THE JOURNAL

OF

CHEMICAL PHYSICS

Reactions of High-Energy, Excited I^{128} Ions with Gaseous Molecules*

EDWARD P. RACK† AND ADON A. GORDUS

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan

(Received June 29, 1961)

The manner in which molecular additives inhibit the reaction of (n, γ) activated I^{128} with CH_4 was determined in an effort to observe indirectly reactions of I^{128} with the additives. The data suggest that (1) O_2, N_2, and CF_4 serve only to remove excess I^{128} kinetic energy; (2) the ionization potential of O_2 is greater than 12.16 ev, the potential energy of $I^+(^1D_2)$; (3) the ionization potential of C_2F_6 is less than 12.16 ev; (4) CH_3I, CF_3I, $n\text{-}C_3H_7I$, and C_6H_6 inhibit the reaction principally as a result of I^++additive ion-molecule reactions and/or physical quenching.

INTRODUCTION

AS a result of gamma-ray recoil, I^{128} atoms activated by the $I^{127}(n,\gamma)I^{128}$ reaction acquire kinetic energies having a range of values with a maximum of 182 ev. In addition, at least 50% of the I^{128} atoms are positively charged[1] and at least 25% of the iodine ions are in an excited state.[2]

The reaction of the I^{128} with gaseous methane is a unique and important example of a chemical reaction activated by a nuclear process. $54.4\pm0.5\%$ of the I^{128} becomes stabilized as organic activity.[2-5] This yield of organic activity is the largest observed for any gas-phase reaction activated by a nuclear process and exceeds that of most liquid or solid-phase reactions. Gas chromatographic data[5] indicate that >97% of the organic activity is CH_3I^{128}. It has been suggested[2-4] that the reaction occurs in one step as a result of hydrogen displacement. Of the 54.4% organic I^{128}, about 18% results from the reaction of I^{128} atoms or ions possessing excess kinetic energy, about 25% from the thermal reaction of $I^+(^1D_2)$ ions, and about 11% from the

thermal reaction of excited I^{128} atoms or I^+ ions in $^3P_2$, $^3P_1$, and/or $^3P_0$ states.[2]

The reaction of (n,γ) activated I^{128} with CH_4 affords a means of investigating the reactions of excited, ionized, high-energy iodine with other molecules. By introducing varying amounts of gaseous molecules to the iodine-methane reaction system it is possible to determine the manner in which these additives affect the $I^{128}+CH_4$ reaction and, thus, determine indirectly the manner in which the I^{128} interacts with the additives.

To examine the interaction of the I^{128} with the additives we determined the extent of reaction of I^{128} with CH_4 to yield organic I^{128} as a function of the mole-fraction of the additive. These data were then extrapolated to unit mole-fraction additive to determine the maximum effect produced by the additive. Based on the moderation of the $I^{128}+CH_4$ reaction with inert gases,[2] it is expected that all additives, regardless of their nature, would extrapolate to 36%, 11%, or to a value less than 11%, depending on the nature of the reactive iodine. If the yield at unit mole-fraction additive is reduced by 18% to about 36%, this would indicate that the additive inhibited the $I^{128}+CH_4$ reaction principally by removing excess kinetic energy from the I^{128}. If, instead of 36%, the yield is reduced an additional 25% to about 11%, this would indicate that, in addition to removal of I^{128} excess kinetic energy, the additive interacts with thermal $I^+(^1D_2)$ ions. If the additive completely suppresses the reaction of I^{128} with CH_4, then the additive must also interact with thermal excited I^{128} atoms or $^3P_2$, $^3P_1$, and/or $^3P_0$ ions.

[1] S. Wexler and H. Davies, J. Chem. Phys. 20, 1688 (1952).
[2] E. P. Rack and A. A. Gordus, J. Chem. Phys. 34, 1855 (1961).
[3] J. F. Hornig, G. Levey, and J. E. Willard, J. Chem. Phys. 20, 1556 (1952).
[4] G. Levey and J. E. Willard, J. Chem. Phys. 25, 904 (1956).
[5] A. A. Gordus and J. E. Willard, J. Am. Chem. Soc. 79, 4609 (1957).

