

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND]

## Chemistry of $N^{13}$ Recoils in Some Carbon Compounds<sup>1</sup>

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The chemistry of  $N^{13}$  recoils produced by the  $C^{12}(d,n)N^{13}$  reaction in methyl bromide, methyl chloride, chloroform and carbon tetrachloride has been studied. A combination of gas chromatographic and chemical methods has been used to analyze the different reaction products. The main product in the  $CH_3Br$  and  $CH_3Cl$  cases was HCN. In  $HCCl_3$ ,  $CICN$  was found in addition to HCN. In carbon tetrachloride  $CICN$  was the main product. In addition, three other radioactive compounds were observed. Nitrogen,  $NO_2$  and one other unidentified nitrogen-oxygen compound were detected. The compounds probably arise from the reactions of  $N^{13}$  with nitrogen and oxygen which originally were absorbed on the surface of the reaction vessel. No significant amounts of  $NH_3$  were detected indicating that probably no abstraction of hydrogen takes place.

### Introduction

When a carbon-containing compound is bombarded with deuterons of appropriate energy, the nuclear reaction  $C^{12}(d,n)N^{13}$  occurs. The nitrogen recoils as a positively charged ion with a considerable amount of translation and electronic energy. The recoil energy is calculated to have a maximum value of 0.7 Mev. for 2 Mev. deuterons if the  $Q$  of the reaction is  $-0.28$  Mev.<sup>2</sup> The recoiling fragment loses its energy by colliding with gaseous molecules, or the walls, to produce ions, free radicals and excited molecules. Finally, when its energy has been reduced sufficiently, it undergoes chemical reactions. This paper reports some results obtained from the study of the compounds produced by  $N^{13}$  recoils in methyl bromide, methyl chloride, chloroform and carbon tetrachloride. The identification of the final radioactive compounds was made through a combination of chemical and gas chromatographic techniques.

### Experimental

The bombardments were made with one microampere of 2 Mev. deuterons obtained from an electrostatic generator in our Laboratory. Bombarding time did not exceed 20 minutes. Methyl bromide and methyl chloride obtained from the Matheson Company, East Rutherford, New Jersey, were dried over  $CaCl_2$  and purified by careful vacuum distillation. During the irradiation the gas was confined in a cylindrical brass cell 1.5 cm. in diameter and 10 cm. long. The cell was equipped with a vacuum gauge and was mounted directly under the beamport of the electrostatic generator. The irradiation was made through a 0.0001 inch nickel window mounted with a Neoprene O-ring. The gases used for irradiation were handled in a small vacuum line mounted under the target. After completion of the bombardment the gas was removed by condensation with liquid air or swept directly into a chromatograph. The radioactive products were then analyzed by gas chromatography. In cases where chemical identification was made, the irradiated gas was shaken with an aqueous solution containing different carriers, such as  $NH_4Cl$  and  $KCN$ . The ammonia was then distilled out of alkaline solution and its activity and half-life measured with a scintillation counter. HCN was distilled out of acidic solutions by sweeping it with carbon dioxide. The cyanide ion also was detected by precipitation as silver cyanide and counted using a flow counter operating in the proportional region.

The gas chromatograph was an all glass instrument and for these experiments it was operated at  $86^\circ$ . A 12-foot column packed with "Celite" and coated with silicone grease was used. Helium was used as a carrier gas and a flow of 40 cc./min. was maintained by a pressure regulator. Detection of macro amounts of material was realized with a thermal-conductivity cell. The radioactive gases were de-

tected with two  $2\pi$  methane proportional counters viewing diametrically opposite Mylar windows of a glass cell through which the gas passed on exit from the chromatograph. The responses of the thermal-conductivity cell and the counter were recorded simultaneously with a two-pen recorder. The difference between the time responses of the two pens was determined for various conditions by running radioactive  $CO_2$  through the instrument. Identification of the compounds was made through comparison of their retention times with those of the reference compounds. The decay curve of each peak was measured to determine that one was dealing solely with the 10 min.  $N^{13}$  activity. The absence of any chlorine or bromine activity was checked by gamma-ray analysis using a multichannel pulse height analyser.

