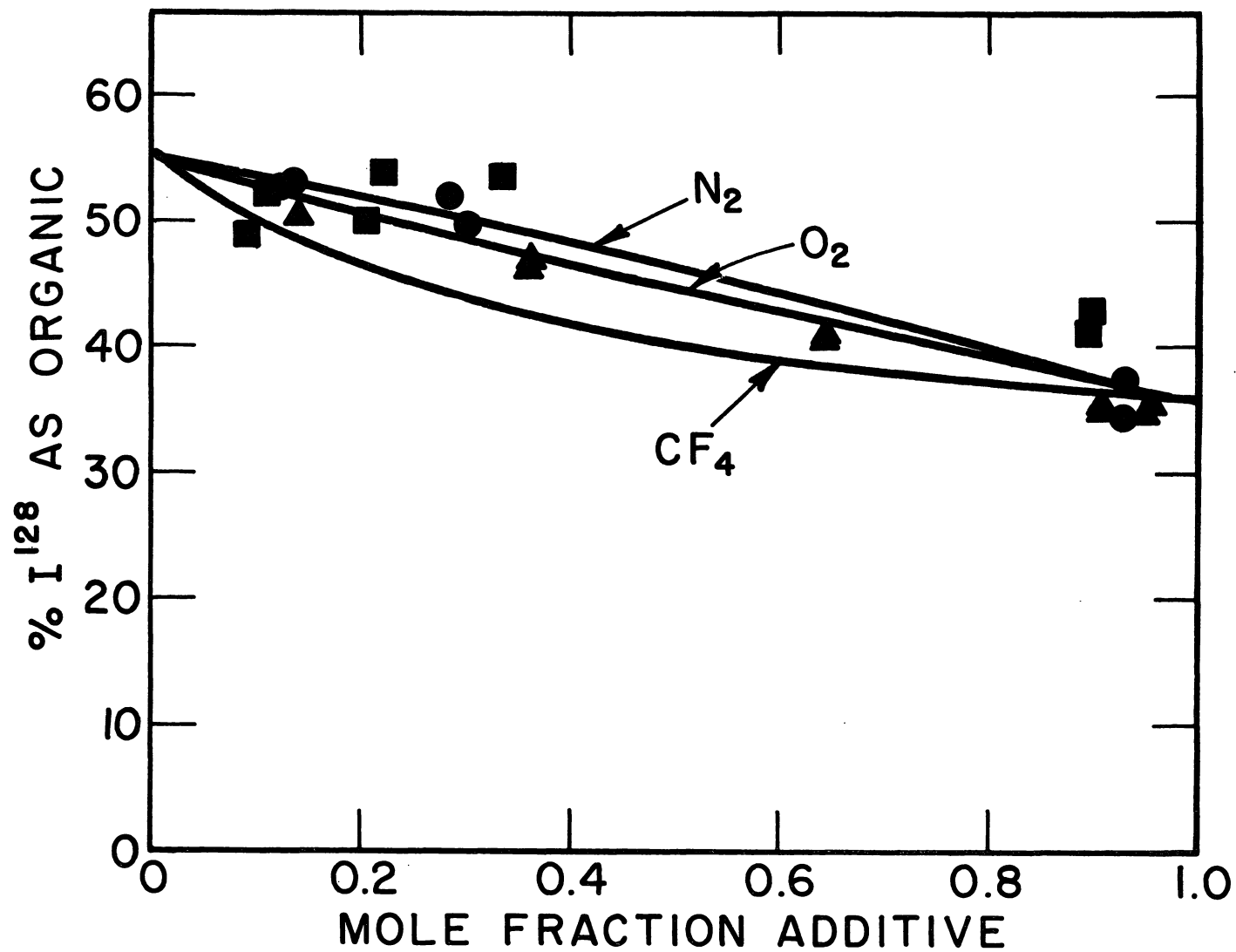


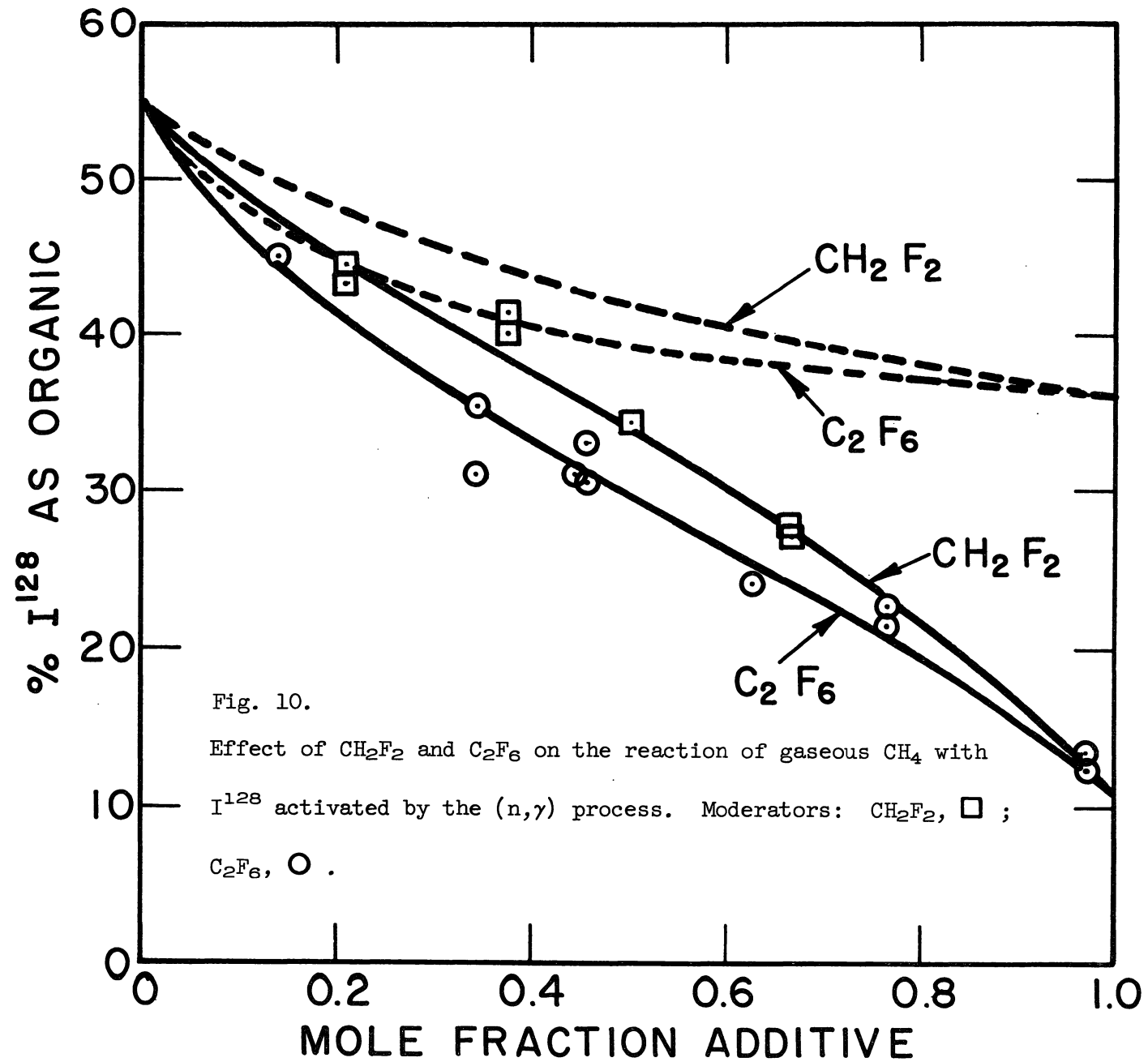
Fig. 9. Effect of N_2 , O_2 , and CF_4 on the reaction of gaseous CH_4 with I^{128} activated by the (n,γ) process. Moderators: N_2 , \blacksquare ; O_2 , \bullet ; CF_4 , \blacktriangle .

with the additive are very small. Iodine atoms do not undergo chemical reactions with N_2 and O_2 . The ionization potential for N_2 being 15.58,⁵⁸ the cross-section for charge transfer is negligible under the experimental conditions. The spectroscopically determined ionization potential for O_2 is 12.2 ± 0.2 ev⁵⁹ while the value determined by photoionization is 12.08 ± 0.01 ev.⁵⁵ From the moderation curve (extrapolating to 36%) it would appear that the ionization potential for O_2 is greater than 12.16 ev.

$I^+(^1D_2)$ cannot undergo thermal reactions with CF_4 because the energy required for reaction is greater than that possessed by the excited ion. Although the ionization potential for CF_4 is not known, that for CH_3F (12.84)⁶⁰ is. In a series of compounds such as CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CCl_4 the ionization potential increases in that order. It is estimated that the CF_4 ionization potential is greater than that for CH_4 (12.99 ev). Therefore, it is extremely unlikely that charge-transfer occurs between CF_4 and $I^+(^1D_2)$. Since the CF_4 moderation curve extrapolates to 36%, the cross-section for physically quenching the excited iodine states is rather small.

