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ANN ARBOR, MICHIGAN

Final Report On

THE EFFECT OF RADIATION ON CHEMICAL REACTIONS

by

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Project 1943-4
U.S. Atomic Energy Commission
Contract AT (11-1)-162
Chicago 80, Illinois
August, 1957

ABSTRACT

This report is a summary of the work done for the U.S. Atomic Energy Commission during the past six and a half years. Primarily the studies have been devoted to a search for chemical reactions which are promoted by gamma radiation. The underlying purpose behind the studies has been to develop uses for the radiation available from waste fission products.

A brief description of all the reactions studied during the program is presented along with appropriate references to the original reports and publications. These give the detailed account of the work done on each reaction and the reader is referred to them for more complete information.

I. INTRODUCTION

The purpose of this project was to carry out research on chemical reactions promoted by gamma radiation. This was part of a broader program to develop uses for waste fission products. By demonstrating the use of radiation in accelerating chemical reactions, it has been possible to interest industry in investing its own capital in further research and development in this area. Thus, it is expected that when large supplies of fission products become available from the operation of the nuclear power reactors of the future, a demand for these radioactive materials will have been developed.

This program of research has been carried out in the Fission Products Laboratory of the Engineering Research Institute of the University of Michigan. In addition to the usual chemical laboratory equipment, two powerful cobalt-60 sources, nominally rated at one and ten kilocuries respectively, were employed. As part of the program a complete analysis of the gamma radiation fields of these sources was made (1,2e,3). All of the chemical reaction studies were made with these two sources.

After an initial literature survey (2a), a number of reactions were screened in the laboratory by simple batch irradiation. Where significant radiation effects were observed, a more complete study was made. Three of the more successful reactions studied were the addition of chlorine to aromatic hydrocarbons, the polymerization of ethylene, and the copolymerization of sulfur dioxide with onefins. All of the reactions investigated

have been reported to the Atomic Energy Commission at various times. From these reports articles on many of the reactions have been submitted to the technical journals. Two articles of a more general nature were also published (4,5).

In the following sections there is presented a brief description of all the reactions which received attention on this project. References are given to the reports and papers in which this work is thoroughly discussed. The Bibliography is a complete list of all reports, manuscripts, and publications covering the experimental work.

II. SUMMARY OF REACTIONS STUDIED

A. Polymerization of Various Individual Hydrocarbons

1. Preliminary Investigations

Preliminary investigations (1,2b,2c,2d,2e), including studies of the polymerization of natural oils (1,2c), soya oil (1,2c), acetylene (1,2b,2c,6), isobutylene (1,2b,2c), propylene (1,2e), styrene (2b,2c,2d), and ethylene (1,2d,2e) indicated that the polymerization of ethylene was a promising reaction in this category for further study.

2. Polymerization of Ethylene

Following the preliminary investigations, ethylene was polymerized under gamma radiation at pressures of 250 to 1600 psi at room temperature (1,2f,7). Radiation doses of 5 to 7 megarep produced a hard, tough polymer. Lesser doses produced a soft, brittle, waxy polymer. The study of the polymerization was then continued (2g,8,9) to include a wide range of temperature and pressure. The products of polymerization ranged from an oily

liquid at 220°C. to waxes and solids at lower temperatures. The radiation yields ("G" values) were fairly high, indicating chain-reaction mechanisms. The effect of radiation intensity upon the rate of polymerization of ethylene was studied (10). For the uninhibited reaction, the reaction rate constant was found to vary as the 0.6 power of the intensity.

A study was made of the process design considerations for the radiation polymerization of ethylene (11). A rough estimate, giving some comparative figures on the cost of polyethylene produced by the radiation and the conventional process, indicated that the proposed process would be competitive with conventional processes for manufacturing polyethylene.

B. Copolymerization of Various Hydrocarbons

1. Copolymerization of Mixtures of Butadiene and Styrene, and Ethylene and Propylene

Preliminary investigations (8,12), were made on the effect of gamma radiation upon the copolymerization of 1,3-butadiene and styrene and upon emulsions of 1,3-butadiene and styrene in various soap solutions. Although the yields obtained were small, the percent yield of the controls were relatively insignificant when compared to those of the irradiated samples. Preliminary work was also done on the copolymerization of ethylene and propylene (6).