### Results and Discussion

A typical gas chromatogram of the deuteron irradiated methyl bromide is given in Fig. 1a. The full line gives the response of the recorder to the output of the thermal-conductivity cell. The large peak is due to methyl bromide and the others are due to products produced by radiation damage. The first peak is due to methane produced during the radiation and to air which is given off by the walls during irradiation. Methane was identified by use of another gas chromatographic column. The counter output is given by the dotted line and four peaks are evident. Referring to the peaks in the order of their increasing retention times, it will be noted that peak IV is small and sometimes not detectable.

These peaks probably are due to compounds formed between recoiling  $N^{13}$  and methyl bromide. The "start" of each pen is also given and will be given in all other figures. The difference is due to the fact that the two pens are displaced from each other. Figure 1a also includes the retention times as obtained from macro-sized samples of various nitrogen compounds which might be products of the reaction of  $N^{13}$  with the bombarded material. Although some uncertainty exists as to the relative behavior of macro and tracer amounts of a gas in a chromatographic column, it will be assumed that they are the same. Retention times will thus serve as a basis for the identification of the unknown compounds.

Figure 1b represents the results obtained with methyl chloride using the same pressure of gas, namely, 390 mm. It is apparent that only peak III is present, with only a slight indication of the presence of peak IV.

Figure 1c represents the gas-chromatographic analysis of the products formed in deuteron irradiated methyl bromide to which HCN carrier

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) T. W. Bonner, J. E. Evans and J. E. Hill, *Phys. Rev.*, **75**, 1398 (1949).