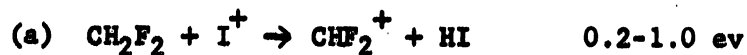
C_2F_6 , CH_2F_2 , and CHF_3 moderation. Depicted in figure 10 are the data for the moderation of the $I^{128} + CH_4$ reaction by CH_2F_2 and C_2F_6 . The dotted curves were calculated according to the Estrup-Wolfgang moderation equation, using the values for I and K determined by inert-gas moderation. They represent the moderation of the 18.4% "hot" reaction by kinetic energy cooling. The diameters for C_2F_6 , CH_2F_2 , and CHF_3 were estimated as 6.8, 4.9, and 5.2 Å, respectively. The solid curves were calculated by the method described below. Since the data tend to extrapolate to 11%, it would indicate that CH_2F_2 and C_2F_6 inhibited the $I^+(^1D_2) + CH_4$ reaction.

Because CF_4 does not physically quench excited iodine species and



alkanes are poor quenchers of excited states,⁴⁸ it is not expected that CH_2F_2 and C_2F_6 would quench excited $\text{I}^+(\text{}^1\text{D}_2)$. Therefore, the moderation to 11% must be due to either charge transfer or ion molecule reactions between $\text{I}^+(\text{}^1\text{D}_2)$ and the additive.

Charge transfer cannot occur between CH_2F_2 and $\text{I}^+(\text{}^1\text{D}_2)$ since the ionization potential of CH_2F_2 is about that of CH_4 . Its moderation must be due to a thermal ion-molecule reaction with $\text{I}^+(\text{}^1\text{D}_2)$ forming inorganic I^{128} . Although there is a lack of fluorocarbon thermodynamic data and ionization potentials for such radicals as CHF_2 , which make it impossible to determine exactly the energy requirement for the various reactions, their energies can easily be estimated. Reactions between $\text{I}^+(\text{}^1\text{D}_2)$ and CH_2F_2 leading to organic I^{128} formation require more energy than is supplied by the $\text{I}^+(\text{}^1\text{D}_2)$ excitation energy. One-step abstraction reactions between $\text{I}^+(\text{}^1\text{D}_2)$ and CH_2F_2 with their accompanying endothermicities, which lead to inorganic I^{128} formation are:



The energy requirement for reaction (a) was calculated assuming that the ionization potential of CHF_2 is comparable to CF_3 . Two values are listed in the literature for the ionization potential of CF_3 , 9.3 ev⁶¹ and 10.10 ev.⁶²

Within the uncertainty in the estimates for the reaction energy, it would appear that thermal reactions are possible between $\text{I}^+(\text{}^1\text{D}_2)$ (1.70 ev excitation energy) and CH_2F_2 forming inorganic I^{128} . It is suggested that the observed moderation of the $\text{I}^+(\text{}^1\text{D}_2) + \text{CH}_4$ reaction is a result of ion-molecule reactions involving $\text{I}^+(\text{}^1\text{D}_2)$ and CH_2F_2 forming inorganic I^{128} .

Reactions (a) and (b) are such possible reactions. The relative cross-section, C , for the $I^+(^1D_2) + CH_2F_2$ reaction compared to the $I^+(^1D_2) + CH_4$ reaction was calculated. (This calculation is discussed on page 58). The C value was found to be 0.49 ± 0.3 . Qualitatively it would be expected that the cross-section for the $I^+(^1D_2)$ reaction with CH_2F_2 be less than that for CH_4 . CH_4 has 4 H's available for displacement reaction with I , while CH_2F_2 has only 2 for abstraction. Since $I^+(^1D_2)$ can only undergo a few collisions before it either loses its excitation energy by fluorescence or becomes stabilized in chemical combination, the number of H atoms in the molecule should be a factor in determining its reaction cross section with $I^+(^1D_2)$.

Each point of the solid curve for the CH_2F_2 moderation (figure 10) corresponds to the sum of three I^{128} organic yields, whose maximum values at zero mole fraction CH_2F_2 are 18.4, 25, and 11%, corresponding to the "hot" reaction, the $I^+(^1D_2)$ thermal reaction, and the thermal excited atom or ion reaction with CH_4 , respectively.

(a) The "hot" $I^{128} + CH_4$ reaction contribution at each mole fraction of CH_2F_2 was calculated from the Estrup-Wolfgang moderation equation, which corresponds to the I^{128} organic yields of the dotted CH_2F_2 curve in figure 10 minus 36 at each individual mole fraction CH_2F_2 . This contribution is zero at unit mole fraction CH_2F_2 .

(b) The $I^+(^1D_2) + CH_4$ reaction contribution at various mole fractions of CH_2F_2 is calculated from the C equation (page 58) using a value of 0.49 for C . This contribution is zero at unit mole fraction CH_2F_2 .

(c) The value 11% I^{128} organic yield, which is unaffected by the CH_2F_2 moderator, corresponds to the I^{128} excited atom or ion (3P_2 , 3P_1 , or 3P_0 I^+ ions) organic reactions with CH_4 .

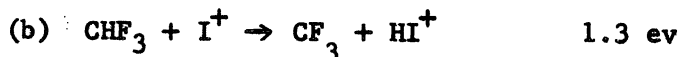
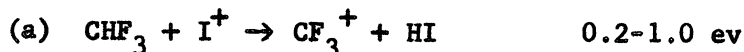
The ionization potential of C_2F_6 is not known, but should be equal to or greater than the value for C_2H_6 (11.65).⁵⁵ If the C_2F_6 ionization potential is less than 12.16 charge transfer between C_2F_6 and $I^+(^1D_2)$ is possible. Charge transfer between such ions as $I^+ 3P_0$ and $3P_1$ can be eliminated from consideration since the ionization potential of C_2F_6 is undoubtedly greater than 11.33 ev. All possible reactions between I^+ and C_2F_6 have an energy requirement which is greater than the excitation energy of $I^+(^1D_2)$. Therefore, the observed moderation of the $I^{128} + CH_4$ reaction to 11% at unit mole fraction C_2F_6 must be the result of a charge transfer reaction between C_2F_6 and $I^+(^1D_2)$.

The relative cross-section, G , for $I^+(^1D_2) + C_2F_6$ charge transfer reaction, compared to the $I^+(^1D_2) + CH_4$ reaction to yield CH_3I^{128} , calculated from the data (see page 58), was found to be 0.57 ± 0.3 . It is estimated that the ionization potential of C_2F_6 is between 11.65 and 12.16 ev.

There are several possible reasons why the charge transfer cross-section for C_2F_6 is smaller than that of Xe (2.2). One possibility is that the energy defect for the $C_2F_6 + I^+(^1D_2)$ charge transfer reaction could be larger than that for the Xe charge transfer reaction, resulting in a smaller cross-section or probability for charge transfer. In charge exchange between Xe and $I^+(^1D_2)$ there are no steric factors involved. The ionization potential of C_2F_6 is believed to be due to the removal of an electron localized in the C-C bond.⁶⁰ Therefore, the presence of fluorine groups in the molecule can sterically hinder charge-transfer reactions involving the removal of an electron from the C_2F_6 molecule.

Since the ionization potential of CHF_3 is about that of CH_4 , charge transfer cannot occur between CHF_3 and $I^+(^1D_2)$. As in the case of CH_2F_2 moderation, possible inhibition of the $I^+(^1D_2) + CH_4$ thermal reaction may

be due to thermal ion-molecule reactions between $I^+(^1D_2)$ and CHF_3 . One step abstraction reactions between $I^+(^1D_2)$ and CHF_3 leading to inorganic I^{128} formation are:



Experimentally it is observed (Table V) that the CHF_3 moderation data tend to extrapolate to 36%. This indicates that the cross-section for $I^+(^1D_2)$ thermal ion-molecule reactions with CHF_3 is quite small. One would expect that CHF_3 be a less effective moderator of the $I^+(^1D_2) + CH_4$ reaction because of its smaller H content than CH_2F_2 , but not to the extent observed. No reason is evident for this behavior of CHF_3 .

NO, CH_3I , CF_3I , $n-C_3H_7I$, and C_6H_6 moderation. Depicted in figure 11 are the data for the moderation of the $I^{128} + CH_4$ reaction by NO, CH_3I , CF_3I , $n-C_3H_7I$, and C_6H_6 . The solid curves are the best curves through the experimental data. Moderation by these additives extrapolates to zero percent I^{128} organic yield at unit mole fraction additive, which indicates that these additives moderate all of the thermal I^{128} reactions with CH_4 .

The ionization potentials of these additives (see Appendix I) are all less than that of the iodine atom. If the 11% thermal reaction of I^{128} and CH_4 is due to reactions of I^+ ions (3P_0 , 3P_1 , and 3P_2), these moderators can inhibit the $I^{128} + CH_4$ reaction by charge transfer reactions with the I^+ ions.