2. Copolymerization of Sulfur Dioxide with Various Hydrocarbons

Preliminary experiments (8,12) carried out on the copolymerization of sulfur dioxide with propylene, butene-1,

butene-2, isobutylene, 1,3-butadiene, nonene, dodecene, and styrene indicated that the reactions proceeded fast enough to warrant further investigation. Larger scale reactions were then conducted (8,12) with the same reactants, but using much smaller radiation dosages. A description of the characteristics of the copolymers formed and of significant observations made during the large scale experiments was presented.

Further investigations (13), were made on the effects of gamma radiation on the polymerization of sulfur dioxide with ethylene, propylene, butene-1, butene-2, isobutylene, hexene-1, decene-1, dodecene-1, 1,3-butadiene, and cyclopropane. Reaction times and radiation doses were varied for each of the reactions. The effect of radiation on some of the properties of the copolymer products was investigated. A correlation of the kinetic data of hexene-1 in the radiation field was obtained from expressions derived from a free radical type reaction.

Additional polysulfones have recently been prepared with allyl bromide, allyl chloride, hexene-2, and 2-methyl-pentene-1 (6). This work will be continued.

C. Halogenation

As used in this work, halogenation (chlorination, bromination, or iodination) refers to the reaction of an organic compound with a halogen. The products may be the result of addition or substitution or a combination thereof.

1. Preliminary Work

In early experiments (1,2d) the chlorination of pure benzene in the presence of gamma radiation was found to proceed

so rapidly that temperature control was virtually impossible and the inlet lines soon became plugged with solid product. The reaction was primarily the addition of chlorine to the benzene ring. The chlorination of toluene was also attempted (2d) and early work indicated that both addition and substitution took place under gamma radiation.

Because of the success in the promotion of chlorine addition to benzene, experiments were tried using bromide and iodine (2d,2e). Evaporation of a solution of bromine in benzene which had been exposed to gamma radiation left a residue of a small quantity of crystals in a liquid having noticeable lachrymatory properties. There were no noticeable reactions in solutions of iodine in toluene exposed to gamma radiation. A solution of linseed oil, benzene, and iodine was found to become lighter in color when irradiated.

In a cooperative program with the Michigan Memorial Phoenix Project No. 98 the preparation of trichloroacetic acid by chlorinating chloral hydrate in the presence of gamma radiation was tried (8). Excellent yields were obtained using radiation whereas repeated experiments at different temperatures gave no conversion of chloral hydrate to trichloroacetic acid by the action of chlorine alone. The kinetics of the radiation reaction were studied further in this project.

2. Chlorination of Aromatics

More extensive work (2e,8,9,14,15) showed that radiation yields for the addition of chlorine to benzene were of the order of 19,000 to 114,000 molecules reacted per 100 electron

volts absorbed by the system (G values). The product of the radiochlorination of benzene was found to be the several isomers of 1,2,3,4,5,6-hexachlorocyclohexane, including 11-13 percent of the commercially important gamma isomer.

A design (2g,8,9) was developed for a chemical plant to chlorinate benzene under gamma radiation for the production of insecticides. Radiation sources of cesium-137, 6-month old mixed fission products, and cooling reactor fuel elements were compared.

The radiochlorination of toluene (2e,2f,2g,8,9,14,15,16,17) proceeded rapidly, although not as fast as the benzene reaction. Most of the chlorine was consumed by addition to the ring, although substitution also occurred. The addition product was separated from the other reaction products in good yields, and appeared to be similar to materials previously reported to be formed in minor amounts during the photochlorination of toluene. An equation was developed for the partial kinetics of the chlorination of toluene.

Chlorobenzene (2f,14,15,16,17) was found to undergo a rapid addition of chlorine under gamma radiation. Benzyl chloride, benzal chloride, and benzotrichloride (2e,15,16,17), however showed no reaction under the same conditions. Benzyl chloride (2e,15,16,17) and oxygen (16,17) were found to inhibit the radiochlorination of both toluene and benzene.

The work done on the chlorination of aromatics was later extended to include the xylene mixture of three isomers (8,9), meta-xylene (18), mesitylene (8,9,19), ethyl benzene (8,

9,20), naphthalene (8,9,19), 1-methyl naphthalene (18), and 2-methyl naphthalene (18). The later work (18,19,20) was more extensive and is believed to be more reliable. Reports of the earlier work (7,8) concluded that the ratio of addition to substitution was increased in general by radiation and decreased by increasing the temperature. More recent work (19) supports only the latter conclusion.

D. Miscellaneous Reactions

1. Synthesis of Ammonia

Attempts were made to synthesize and to decompose ammonia at atmospheric pressure by gamma radiation (1,2b). No formation or decomposition of ammonia was detected. Further experiments using palladium-109 beta radiation (1,2b) also indicated no measurable formation of ammonia.