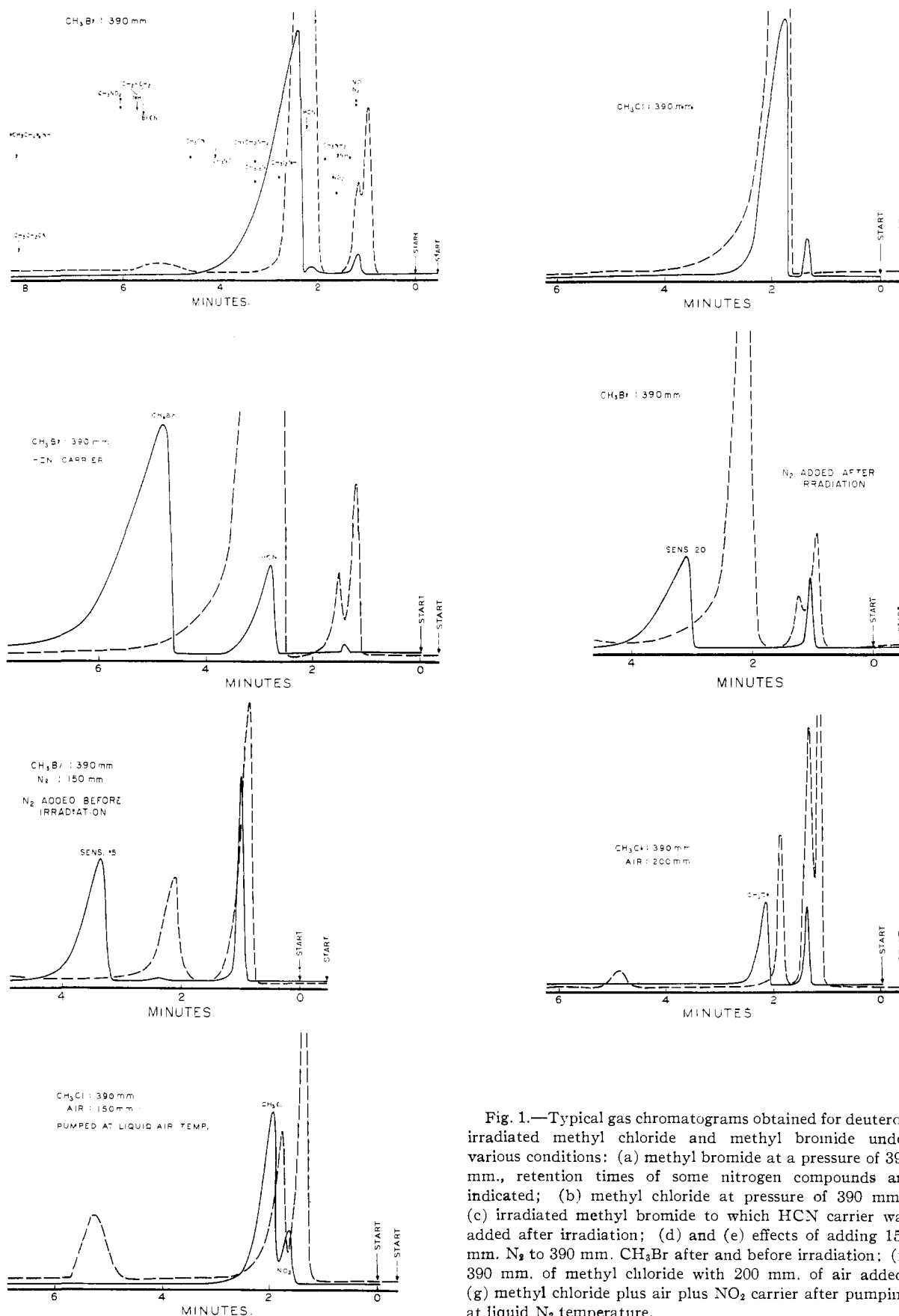


Fig. 1.—Typical gas chromatograms obtained for deutron irradiated methyl chloride and methyl bromide under various conditions: (a) methyl bromide at a pressure of 390 mm., retention times of some nitrogen compounds are indicated; (b) methyl chloride at pressure of 390 mm.; (c) irradiated methyl bromide to which HCN carrier was added after irradiation; (d) and (e) effects of adding 150 mm. N<sub>2</sub> to 390 mm. CH<sub>3</sub>Br after and before irradiation; (f) 390 mm. of methyl chloride with 200 mm. of air added; (g) methyl chloride plus air plus NO<sub>2</sub> carrier after pumping at liquid N<sub>2</sub> temperature.

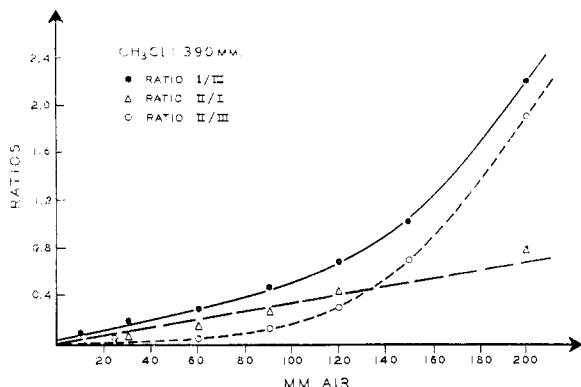


Fig. 2.—Variation with air content of various radioactive  $N^{13}$  products formed from deuteron irradiation of methyl chloride and air: I/III, ratio of nitrogen to HCN; I/II, ratio of  $NO_2$  to nitrogen; II/III, ratio of  $NO_2$  to HCN.

has been added after irradiation. The same retention times of the HCN thermal-conductivity peak and the radioactive peak III are taken as evidence that it is due to HCN. The presence of hydrogen cyanide was confirmed by dissolving the products in water containing KCN and  $NH_4Cl$  as carriers. The cyanide was precipitated as  $AgCN$  and counted. It was found that  $N^{13}$  activity was present in that form. The question may, of course, arise as to whether nitrogen exchange occurs between  $NH_4Cl$  and HCN under experimental conditions. To check this point, an exchange experiment was performed by mixing  $N^{15}H_4Cl$  and KCN solutions, then separating and analyzing them mass spectroscopically. No nitrogen exchange was detected. Nitrogen activity could also be swept out of an acidic solution of the radioactive materials by  $CO_2$ . Furthermore the radioactive peak III can be made to disappear completely if the irradiation is made in a clean copper or brass vessel by running the irradiated gas through metal containers before chromatographic analysis. The radioactive compound producing peak III is a reactive material which reacts with a metal surface causing the nitrogen activity to stay on the metal wall. It is also eliminated when the reaction products are passed over soda-lime. The only detectable peak present in irradiated methyl chloride also was shown to be due to hydrogen cyanide.