The thermal ion-molecule reaction $I^+ + CH_3I \rightarrow I_2^+ + CH_3$ ($\Delta H = -15 \text{ kcal mole}^{-1}$) has been observed⁴⁹ in the mass spectrometer. It is possible that the moderation by the iodides is due to such a process.

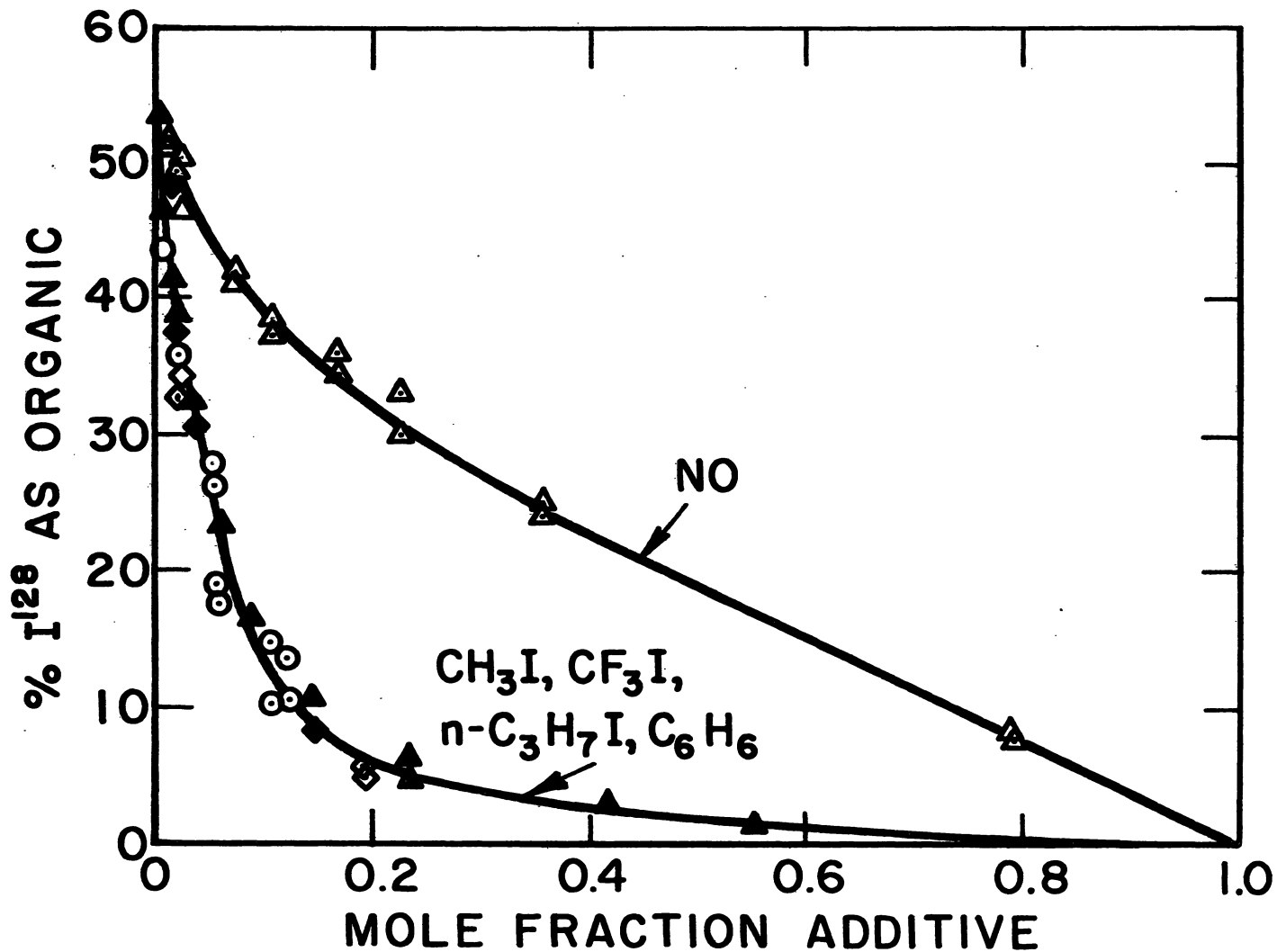


Fig. 11. Effect of NO, CH₃I, CF₃I, n-C₃H₇I, and C₆H₆ on the reaction of gaseous CH₄ with I¹²⁸ activated by the (n,γ) process. Moderators: NO, Δ ; CH₃I, \blacktriangle ; CF₃I, \diamond ; n-C₃H₇I, \odot ; C₆H₆, \blacklozenge .

Unfortunately, there is no information concerning quenching of excited states by these additives which could be of value in determining the relative importance of physical quenching of excited states. As a result, physical quenching can not be ruled out as a possibility in the inhibition of the $I^{128} + CH_4$ reaction.

It is obvious from the above discussion that the problem of interpreting these moderation curves is quite difficult in view of all the moderation possibilities. C values calculated in the usual manner indicate a value ranging from 2 to 5 for NO and about 23 for CH_3I , CF_3I , $n-C_3H_7I$, and C_6H_6 .

No known compounds have been found by reaction of I and NO. The observed moderation of NO may be due to both charge transfer of the I^+ ions and physical quenching of excited I species.

The approximate C value for the iodides and C_6H_6 is much larger than that for NO. It may be that this is due to an ion-molecule reaction which has a much larger cross-section than the $I^{128} + CH_4$ reactions. In order to determine if the H groups were responsible for the high moderation cross-section, moderation by CF_3I , having the H groups substituted by the more inert F groups, was studied. It was found (see Figure 11) that CF_3I moderated the $I^{128} + CH_4$ reaction with the same efficiency as CH_3I . Since the C_2F_6 relative charge-transfer cross-section, C, was about 0.5, it is difficult to imagine that the relative charge-transfer cross-section for the iodides and C_6H_6 is 23. Probably the largest contribution to the reaction inhibition efficiency is either physical quenching or ion-molecule reactions or both. Possibly, when more is learned about charge-transfer reactions and physical quenching efficiencies of the iodides and C_6H_6 , a more definite interpretation of their moderation curves will be made.

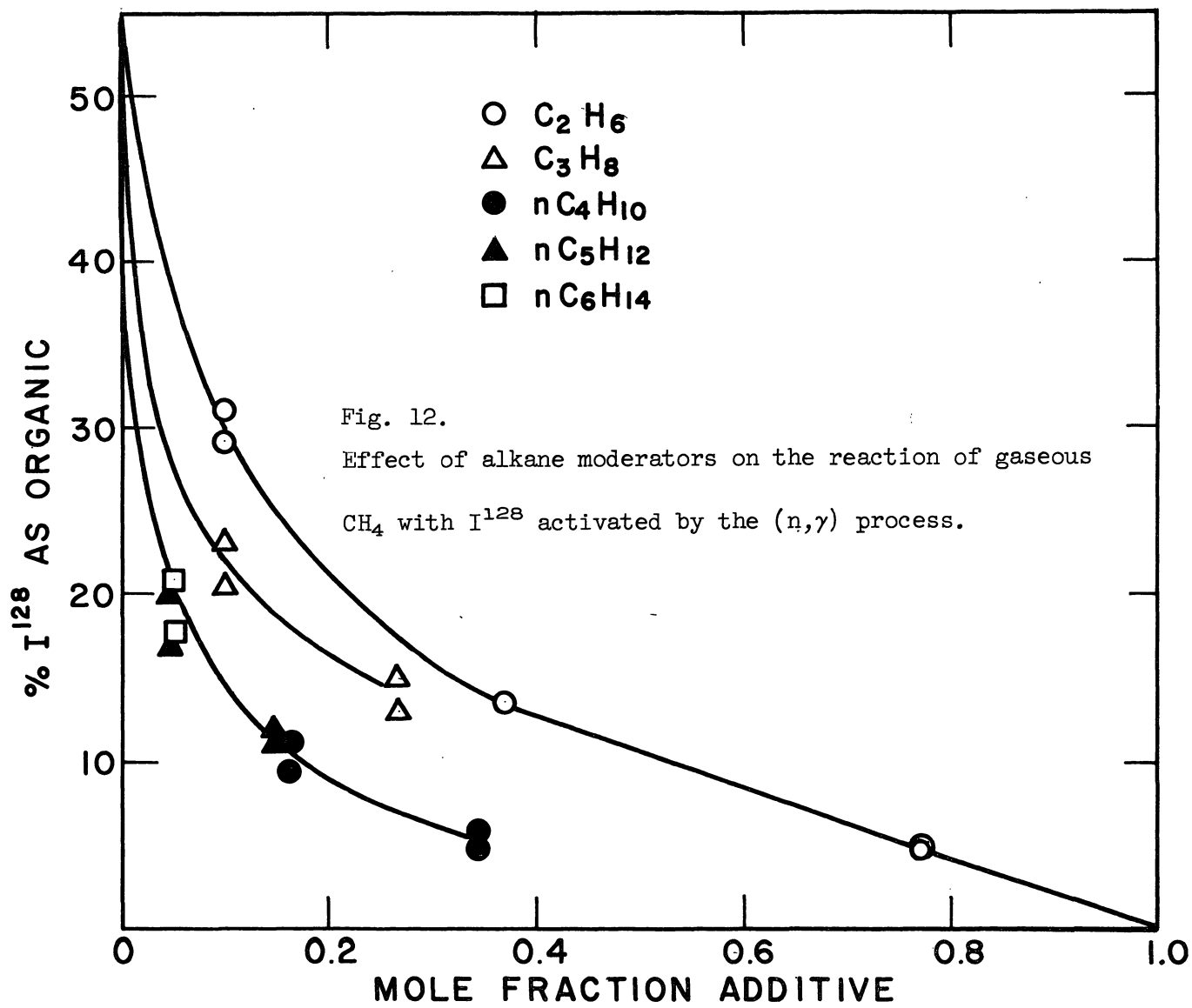
Alkane moderation. Depicted in Figure 12 are the data for the moderation of the $I^{128} + CH_4$ reaction by the alkanes. The solid curves are the best curves through the data. The inhibition of the $I^{128} + CH_4$ reaction by the alkanes tends to extrapolate to 0% at unit mole fraction additive, indicating that the alkanes inhibit all the thermal I^{128} reactions with CH_4 .