TABLE I. Percent I^{128} in organic combination for systems containing CH_4 and additive.[a]

Additive	Pressure CH_4-mm	Mole fraction additive[e]	Observed % organic I^{128}
O_2[b]	574	0.122(11)	53.5
	574	0.132(6)	53.5
	459	0.282(19)	53.0
	459	0.295(13)	50.8
	35	0.932(7)	40.5, 43.0
N_2[b]	608	0.089(9)	49.6
	608	0.097(6)	53.6
	529	0.200(16)	51.1
	529	0.219(9)	54.9
	411	0.335(26)	54.5
	35	0.890(120)	48.2, 46.8
CF_4[b]	577	0.139(2)	52.7, 52.7
	445	0.359(2)	50.0, 50.1
	247	0.635(3)	47.3, 47.6
	67	0.905(4)	42.6, 42.8
	35	0.950(3)	42.2, 42.7
CH_2F_2[b]	545	0.211(2)	45.3, 46.6
	282	0.373(3)	42.7, 44.1
	284	0.499(3)	37.1
	229	0.663(3)	31.0, 31.5
C_2F_6[b]	590	0.135(2)	48.8, 49.2
	367	0.339(2)	39.7, 44.0
	389	0.444(4)	42.0
	399	0.453(2)	42.0, 44.3
	171	0.627(4)	39.5
	150	0.776(3)	40.2, 41.4
	14	0.979(4)	37.2, 37.3
NO[c]	679	0.013(1)	52.9, 51.8
	674	0.019(1)	49.4, 51.0
	652	0.024(1)	47.2, 51.6
	454	0.077(2)	42.6, 43.0
	373	0.106(2)	39.6, 39.3
	562	0.166(1)	35.5, 36.8
	457	0.224(2)	34.1, 31.1
	289	0.337(2)	26.2, 25.1
	149	0.790(1)	9.2, 9.9
CH_3I[d]	721	0.001(1)	54.8
	710	0.003(1)	55.0, 53.4
	665	0.005(1)	54.2, 53.9
	659	0.011(1)	47.1, 47.8
	558	0.018(1)	42.2, 42.3
	532	0.022(1)	39.2, 40.6
	460	0.023(2)	38.5, 37.9
	342	0.034(2)	33.5, 33.1
	186	0.061(4)	24.5
	233	0.086(3)	17.6, 17.6
	131	0.144(5)	11.7
	111	0.234(6)	7.4, 5.9
	197	0.417(5)	4.2, 3.9
	132	0.553(5)	2.9, 2.5
n-C_3H_7I[d]	684	0.010(1)	44.7, 44.8
	678	0.022(1)	37.4, 35.2
	482	0.055(1)	28.9, 27.3
	288	0.068(2)	20.1, 18.6
	187	0.105(1)	15.9, 11.4
	181	0.121(4)	14.9, 11.8
CF_3I[d]	620	0.025(1)	35.4, 33.7
	178	0.191(4)	6.6, 5.9
C_6H_6[c]	646	0.015(1)	46.4, 48.4
	659	0.022(1)	37.7, 37.6
	675	0.039(1)	31.4, 32.4
	155	0.148(2)	9.7, 9.2

[a] All samples, except when an iodide was the main source of I^{128}, contained 0.5–2 mm CH_3I and 0.1 mm I_2.

[b] Except for a few samples which were irradiated for about 15 sec, samples were irradiated for 7 sec.

[c] Samples were irradiated for 15–20 sec.

[d] Samples were irradiated for 2–30 sec.

[e] Uncertainty in last figure or figures (given in parentheses) is based on estimates of the uncertainties in individual pressures.

EXPERIMENTAL

Samples were prepared by vacuum-line techniques and analyzed in a manner described previously.[2,5] Airco assayed-reagent N_2, Matheson extra-dry grade O_2 (99.6% minimum purity), and Phillips research-grade CH_4 (99.65% purity) were used. By mass-spectral analysis, du Pont research sample C_2F_6 was found to contain about 0.1% N_2 impurity, du Pont research sample CH_2F_2 contained about 0.1% N_2, 1.7% CHF_3 or CF_4, and Matheson CF_4 contained about 0.2% N_2 and 0.1% O_2. Matheson NO, >99% purity was also used. I_2 was sublimed from a mixture of I_2, KI, and CaO. Other additives were purified prior to use.

The samples were irradiated in the University of Michigan Megawatt reactor for 2 to 30 sec at a thermal-neutron flux of about 2×10^{12} n/cm^2-sec.

RESULTS

Contained in Table I are the percent I^{128} found as organic for various mixtures of molecular additive, methane, 0.5–2 mm CH_3I, and 0.1 mm I_2. Table II is a summary of the percent I^{128} stabilized in organic combination in various nonmethane systems where the additive molecule was in great excess.