Figures 1d and 1e show the effect of adding 150 mm. of nitrogen to methyl bromide after and before deuteron irradiation, respectively. Clearly the addition of  $N_2$  after irradiation has no effect on the ratio I/III. However,  $N_2$  addition prior to deuteron irradiation results in an increase of the ratio I/III. It also will be noted that peak II is not evident. This behavior can be explained if the  $N_2$  acts as a sink for the  $N^{13}$  atoms, thus reducing the number of  $N^{13}$  atoms available for HCN production. If this is the case, peak I formed in methyl bromide must be due to the reaction of  $N^{13}$  with some nitrogen impurity, such as air, in the system. Peak I also could be due to NO since the column does not separate  $N_2$  from NO, and the two compounds have the same retention times. In the case of methyl bromide, it appears that peak I is mostly due to  $N_2$  judging from results obtained with a

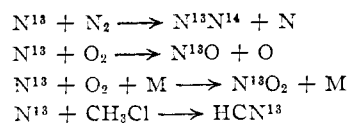
molecular sieve column that separated  $N_2$  and NO. Since the activity due to nitrogen cannot be due to doubly labelled nitrogen molecules and since considerable care was taken to remove any air from the starting material, it seems reasonable to assume that the  $N_2$  activity present in the case of methyl bromide, in which no nitrogen was deliberately added, is the effect of  $N^{13}$  reacting with nitrogen adsorbed on the walls of the container. Gas chromatographic analysis of the gases after performing the same manipulations, but without deuteron irradiation, showed no detectable amounts of air. This wall effect would be expected to show a pressure dependence because the process would be a function of the diffusion of the nitrogen atoms to the walls of the reaction vessel. This was found experimentally in that the ratio of peak I to III decreased as the methyl bromide pressure increased. At 300 mm. the ratio was 2.8 and at 600 mm. it was 0.7. A similar behavior has been observed for methyl chloride; however, at 300 mm. pressure of methyl chloride no evidence of peaks I and II was obtained. However, the peaks began to appear as one lowered the pressure to 50 mm. or lower.

Figure 1f shows the effect of adding air to 390 mm. of methyl chloride. It is immediately apparent that peaks I and II have become prominent. Figure 2 shows the effects of adding different amounts of air to a fixed quantity of methyl chloride. As can be seen peaks I and II become more and more important relative to peak III as the pressure of air is increased. Since the addition of nitrogen only influences peak I, peak II might be due to a nitrogen-oxygen compound.

Figure 1g shows the results obtained when the reaction products and  $NO_2$  carrier have been vacuum pumped at liquid air temperature so as to remove all nitrogen, air and methane. Peak II does correspond to  $NO_2$ . This is indicated by the disappearance of the first thermal-conductivity peak. It is seen that radioactive peak I has disappeared leaving only peak II due to  $NO_2$ . Pumping on the frozen reaction products at liquid air temperature without having added  $NO_2$  carrier removed peak II as well as peak I. The vapor pressure of these materials at tracer concentration is sufficiently high so they are eliminated by pumping. Addition of a carrier would of course change this behavior. It therefore appears that oxygen as well as nitrogen can act as a scavenger for the nitrogen-13 atom. The presence of oxygen or nitrogen on the walls of the reaction cell might be expected to have a similar effect.

Figure 2 also shows the ratio of peaks II/I as a function of different amounts of air added to 390 mm. of methyl chloride. It is seen that the amount of  $NO_2$  increases linearly relative to  $N_2$  as more air is added.