Since CH_4 is undoubtedly a poor quencher of excited I states (as indicated by the high thermal I^{128} organic yield in CH_4) and alkanes have been found generally to be poor quenchers⁴⁸ of excited atoms, it will be assumed that the physical quenching correction of excited I by the alkanes is very small. Therefore, the observed moderation of the thermal $I^{128} + CH_4$ reactions must be due to ion-molecule or charge-transfer reactions, or both.

The ionization potentials of the alkanes are listed in Appendix I. It can be seen that all the alkane additives (other than CH_4) can undergo charge-transfer reactions with $I^+(^1D_2)$ while C_3H_8 and the higher hydrocarbons can undergo charge transfer with $I^+ ^3P_1$ and 3P_0 . $n-C_6H_{14}$ can undergo charge transfer with all I^+ species.

I^{128} reactions with the alkanes to form organic and inorganic I^{128} have comparable energy requirements with CH_4 . For example the reaction $I^+ + C_2H_6 \rightarrow C_2H_5I^+ + H$ has an endothermicity of at least 0.9 ev which is comparable to 0.78 ev endothermicity for $I^+ + CH_4 \rightarrow CH_3I^+ + H$.

Since C_2H_6 can only moderate the $I^+(^1D_2) + CH_4$ reaction by charge transfer, C_2H_6 inhibition should extrapolate to 11%. But the data extrapolates to 0%, indicating that C_2H_6 is inhibiting other I thermal reactions, involving $I^+ ^3P_0$ and 3P_1 and 3P_2 and/or excited I atoms, probably by ion-molecule reactions. Because the endothermicity for organic I^{128} formation with the higher alkanes is comparable to CH_4 , it is difficult



to believe that I^{128} preferentially undergoes only reactions of the type $RH + I^+ \rightarrow R^+ + HI$, which have comparable energy requirements with such reactions as $RH + I^+ \rightarrow RI^+ + H$.

If the 11% $I^{128} + CH_4$ reaction is a result of excited $I^+ \ ^3P_0$ and $\ ^3P_1$ reactions then the observed inhibition by C_3H_8 and the higher alkanes to 0% can be explained on the basis of charge-transfer reactions.

It is observed experimentally (see Figure 12), that the order of increasing efficiency of the inhibition of the $I^{128} + CH_4$ reaction by the alkanes is C_2H_6 (~ 5) $<$ C_3H_8 (~ 10) $<$ C_4H_{10} , C_5H_{12} , and C_6H_{14} (~ 23). (Approximate C values which have been calculated for the corrected I^{128} organic yields of Table V are listed in parentheses.) Except in the case of C_4H_{10} , C_5H_{12} , and C_6H_{14} , where the error spread in the C values is quite wide, the calculated C values are not constant for all the experimental values, tending to decrease with increasing alkane mole fraction.

It is difficult to imagine that such a range of C values is possible for the alkanes if charge transfer is the only reaction inhibition. Besides, C_2H_6 inhibits the reaction, as noted above, probably by ion-molecule reactions as indicated by its extrapolation at 0%. In the C_2F_6 moderation of the $I^{128} + CH_4$ reaction the C_2F_6 charge-transfer relative cross-section, C, was about 0.5. It seems, from the above discussion, that moderation by charge transfer, only, can not explain all the facts.

Gordus and Willard¹⁰ determined chromatograms for I^{128} reactions in excess alkanes. For the reaction of I^{128} in excess C_2H_6 , the organic iodides were CH_3I , 0.5; CH_2I_2 , 0.1; C_2H_3I , 0.1; and C_2H_5I , 1.3%; for I^{128} in excess C_3H_8 they were CH_3I , 1.3; CH_2I_2 , 0.1; C_2H_3I , 0.1; C_2H_4I , 0.3; *i*- C_3H_7I , 0.5; and *n*- C_3H_7I , 0.3%; for I^{128} with *n*- C_4H_{10} the data indicate even a larger fraction of C-C bond rupture. The organic iodides formed in this system

were CH_3I , 2.1; CH_2I_2 , 0.1; $\text{C}_2\text{H}_3\text{I}$, 0.1; $\text{C}_2\text{H}_5\text{I}$, 0.8; and $\text{C}_4\text{H}_9\text{I}$, 0.8%.

It is observed that the moderating efficiencies increase with the increasing molecular complexity of the alkane. One rationalization of the data is that I^+ (excited states) reacts with the alkane (R-H) to form RI^+ . By neutralization of the charge of RI^+ , RI could decompose forming the smaller iodides observed by gas chromatography and inorganic I. These types of reactions, in addition to charge-transfer reactions in the pure alkane, may explain why I^{128} has an anomalously low organic yield in the higher alkanes in the gaseous state.

Chloromethane moderation. On the basis of the limited data of chloromethane moderation (see Table V) of the $\text{I}^{128} + \text{CH}_4$ reaction, the moderation efficiencies of the chloromethanes lie between C_2H_6 and C_3H_8 . The order of moderating efficiencies are $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CH}_3\text{Cl}$.

The ionization potentials of the chloromethanes are listed in Appendix I. It is seen that CH_3Cl and CH_2Cl_2 can inhibit, by charge transfer, $\text{I}^+(\text{}^1\text{D}_2)$ and ${}^3\text{P}_0$ reactions, while CHCl_3 and CCl_4 can only inhibit $\text{I}^+(\text{}^1\text{D}_2)$ reactions by charge transfer.

On the basis of ionization potential it would be expected that CH_2Cl_2 and CH_3Cl be more effective than CCl_4 and CHCl_3 in quenching of the thermal $\text{I} + \text{CH}_4$ reactions. The observed moderation by the chloromethanes could be due to both charge transfer and ion-molecule reactions, with ion-molecule reactions being the more efficient inhibitors. Since the efficiency of moderators increases with the Cl content, it may be that the I^{128} reacts with the additive to abstract Cl, for example, the reaction $\text{I}^+ + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{ICl}$, endothermic by only 0.4 ev.

Chapter VI. I^{128} (n, γ) ACTIVATED REACTIONS WITH
 CD_4 AND MOLECULES OTHER THAN CH_4

Introduction

It was seen that Br^{80} reacts with CH_4 by virtue of its kinetic energy and that a positive charge is not a requirement for reaction. The $I^{128} + CH_4$ reaction is more complex, being activated by kinetic energy, electronic excitation energy, and a positively charged I^{128} . The purpose of this chapter is to discuss I^{128} reactions with molecules other than CH_4 , in the light of CH_4 reaction mechanisms of I^{128} and the influence of moderators on the CH_4 reactions. Because of the obvious complexity of multi-carbon reactions, as evidenced by the anomalous I^{128} organic yields in the higher alkanes, only mono-carbon molecules will be discussed.

Results and Discussion

$I^{128} + CD_4$ Reaction.

The moderation data of the $I^{128} + CD_4$ reaction for CH_3I , Kr, and Xe are listed in Tables VII and VIII.

Figure 13 is a log-log plot of the I^{128} organic yield as a function of mole fraction of CD_4 (CH_3I additive). The straight line was calculated by the "method of averages." The limiting organic yield of I^{128} in CD_4 is $52.3 \pm 1.0\%$ as compared to $54.4 \pm 0.5\%$ for the $I^{128} + CH_4$ reaction.

In order to determine whether the "hot" or thermal reactions were effected by the CD_4 , limiting organic yields at unit mole fraction Kr and Xe were determined. These data are listed in Table VIII.

The average limiting I^{128} organic yield at unit mole fraction additive for Kr and Xe are (see Table VIII) $36.6 \pm 2\%$ and $11.6 \pm 2\%$, which are comparable to the values for CH_4 . Therefore, only the "hot" fraction of the

Table VII.