In order to interpret properly the relative effects of the additives on the $I^{128}+CH_4$ reaction it is necessary to correct the data of Table I for three effects:

(1) As a result of cancellation of gamma-ray momenta in (n,γ) cascade-gamma emission, a small fraction of the activated I^{128} will receive a net gamma-recoil which is less than that required for the I^{128} to rupture from its parent molecule. The percent failure to bond-rupture used in correcting the data of Table I are[6]: CH_3I—1.1, n-C_3H_7I—0.7, and CF_3I—0.1%.

TABLE II. Percent I^{128} reacting with additive to yield organic activity.[a]

Additive	Pressure additive-mm	% I^{128} as organic
CF_4[b]	618	4.4, 4.6
CH_2F_2	650[c]	3.5, 3.0
	693[d]	3.4, 2.9
C_2F_6[e]	621	8.9, 8.8
CH_3I	18	1.2, 1.3
	28	1.4
CF_3I	44	1.1, 1.2
n-C_3H_7I	19	1.3
C_6H_6[f]	30	1.4, 1.3

[a] All samples contained in 0.1 mm I_2 and were irradiated for 2–25 sec.
[b] Contained 4 mm CH_3I.
[c] Contained 10 mm CH_3I.
[d] Contained 17 mm CH_3I.
[e] Contained 2 mm CH_3I.
[f] Contained 1 mm CH_3I.

[6] A. A. Gordus (unpublished data).

(2) As a result of the 8000 r/min gamma-radiation flux associated with the neutron irradiations, any radiation-induced reactions will result in the transfer of some inorganic I^{128} to organically bound I^{128}. The extent of radiation-induced organic pickup may be determined by incorporating, prior to irradiation, I_2 tagged with I^{131} and determining, following the neutron irradiation, the percent I^{131} as organic activity. Under the conditions of the irradiations less than 1% of the I^{131} was found as organic activity in systems which did not contain an additive.[2] For systems containing inert-gas additives, the percent I^{131} organic pickup appeared to be a linear function of the mole fraction of the inert gas. At unit mole fraction of inert gas the radiation-induced pickup was[2]: Xe—17, Kr—12, Ne and Ar—5%. For C_2F_6 a value of 17% was found, for CF_4, a value of 3%. The value of 5% for Ne and Ar was assumed to apply to the N_2 and O_2 systems. On the basis of the 3% value for CF_4, a value of 2% was chosen for CH_2F_2. Since the data for CH_3I, $n\text{-}C_3H_7I$, CF_3I, NO, and C_6H_6 all extrapolate to zero percent I^{128} as organic at unit mole-fraction additive, it would appear that radiation effects are not important in these five systems. The extent of radiation-induced pickup was assumed equal to the product of the mole fraction of the additive times the maximum value given above. Since the radiation results in a lowering of the percent I^{128} as inorganic and results in a numerically equal increase in the percent I^{128} as organic, to correct for this effect, it is only necessary to subtract the percent value calculated above from the observed percent organic I^{128}.

(3) As indicated in Table II, I^{128} reacts with the additives forming organic I^{128}. In the presence of essentially pure additive these values (Table II), corrected for failure to bond rupture, are: CF_4—3.4, CH_2F_2—2.2, C_2F_6—7.8, C_6H_6—0.1, $n\text{-}C_3H_7I$—0.6, and CH_3I—0.2%. We assumed that the extent of reaction of I^{128} with the additive was equal to the mole fraction of the additive times the maximum extent of reaction given above. The I^{128} which reacts with the additive to form organic activity is removed from the reaction system. As a result, the I^{128} available for reaction with CH_4 is less than the
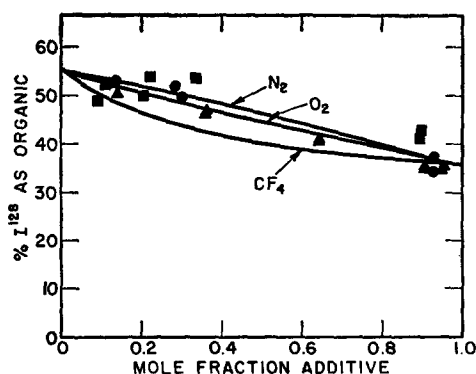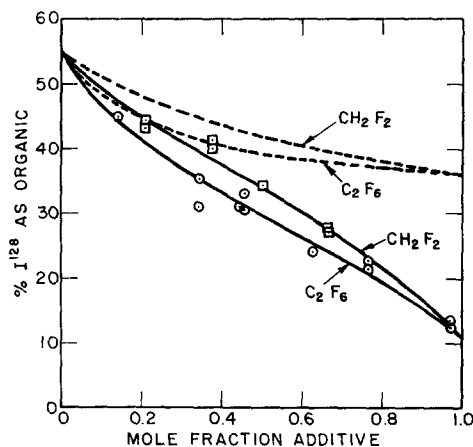