2. Oxidations

a. Oxidation of Sulfur Dioxide

The oxidation of sulfur dioxide was attempted by three procedures (1,2d). Irradiation did not significantly accelerate the oxidation of either gaseous or liquid sulfur dioxide. However, it was found that sulfurous acid can be converted to sulfuric acid by passing oxygen through the sulfurous acid in the presence of gamma radiation.

b. Oxidation of Benzene and Toluene

Several attempts were made to oxidize benzene and toluene by bubbling oxygen through the hydrocarbons in the presence of gamma radiation (2e). No measurable reaction occurred

in any of the runs.

c. Oxidations Using Oxidizing Agents Other than Elemental Oxygen

Solutions of potassium permanganate in acetone and in an acetone-benzene mixture were exposed to gamma radiation (2d). The solutions containing benzene were decolorized and yielded a dark precipitate. No change was apparent in irradiated solutions of permanganate in acetone.

Potassium iodide solutions were also irradiated in the cobalt-60 source (2d). In one run, using acetone as a mutual solvent, a crystalline product with a sharp melting point was obtained. Subsequent runs produced explosive products which were probably organic peroxides.

3. Oxo-Type Reactions

Preliminary runs were made on the Oxo reaction (7). Ethylene, butene-1, butene-2, propylene, and isobutylene were subjected to Oxo conditions (i.e., mixed with CO and H₂) under the influence of gamma radiation. In general the yields were low and the required radiation doses so high that further investigations were not warranted.

4. Hydrogen Sulfide Addition to Olefins

The addition reactions of hydrogen sulfide to olefins indicate significant yields with gamma radiation (6). The products of these reactions are predominantly mercaptans and sulfides.

III. DISCUSSION AND CONCLUSIONS

During the six and a half years of this project the effect of gamma radiation on many chemical reactions has been

studied. In most cases the effect is small and not of particular significance. In a few cases the effect is pronounced, and therein lies the possibility of a radiation processing industry. A number of reports and papers have been published describing these results in a conservative manner and emphasizing the reactions accelerated by radiation, but not trying to sell radiation as a panacea for the chemical process industry.

As a result of the publications from this laboratory, and of course from others also, many private companies have inaugurated their own research programs in this area. Some of them have even built their own radiation laboratories with very considerable outlays of capital. It can be expected that this research will produce results in the future and form the foundation of a radiation processing industry. Because of that a demand will have been developed for radiation sources such as those produced from fission products. This should solve at least part of the problem of what to do with these waste radioactive materials.

It can be concluded that this project has been successful in getting the chemical industry interested in using the radiation that is a by-product of nuclear power reactors. The next step is to make fission product radiation sources available at a low enough cost so that industry can use them profitably to promote the reactions that have been discovered. Naturally, there will be competition between various sources of radiation, such as fission products, artificial isotopes, and accelerators. However, because radiation is a necessary by-product of the uranium fission process, it is very probably that this source of radiation will be the cheapest in the end. This by-product radiation may be that associated with the primary fission process

in the reactor, it may be from the fission products in spent fuel, or it may be from fission products such as cesium-137 that have been separated from the unburnt fuel and other inert materials. The preparation of practical fission product radiation sources is only starting at this time. A plant is being constructed at Oak Ridge National Laboratory to separate and package $Cs^{137}Cl$. When its output becomes available on the market, there will be a further stimulus for research in the field of radiation chemistry. Another project here at the University of Michigan has been studying the feasibility of making radiation sources by absorbing radioactive fission products in montmorillonite clay. It is hoped that the studies of the clay sources may be continued so that they can be furnished on a trial basis to industry. With more and more kinds of radiation sources being developed, it can be expected that radiation chemistry will expand on both a fundamental basis and in its practical applications. Production of cheap radiation sources is necessary if a radiation processing industry is to be developed. It is doubtful that nuclear reactors can ever be operated to make artificial isotopes, such as cobalt-60, very cheaply. Fission products, being a true waste by-product of the nuclear power industry, have the potential, at least, of being made available at comparatively low cost.

IV. ACKNOWLEDGEMENT

The personnel who worked on this investigation and the University of Michigan greatly appreciate the support of the Atomic Energy Commission. Not only has the project stimulated research, but it has afforded valuable training and employment opportunities for project personnel. Facilities for training students in various phases of nuclear engineering have also been provided in the Fission Products Laboratory where this work has been conducted.

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