Percent I^{128} Stabilized in Organic Combination
in Mixtures of CD_4 and CH_3I^a

Additive	Pressure CD_4 (mm)	Pressure Additive (mm)	Mole Fraction CD_4^b	Uncorrected % I^{128} as Organic	Corrected % I^{128} as Organic ^c
CH_3I	639.0	1.0	$0.9984 \pm .0024$	49.8	48.7 ± 0.5
				54.7	53.6 ± 0.2
	677.0	5.0	$0.9927 \pm .0023$	48.2	47.1 ± 0.2
				49.9	48.8 ± 0.5
	596.0	10.0	$0.9835 \pm .0025$	40.0	38.9 ± 0.4
				41.6	40.5 ± 0.5
571.0	15.0	$0.9744 \pm .0026$	34.1	33.0 ± 0.4	
			34.2	33.1 ± 0.4	
562.0	25.0	$0.9574 \pm .0026$	26.8	25.7 ± 0.4	

- a. All samples contained 0.1 mm I_2 and irradiated for 7 seconds.
- b. In order to reduce the error due to the vapor pressure of CD_4 at liquid N_2 temperature, large quartz bulblets were used (about 6 ml. in size).
- c. Uncertainty based on estimates of uncertainty in positioning 25.0 minute slope through the decay data for inorganic and organic fractions for each run. Data corrected for failure to bond-rupture.

Table VIII.

Percent I^{128} Stabilized in Organic Combination
in Mixtures of CD_4 and Inert Gases^a

Additive	Pressure CD_4 (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % I^{128} as Organic	Corrected % I^{128} as Organic ($\pm 2\%$)
Kr	153	489	$0.762 \pm .004$	47.4	34.8^b
				50.8	38.2^b
	62	493	$0.888 \pm .005$	50.7	38.7^b
Xe	47	425	$0.900 \pm .005$	47.2	34.6^b
				28.0	10.6^c
	45	516	$0.920 \pm .005$	29.9	12.5^c

- a. All samples contained about 0.5 mm CH_3I and 0.1 mm I_2 , and were irradiated for 7 seconds.
- b. Organic yields corrected for 1.1% failure to bond-rupture of I^{128} from CH_3I^{128} , for radiation-induced reactions (using Figure 5 of Chapter V, since experimental conditions were comparable), and for the 16.3% hot I^{128} reaction at each mole fraction of Kr (using the Estrup-Wolfgang moderation equation of Chapter V).
- c. In addition to correcting for the failure to bond-rupture of I^{128} and for radiation-induced reactions (Figure 5, Chapter V), a correction term corresponding to the 25% $^1D_2 I^{128}$ reaction (using the C equation, $2.2 = (25 - R)(1 - N)/RN$, of Chapter V).

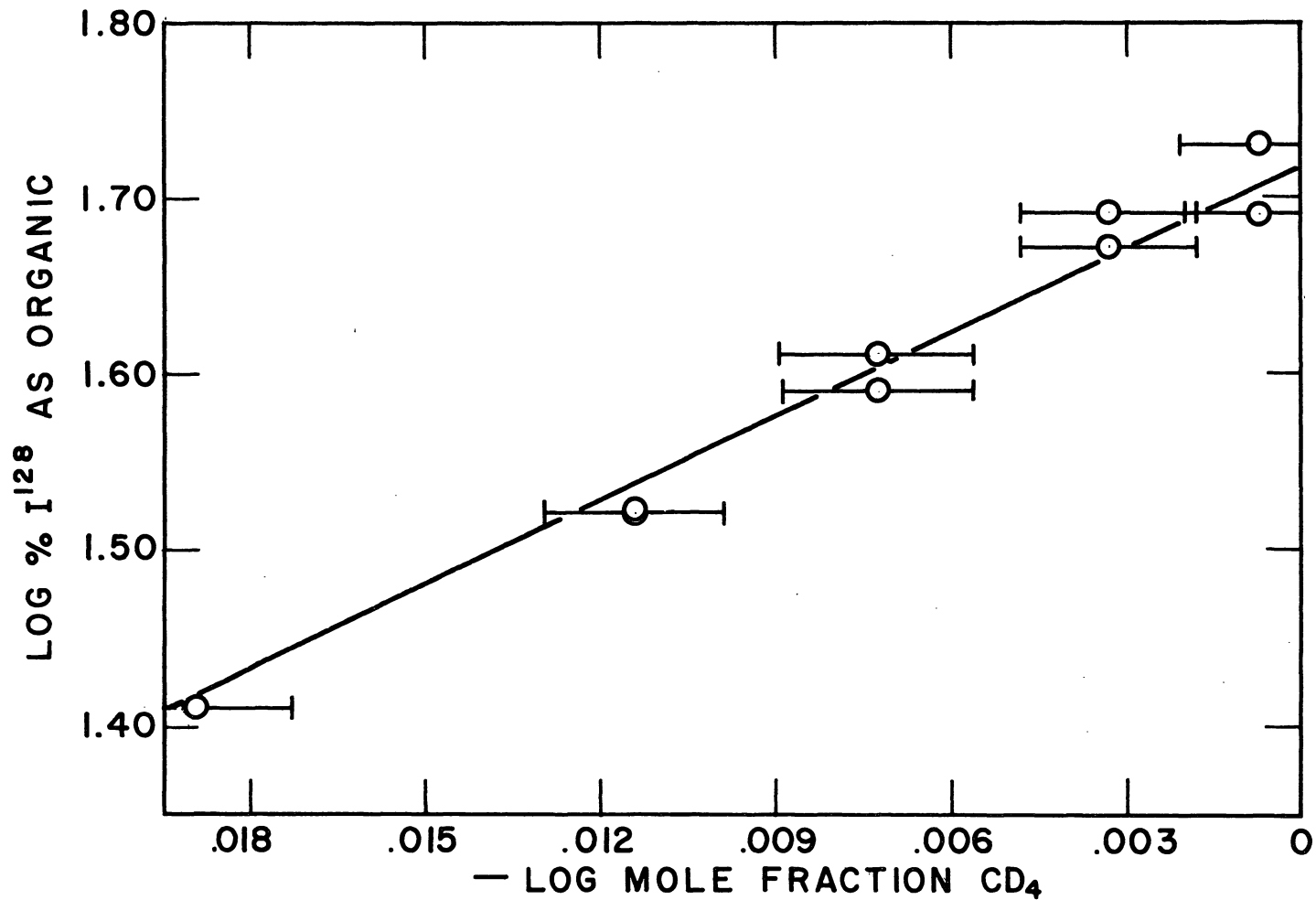


Fig. 13. The determination of limiting I^{128} organic yield in CD_4 .

Limiting organic yield in CD_4 is $52.3 \pm 1.0\%$.

I^{128} organic yield in CD_4 is influenced by the presence of D in the molecule.

The only significant difference between CH_4 and CD_4 is the I^{128} collision energy decrement. The maximum fractional energies which can be lost in one collision between I and CH_4 and CD_4 are 0.395 and 0.468, respectively. It can be seen qualitatively that the organic yields should be lower in a system which has a higher collision energy decrement when the reaction is endothermic. More effective energy-removing collisions will decrease the probability that the I^{128} will reach the reactive energy range (lower energy limit dictated by reaction endothermicity and the upper limit governed by the maximum energy which will allow compound formation without disrupting the molecule with excess energy). It would appear that the "hot atom" collision energy decrement is an important factor in determining the magnitude of "hot" organic yields.

$I^{128} + CHF_3$ Reaction.

Listed in Table IX are the data for the moderation of the $I^{128} + CHF_3$ reaction by CH_3I and Kr. The data are depicted in Figure 14. The solid curve for Kr moderation was calculated according to the Estrup-Wolfgang moderation equations described below. The solid curve through the CH_3I points is the best curve through the data.

The limiting organic yield of I^{128} in CHF_3 is 5.9% as determined from visual inspection of Figure 14.

All reactions of I^{128} (whether they involve positively charged or neutral iodine) with CHF_3 forming organic I^{128} require more energy than is supplied by electronically excited I^+ ions. For example the reaction $I^+ + CHF_3 \rightarrow CF_3I^+ + H$ is endothermic by at least 1.83 ev.* Therefore, it

* Endothermicity calculated using $D_{CF_3-H} = 102$ kcal/mole. $D_{CF_3-I} = 48.5$ kcal/mole,⁶¹ and ionization potential of $CF_3I = 10.0$ ev.⁶¹

Table IX.