FIG. 2. Effect of additives on the reaction of I^{128} with gaseous CH_4. Additives: CH_2F_2, ☐; C_2F_6, ☉.

total observed activity. To adjust the observed percent I^{128} as organic P_0 for the percent organic I^{128} resulting from reaction with the additive x it would appear more correct to calculate the adjusted value by the expression $100(P_0-x)/(100-x)$. However, since x will generally be small (a maximum of 7.8 for C_2F_6) we have chosen to neglect the quantity x in the denominator.

DISCUSSION

The data, corrected for the three effects described above, are plotted graphically in Figs. 1–3. An uncertainty of the percent I^{128} as organic $\pm 2\%$ is ascribed to these data.

O_2, N_2, and CF_4

The data of Fig 1 approach 36% at unit mole-fraction additive suggesting that these additives are effective only in moderating the 18% "hot" reaction. The solid curves were calculated according to the Estrup and Wolfgang[7] kinetic theory of hot-atom reactions using parameters determined in our previous study[2] of the effects of inert gases on the $I^{128}+CH_4$ reaction.

Since these data extrapolate to 36%, rather than 11% or 0%, this indicates that any charge transfer between $I^+(^1D_2)$ and the additives must be of minor importance. The potential energy of $I^+(^1D_2)$ is 12.16 ev[8]; the ionization potential of N_2 is 15.58 ev.[9] Thus, even for 182 ev $I^+(^1D_2)$ ions, charge transfer with N_2 should be negligible.[10] Within the last ten years, 17 separate values of the ionization potential of O_2 have been reported.[11] The values range between 12.04 and 12.45 ev. If the ionization potential of O_2 were approximately equal to or less

FIG. 1. Effect of additives on the reaction of I^{128} with gaseous CH_4. Additives: N_2, ■; O_2, ●; CF_4, ▲.

[7] P. J. Estrup and R. Wolfgang, J. Am. Chem. Soc. 82, 2665 (1960).
[8] C. E. Moore, "Atomic energy levels," NBS Circ. 467 (1958), Vol. III, p. 108.
[9] K. Watanabe, J. Chem. Phys. 26, 542 (1957).
[10] E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237 (1957).
[11] R. W. Kiser, "Tables of ionization potentials," Office of Technical Services, Department of Commerce, Washington, D. C., U. S. Atomic Energy Commission Rept. TID-6142 (1960).
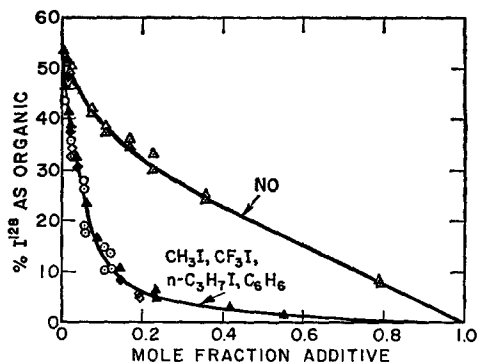
FIG. 3. Effect of additives on the reaction of I^{128} with gaseous CH_4. Additives: NO, $\triangle$; CH_3I, $\blacktriangle$; CF_3I, $\lozenge$; n-C_3H_7I, $\odot$; C_6H_6, $\blacklozenge$.

than the potential energy of $I^+(^1D_2)$ the charge transfer cross section should be very high. Apparently, then, the ionization potential of O_2 is greater than 12.16 ev. The ionization potential of CF_4 is 17.81 ev.[12] Thus, $I^+(^1D_2)$ would not be expected to undergo charge exchange[10] with CF_4.

In addition, it would appear that physical quenching of excited iodine atoms or reaction of the iodine with these additives must be of minor importance.

C_2F_6 and CH_2F_2

The dashed curves in Fig. 2 were calculated according to the Estrup and Wolfgang[7] equation.[13] The solid curves were calculated according to the method described below. Since the data extrapolate to 11%, it appears that, in addition to the removal of I^{128} excess kinetic energy, these two additives inhibit the $I^+(^1D_2)+CH_4$ reaction.