The Percent of I^{128} Stabilized in Organic Combination
in Various Gaseous Mixtures of Fluoroform and Additives^a

Additive	Pressure CHF_3 (mm)	Pressure Additive (mm)	Mole Fraction Additive	Uncorrected % I^{128} as Organic	Corrected % I^{128} as Organic ^c
Kr	587	109	0.157 ± 0.002	5.8	4.7 ± 0.2
				6.9	5.8 ± 0.3
	356	133	0.272 ± 0.002	5.4	4.3 ± 0.3
				6.2	5.1 ± 0.2
159	141	0.470 ± 0.004	4.2	3.1 ± 0.3	
			6.0	4.9 ± 0.1	
92	139	0.602 ± 0.006	2.5	1.4 ± 0.3	
			2.8	1.7 ± 0.4	
I_2	630	0.1	0.001 ± 0.001	4.7	4.7 ± 0.2^b
				6.7	6.7 ± 0.2
CH_3I	691	1	0.001 ± 0.001	5.7	4.6 ± 0.4
				7.0	5.9 ± 0.4
	731	19	0.025 ± 0.004	3.3	2.2 ± 0.1
				3.4	2.3 ± 0.1
	375	40	0.096 ± 0.002	1.8	0.7 ± 0.1
2.4				1.3 ± 0.1	
162	41	0.202 ± 0.005	1.4	0.3 ± 0.1	
			1.6	0.5 ± 0.1	

a. All samples contained 0.1 mm I_2 , and about 1 mm CH_3I in the Kr samples. Irradiation time was 2-15 seconds.

b. Irradiation time was 2 minutes.

c. Uncertainty based on estimates of uncertainty in positioning 25.0 minute slope through the decay data for inorganic and organic fractions for each run. Data corrected for failure to bond-rupture.

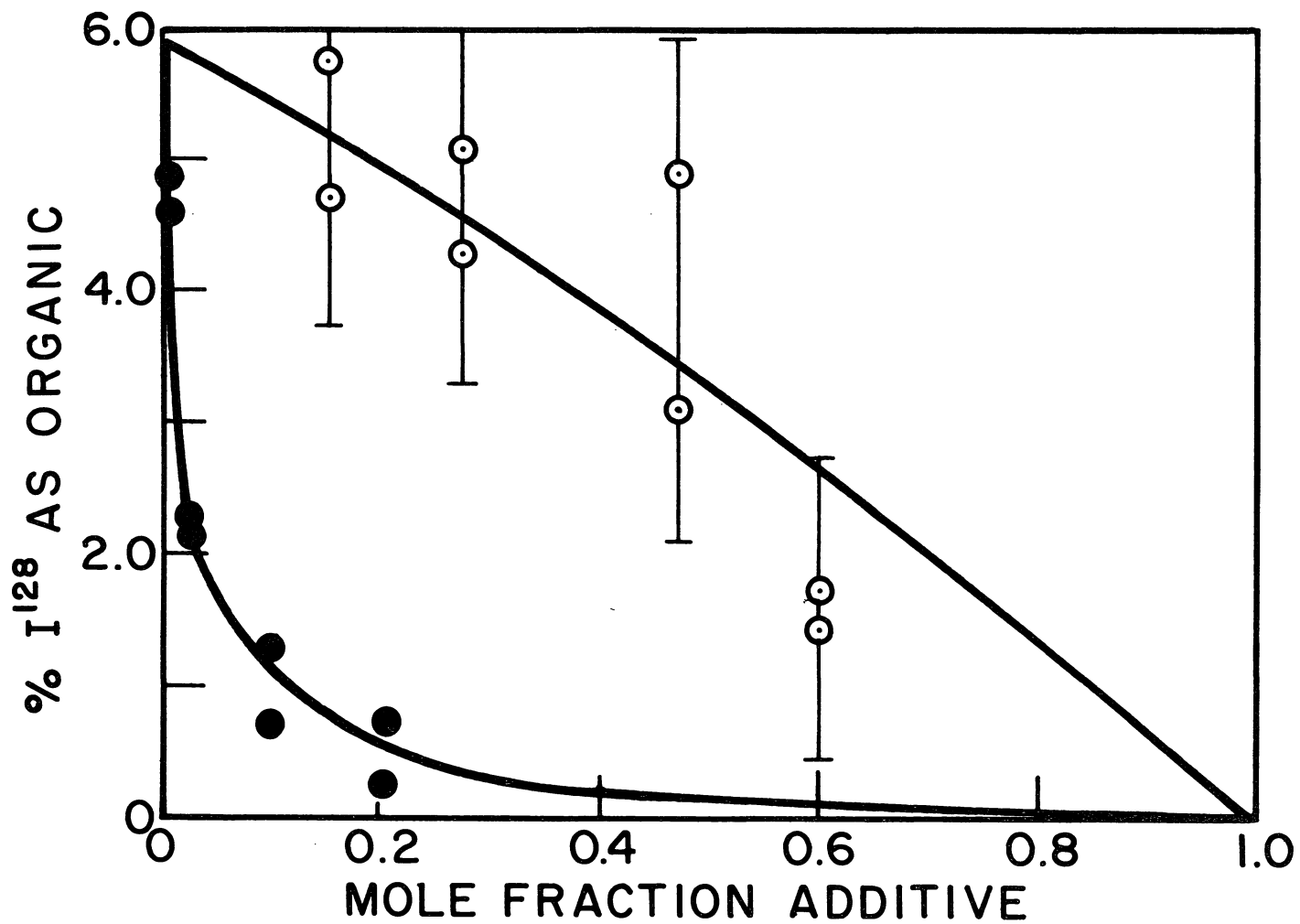


Fig. 14. Effect of Kr and CH₃I moderators on the reaction of gaseous CHF₃ into I¹²⁸ activated by the (n,γ) process. Moderators: Kr, O ; CH₃I, ● .

would be expected that the $I^{128} + CHF_3$ reaction occurs only by virtue of the I^{128} kinetic energy.

The Kr moderation data of the $I^{128} + CHF_3$ reaction was treated according to the Estrup-Wolfgang theory. The collision diameter for CHF_3 used to calculate S^2 was estimated as 5.2 \AA . Figure 15 is a plot of the experimental data corresponding to the Estrup-Wolfgang moderation equation (see Chapter III). For essentially pure CHF_3 , $f_{CHF_3}^{\text{Kr}} = 1.30$ and α/f_{CHF_3} (I^{128} organic yield) = 0.0454. The best straight line through the data and ending at the point (1.30, 0.0454) has an intercept $I = 0.053 \pm 0.015$ and a slope $-K = -(0.006 \pm 0.006)$. The solid curve for Kr moderation in Figure 14 was calculated using the Estrup-Wolfgang moderation equation and the above values of K and I.

It is seen from the Kr moderation that the reaction of I^{128} and CHF_3 is mainly activated by kinetic energy of I^{128} , as expected from reaction energy considerations. CH_3I inhibits the reaction with about the same efficiency as it does the $I^{128} + CH_4$ reaction, suggesting that the I^{128} may be either positively charged or electronically excited (see page 82).

I^{128} Reactions with Molecules other than CH_4

Tabulated in Table VI are the limiting organic yields of I^{128} in various molecular systems.

The data for the $I^{128} + CD_4$ reaction suggest that the collision energy decrement $\Delta E/E$ of the I^{128} in the system is an important factor in determining the organic yield. From the $I^{128} + CH_4$ reaction mechanism it is known that I^{128} reactions are activated by kinetic energy, positive charge and electronic excitation energy.

Knowing a molecule's ionization potential and the various energy requirements of possible I^{128} reactions with the molecules forming organic