Because CF_4 does not physically quench excited iodine species and since alkanes are poor quenchers of excited states,[14] CH_2F_2 and C_2F_6 would not be expected to quench $I^+(^1D_2)$. Therefore, the moderation to 11% must be due either to charge transfer or to reaction between $I^+(^1D_2)$ and the additive.

Charge transfer cannot occur easily between CH_2F_2 and $I^+(^1D_2)$ since the ionization potential of CH_2F_2 is 12.55 ev.[12] Therefore, the 25% additional inhibition by CH_2F_2 must be due to a thermal ion-molecule reaction of $I^+(^1D_2)+CH_2F_2$. Reactions leading to organic I^{128} are endothermic. However, one-step reactions leading to HI are exothermic; for the products: CHF_2^++HI, $\Delta H=-1.0$ ev,[15] for CHF_2+HI^+, $\Delta H=-0.4$ ev. Thus, it would appear that the 25% additional inhibition by

[12] S. Stokes and A. B. F. Duncan, J. Am. Chem. Soc. **80**, 6177 (1958).

[13] The diameters for C_2F_6 and CH_2F_2 were estimated as 6.8 and 4.9 A.

[14] K. J. Laidler, *The Chemical Kinetics of Excited States* (Oxford University Press, Oxford, England, 1955), pp. 102–103.

[15] The ionization potential of CHF_2 is 9.45 ev.[16]

[16] F. P. Lossing, P. Kebarle, and J. B. DeSousa in *Advances in Mass Spectroscopy*, edited by J. D. Waldron (Pergamon Press, Ltd., London, 1959), pp. 431–441.

CH_2F_2 could be due to either of the two reactions yielding HI.

All possible one-step reactions between $I^+(^1D_2)$ and C_2F_6 are endothermic. Therefore, the additional inhibition by C_2F_6 to 11% is probably due to charge transfer. The ionization potential of C_2F_6 is not known, but it would be expected to be equal to or greater than the value for C_2H_6 (11.65 ev). Thus, if the additional inhibition is due to charge transfer, the ionization potential of C_2F_6 would be between 11.65 and 12.16 ev.

We assumed that the inhibition resulting from kinetic-energy removal is independent of the inhibition of the $I^+(^1D_2)+CH_4$ reaction. To determine the magnitude of the inhibition of the $I^+(^1D_2)$ we subtracted from the data of Fig. 2: (a) the 11% organic I^{128} which is not effected by the CH_2F_2 or C_2F_6 and (b) the kinetic-energy moderation which corresponded to the dashed curve minus 36%. We then assumed that this remaining extent of reaction to produce organically bound I^{128}, R, can be related to a cross-section ratio C according to the equation[2] $C=[(25-R)(1-N)]/RN$, where N is the mole fraction of additive and $C=\sigma[I^+(^1D_2)+$additive interaction$]/\sigma[I^+(^1D_2)+CH_4$ to yield $CH_3I^{128}]$. For $I^+(^1D_2)+Xe$ charge transfer, C was found to be[2] 2.2 ± 0.6. For CH_2F_2 inhibition a value of C was found to be 0.5 ± 0.3. For C_2F_6 charge transfer, $C=0.6\pm0.3$. The solid curves of Fig. 2 were calculated by adding together 11%+ the kinetic-energy effect (dashed curve)+the value of R calculated using these C values.

To a first approximation, the cross section for reaction of I^{128} with CH_4 or CH_2F_2 should depend simply on the number of available hydrogen atoms per molecule. Thus, a C value of 0.5 for CH_2F_2 appears reasonable.

There are several possible reasons why the cross-section ratio for C_2F_6 (0.6) is smaller than that for Xe (2.2), even though it is postulated that both additives inhibit the $I^+(^1D_2)+CH_4$ reaction by a charge-transfer mechanism. 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 for C_2F_6 charge transfer. Another possibility for the difference could be ascribed to steric effects. In charge transfer with Xe, no steric factors are involved. However, the primary ionization of C_2F_6 may be due to the removal of an electron localized in the C—C bond[17]; steric hindrance in C_2F_6 could be of importance in charge-transfer reactions.

NO, CH_3I, CF_3I, n-C_3H_7I, and C_6H_6,

The solid curves of Fig. 3 were drawn as the best visual fits through the experimental data. Since the data extrapolate to zero percent organic I^{128} at unit mole-fraction of additive, this indicates that these additives are capable of inhibiting all thermal I^{128} reactions

[17] C. A. McDowell and B. C. Cox, J. Chem. Phys. **22**, 946 (1954).