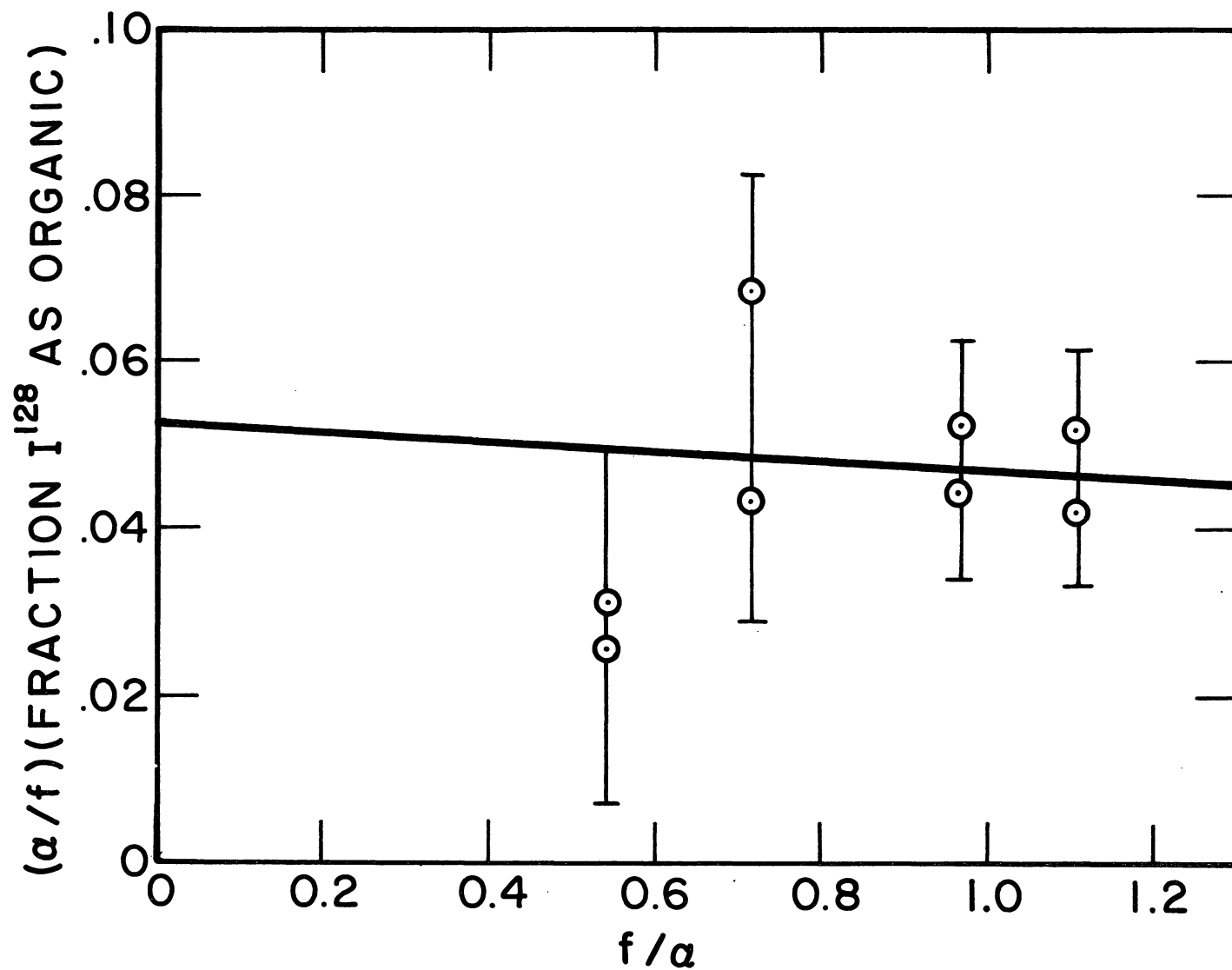


Fig. 15. Plot corresponding to Estrup-Wolfgang moderation equation for the I^{128} in organic combination. Moderator: Kr, O .

I^{128} , one can predict the magnitude of the organic yield. Unfortunately, with many of the molecules there is a scarcity of thermodynamic and ionization potential data for the reactions of interest.

Listed in Table X are various parameters for the I^{128} reactions with different molecules. Considering only I^{128} reactions with the molecules, only "hot" reactions are possible for I^{128} systems of CH_3Cl , CH_3Br , CF_3I , CH_3I , CH_2F_2 , CHF_3 and CF_4 . There are insufficient data to predict whether thermal reactions (involving excited ions) can occur in CCl_4 , $CHCl_3$, and CH_2Cl_2 systems.

Plotted in Figure 16 are the limiting I^{128} organic yields versus the collision energy decrement $\Delta E/E$ for the various molecular systems. Seven of the values fall close to a straight line drawn through the points. The very low values for CF_3I and CH_3I are possibly due to the fact that their ionization potentials are lower than that for an I atom. If a positively charged iodine is the reactive species a medium having an ionization potential lower than the iodine atom will remove the I^{128} from organic combination.

It would appear, to a first approximation, from Figure 16, that the most important parameter in determining the magnitude of the I^{128} "hot" organic reaction is the collision energy decrement (or efficiency of removing the "hot atom" kinetic energy).

Although the Estrup-Wolfgang theory is able to describe satisfactorily the moderation of "hot" reactions, it cannot predict the extents of "hot atom" organic reactions. The previous discussions suggested that the magnitude of an I^{128} organic formation can be predicted by considering the ionization potential of the molecule (whether it will inhibit excited I^+ reactions with the molecule by charge transfer) and the energy require-

Table X.

Collision Energy Decrements and Charge Transfer Defects
for Systems of I^{128} and Various Molecules

Molecule	% Organic ^a Yield I^{128}	$\frac{\Delta E}{E} = \frac{4M_A M_B}{(M_A + M_B)^2}$	Charge Transfer Energy Defect $\Delta E'$ (ev) ^c
CH_4^b	18.4 ± 0.5	0.395	+2.55
CD_4^b	16.3 ± 1.0	0.468	+2.55
CF_4	3.4 ± 0.4	0.965	>+2.55
CCl_4	2.9 ± 1.0	0.992	+1.03
CHF_3	5.9 ± 0.4	0.914	>+2.55
$CHCl_3$	7.0 ± 1.0	0.998	+0.98
CH_2F_2	2.2 ± 0.2	0.823	>+2.55
CH_2Cl_2	3.1 ± 1.0	0.958	+0.91
CH_3I	0.1 ± 0.1	0.995	-0.99
CF_3I	0.1 ± 0.1	0.953	-0.44
CH_3Cl	6.5 ± 1.0	0.812	+0.78

- a. Organic yields have been corrected for I^{128} failure to bond-rupture.
- b. Only the "hot" fraction of the I^{128} organic yield listed.
- c. $\Delta E' = I.P. \text{ molecule} - I.P. \text{ iodine}$.

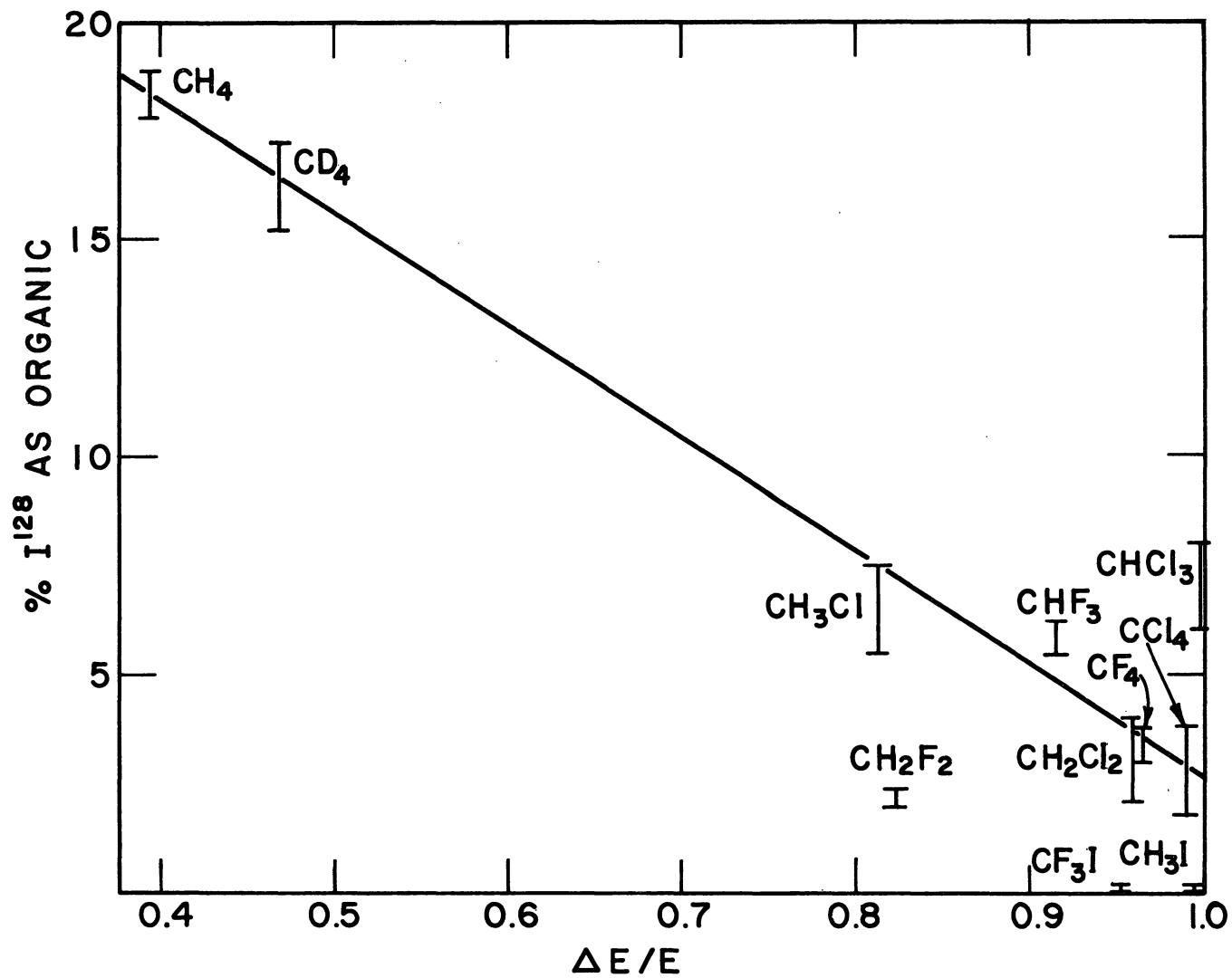


Fig. 16. The influence of collisional energy decrement on the I^{128} organic yield in various molecules.

ments for various I^{128} reactions with the molecule forming organic products. It would seem that the extent of "hot" reactions was governed primarily by the efficiency of kinetic energy removal by the molecule.

APPENDIX I.

Ionization Potential Data and Reaction Energy Requirements

Ionization Potentials.

Listed in Table XI are the ionization potentials which were used throughout the thesis. Most significant is the work of Watanabe⁵⁵ who determined many ionization potentials of interest in the research.

Reaction Energy Requirements.

Various reactions involving Br and I with CH₄ and other molecules have been used throughout the thesis, in which the reaction energy requirements were estimated. The most accurate way of determining heats of reaction is by using heats of formation for the reactants and products. For simple reactions involving molecules such as CH₄ and CH₃Cl, heats of formation, $\Delta H_f^\circ(298.1^\circ\text{K})$ ⁶⁴, were used to calculate the heat of reaction, ΔH_{298} . However, for reactions involving various polyhaloalkanes, heats of formation for many of the reactants and products are unavailable. In these cases the heat of reaction was estimated from bond energies. For example, for the $\text{I} + \text{CH}_4 \rightarrow \text{CH}_3\text{I} + \text{H}$ reaction, $D_{\text{CH}_3-\text{H}} = 102 \text{ kcal/mole}$ ⁶⁵ and $D_{\text{CH}_3-\text{Br}} = 67 \text{ kcal/mole}$,⁶⁶

$$\Delta H_{298} = D_{\text{CH}_3-\text{H}} - D_{\text{CH}_3-\text{Br}} = 35 \text{ kcal/mole}$$

as compared to 35 kcal/mole, determined by using the heats of formation of the products and reactants. Unfortunately, there is a wide spread in bond-energy data in the literature for many of the molecules of interest, which makes it impossible to estimate the heats of reaction with accuracy.

When a reaction takes place, in which one of the reactants is positively charged, as in the reaction $\text{I}^+ + \text{CH}_4 \rightarrow \text{CH}_3\text{I}^+ + \text{H}$, it is necessary to

Table XI.

Ionization Potentials of the Various Molecules

Molecule	Ionization Potential	Molecule	Ionization Potential
He	24.580 ⁶⁷	CF ₃ I	10.0 61
Ne	21.559 ⁶⁷	n-C ₃ H ₇ I	9.41 58
Ar	15.755 ⁶⁷	C ₆ H ₆	9.245 ⁵⁵
Kr	13.996 ⁶⁸	CH ₄	12.99 55
Xe	12.127 ⁵⁴	C ₂ H ₆	11.65 55
N ₂	15.58 58	C ₃ H ₈	11.08 55
O ₂	12.2 59	n-C ₄ H ₁₀	10,80 69
NO	9.25 55	n-C ₅ H ₁₂	10.55 69
CF ₄	≥13 a	n-C ₆ H ₁₄	10.43 69
CHF ₃	≥13 b	Br ₂	10.55 55
CH ₂ F ₂	≥13 b	I ₂	9.28 55
C ₂ F ₆	~12 c	Cl	13.01 67
CCl ₄	11.47 55	Br	11.84 68
CHCl ₃	11.42 55	I	10.454 ⁵⁴
CH ₂ Cl ₂	11.35 55	I → I ⁺ (³ P ₀)	11.254 ^d
CH ₃ Cl	11.28 55	I → I ⁺ (³ P ₁)	11.333 ^d
C ₂ H ₅ Br	10.29 55	I → I ⁺ (¹ D ₂)	12.156 ^d
CH ₃ I	9.54 55	I → I ⁺ (¹ S ₂)	14.498 ^d

a. See page 75.

b. See page 76.

c. See page 79.

d. Calculated from ionization potential of I and the electronic excitation energies of the various states given on page 55.

know the ionization potentials of the charged species. $\Delta H_{298} = 40$ kcal/mole for $I + CH_4 \rightarrow CH_3I + H$. The ionization potentials for I and CH_3I are 10.454 ev and 9.54 ev, respectively. ΔH_{298} for $I^+ + CH_4 \rightarrow CH_3I^+ + H$ is (40 kcal/mole minus the ionization potential of I plus the ionization potential of CH_3I) 18 kcal/mole.

From kinetics it is usually found that in order for reactions to occur they need an additional amount of energy -- the activation energy for reaction. Since the reactions discussed in this thesis have never been studied using standard kinetics, no values for the activation energies have been determined. The ΔH_{298} values quoted in this thesis are actually minimum energy requirements.

APPENDIX II

Error Analysis

Error in the Determination of Mole Fraction of Additive or CH₄.

There are two uncertainties which combine to determine the mole fraction error.

- a. The uncertainty in reading the manometer is about 1 mm.
- b. The uncertainty in estimating the amount of a gas, having a vapor pressure at liquid N₂ temperature, not included in the quartz bulblet (in the preparation of the reaction systems) is estimated to be half of the amount in the stem leading to the stopcock (see Chapter II).

The mole fraction of an additive is equal to:

$$\frac{\text{Pressure Additive}}{\text{Pressure Additive} + \text{Pressure CH}_4}$$

The propagation of error of the pressure uncertainties is given by the following relationship:

$$\text{Error Mole Fraction Additive} = (\text{Mole Fraction Additive}) \left(\frac{\Delta P_A^2}{P_A^2} + \frac{\Delta P_T^2}{P_T^2} \right)^{1/2}$$

where ΔP_A and ΔP_T are the uncertainties in the pressure of the additive and the total pressure of the system, respectively and P_A and P_T are the pressure of the additive and the total pressure of the reaction system, respectively.

Error in Organic Yield Determinations.

There are two uncertainties which combine to determine the error

in organic yield determinations.

- a. The uncertainty based on estimates of uncertainty in positioning slope through decay data for inorganic and organic fraction, for each run.
- b. The uncertainty in estimating the contribution of additive-induced reactions and reactions of additive, wherever occurring, to the observed organic yield. This combined error is estimated to be about 2%.

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GASEOUS REACTIONS OF METHANE AND VARIOUS POLYHALOMETHANES
WITH BROMINE AND IODINE ACTIVATED BY THE (n,γ) PROCESS

Edward Paul Rack

ABSTRACT

The effects of various inert-gas and molecular additives in moderating the reactions of (n,γ) activated I^{128} and Br^{80} with CH_4 and various polyhalomethanes were determined in order to ascertain the reaction mechanisms.

In the absence of additives, it was found that $13.3 \pm 0.5\%$ (all uncertainties are approximately at the 95% confidence level) of the activated Br^{80} reacted with gaseous CH_4 to yield CH_3Br^{80} . Inert gases, Br_2 , C_2H_5Br , CF_4 , and C_2F_6 inhibited the formation of CH_3Br^{80} in a manner which indicated that the reaction of Br^{80} with CH_4 proceeded via a mechanism involving Br^{80} atoms (or ions) possessing excess kinetic energy. The inert-gas and molecular moderation of the reaction was found to be described by a mathematical model for "hot-atom" reactions as developed by Estrup and Wolfgang [J. Am. Chem. Soc., 82, 2665 (1960)].

In the absence of additives, it was found that $54.4 \pm 0.5\%$ of the activated I^{128} reacted with gaseous CH_4 to yield CH_3I^{128} . Excess neon, argon, and krypton reduced the CH_3I^{128} yield to $36 \pm 2\%$. The moderation exhibited by these additives was described by the Estrup-Wolfgang model. Excess xenon reduced the CH_3I^{128} yield to $11 \pm 2\%$. Xenon differs from the

other inert gases in that it may easily undergo charge-transfer with $I^+(^1D_2)$ ions. On the basis of these data it was concluded that of the 54.4% I^{128} found as CH_3I^{128} , $18.4 \pm 2\%$ is formed by a hot reaction or reactions, $25 \pm 3\%$ is formed as a result of the $I^+(^1D_2) + CH_4$ reaction, and $11 \pm 2\%$ is formed as a result of the reaction of I^{128} excited atoms or I^+ ions in the 3P_2 , 3P_1 , or 3P_0 states.

Moderation of the $I^{128} + CH_4$ reaction by the various molecular additives (N_2 , O_2 , CF_4 , CHF_3 , CH_2F_2 , C_2F_6 , NO , CH_3I , CF_3I , $n-C_3H_7I$, C_6H_6 , CH_3Cl , CH_2Cl_2 , $CHCl_3$, CCl_4 , and the alkanes) was discussed in terms of the $I^{128} + CH_4$ reaction processes as given above.

Preliminary studies were made of the I^{128} reactions with various polyhalomethanes and CD_4 . It was possible in certain cases, to predict the magnitude of the organic I^{128} yield of the reaction with various molecules by considering ionization potentials, energy requirements, and the efficiency of collisions between the hot I^{128} and the target molecule. It was found that the extent of any reaction requiring kinetic energy was related to the efficiency of the kinetic-energy removal by the molecule.