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

It is possible, however, that the observed inhibition is due to thermal ion-molecule reaction. For example, the reaction:

$$I^+ + CH_3I \rightarrow I_2^+ + CH_3 (\Delta H = -15 \text{ kcal/mole})$$
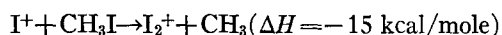
has been observed[18] in the mass spectrometer. No information is available concerning another possible means of inhibition: that of the quenching of excited states of iodine by these additives. As a result, physical quenching cannot be ruled out.

From the above discussions, it is apparent that the problem of interpreting the curves of Fig. 3 would be difficult in view of the various possibilities for inhibition of the reaction. Because of the effectiveness of these moderators, it is questionable whether it is realistic to consider the kinetic-energy moderation as independent of other types of inhibition.

Assuming such separation possible, we determined R values by subtracting from the data of Fig. 3 values corresponding to the expected kinetic-energy moderation. The C values were then calculated according to the equation: $C = [(36-R)(1-N)]/RN$. These values were found to vary considerably; however, except for NO, the C values invariably tended to increase with mole fraction. The calculated values were: NO—10 to 2, CH_3I—7 to 55, CF_3I—about 50, C_6H_6—14 to 40, and n-C_3H_7I—30 to 130.

A better representation is obtained if it is assumed that inhibition by the additive occurs principally by a process which can be described by the relative cross-section equation. Thus, $C = [(54.4-R)(1-N)]/RN$, where R corresponds to data in Fig. 3. According to this calculation C values were found to be 2 to 5 for NO and about 23 for CH_3I, CF_3I, n-C_3H_7I, and C_6H_6.

Iodine is known not to react with NO. Therefore, the observed inhibition by NO may be due to physical quenching and/or charge transfer with I^+ species.

The very large cross-section ratios for the iodides and benzene are most probably not a result of a reaction of $I^{128}+$additive to yield HI since CF_3I and CH_3I both exhibit the same effect. Since much lower C values were found for processes involving charge-transfer (Xe—2.2, C_2F_6—0.5), it would appear unlikely that the iodides and C_6H_6 inhibit principally by charge neutralization. The cross sections for ion-molecule reactions, however, are usually found to be much larger than gas-kinetic or charge-transfer cross sections. As indicated above, an ion-molecule reaction with CH_3I has been reported. Thus, such ion-molecule reactions could be the main cause for the observed inhibition. In addition, physical quenching could be a contributing factor in the inhibition process.

CONCLUSIONS

The above data indicate that it is possible to study indirectly interactions of molecules with atoms and ions activated by nuclear processes. Because of the large yield of organic activity, the (n,γ) activated reaction of I^{128} with CH_4 is particularly suited for such studies.

The $I^{128}+CH_4$ reaction, therefore, may be used as a means of investigating reactions of I^{128} with other alkanes. As Lind has stressed,[19] the reactions of I^{128} with C_2H_6, C_3H_8, and n-C_4H_{10} are particularly interesting since the yields of organic I^{128} (2, 3, and 4%, respectively[5]) are so very low compared with the $I^{128}+CH_4$ reaction. One of the possible reasons for these low yields is that, unlike CH_4, the higher alkanes are capable of undergoing charge transfer with $I^+(^1D_2)$ ions. C_3H_8 and higher alkanes are also capable of undergoing charge transfer with $I^+(^3P_1)$ and ($^3P_0$) ions.

Preliminary data, using C_2H_6 as an additive indicate that C_2H_6 inhibits the $I^{128}+CH_4$ reaction in a manner such that the curve lies between that for NO and CH_3I (Fig. 3). These data extrapolate to zero at unit mole-fraction C_2H_6. Thus, I^{128} reacts or interacts more readily with C_2H_6 than it does with CH_4. The reason for the low organic I^{128} yield with C_2H_6 could be due to a reaction of $I^{128}+C_2H_6$ which proceeds readily but leads to the formation of HI as well as to charge transfer with $I^+(^1D_2)$.

[18] R. F. Pottie, R. Baker, and W. H. Hamill, Radiation Research 10, 664 (1959).

[19] S. C. Lind, *Radiation Chemistry of Gases* (Reinhold Publishing Company, New York, 1961), pp. 133, 203.