The four reactions that can be used to account for the formation of radioactive HCN,  $N_2$ , NO and  $NO_2$  when methyl chloride and air are subjected to deuteron irradiation are



where M is a third body, either another molecule or the wall of the vessel. The formation of NO<sub>2</sub> from a reaction of NO and O<sub>2</sub> was ruled out since this is known to be a termolecular reaction.

The linear increase of radioactive NO<sub>2</sub> over N<sub>2</sub> with increasing air concentration is expected since the formation of NO<sub>2</sub> depends on the presence of a third body (M) which can be molecules of oxygen or nitrogen, consequently the ratio of NO<sub>2</sub> to N<sub>2</sub> would be proportional to the concentration of M.

Although the equations listed above are possibilities which can be used to explain the results, we do not wish to give the impression that they are the only ones. For example, the role of ion-molecule reactions *versus* atom-molecule reactions has not been considered here since there is not a sufficient amount of data to warrant a discussion at this stage of the investigation. Suffice it to say for the time being that if the production of radioactive nitrogen was due to an ion-molecule reaction, and it may well be, and the other products were due to atom-molecule reactions as postulated above, the ratio of the products would depend on the over-all pressure and on the nature of additives. For example, the ionization potentials of the bombarded materials and of oxygen are considerably less than that of nitrogen atoms, making a situation favorable for charge exchange between the recoiling nitrogen ions and other gases in the cell. This situation would tend to reduce the ion-molecule reactions and to favor atom-molecule reactions. The various pressure dependences observed also can be interpreted to favor this arrangement; however, more data are being collected on this phase of the work and will be reported in the near future.

The identity of peak IV has not yet been established; however, on irradiating methyl bromide or chloride with varying amounts of oxygen the ratio of peaks IV/III increases with oxygen content and is not influenced by the presence of nitrogen. Since methyl chloride as well as methyl bromide gives peak IV, it is assumed that no halogen is present in IV. Its dependence on oxygen suggests that it is an oxygen compound. Its retention time does not correspond to CH<sub>3</sub>NO<sub>2</sub> or CH<sub>3</sub>ONO. At any rate it does not appear that peak IV is a very significant product. Similar results and identical products were obtained on irradiation of ethyl bromide. Deuteron irradiation of chloroform gave ClCN and HCN. Carbon tetrachloride gave ClCN as the main radioactive product. The amount of ClCN increased as the number of chlorine atoms in the molecule increased and in methyl chloride there was presumably too little to detect.

In addition to the N<sup>13</sup> recoil process discussed above, there is present various radiation damage occurring as a result of deuteron bombardment. If the beam current is sufficiently high and the irradiation times sufficiently long, it is clear that one can produce considerable decomposition of the target gas. Since the objective in this research was to study the effects of N<sup>13</sup> recoils on the target gas, conditions which led to extensive radiation damage were avoided. The following experiments were performed in order to get an estimate

of the amount of radiation damage. For various conditions of target gas pressure, beam current, beam voltage and irradiation time, a measurement was made of the non-condensable gases produced by the radiation and compared with the amount of target gas present. In addition, spot checks were made from time to time as to what fraction of the target gas remained after irradiation. Quantitative gas chromatographic analysis was used, in the main, for this purpose. In all of the experiments reported here, the decomposition of the target material did not exceed 7%. Furthermore, no peaks were observed in the gas chromatographs corresponding to expected compounds such as ethyl or higher bromides when methyl bromide was a target gas. In general, all chromatographs were run for a considerably longer period than indicated in the figures to monitor any possible higher molecular weight products which might have been produced. One cannot with complete certainty rule out the possibility that the radiation damage materials or fragments are combining with N<sup>13</sup> to form the observed radioactive molecules. However, in view of the small amount of damage produced under the experimental conditions it appears highly probable that one is here dealing in the main with reactions between recoil N<sup>13</sup> and the target materials. The main radiation damage products that were formed under our experimental conditions were methane, hydrogen, probably HBr or HCl. On extensive irradiation where much radiation damage occurred some polymer was deposited on the wall. It was mentioned earlier that the radioactive HCN reacted with freshly cleaned metal surfaces. This was experienced with newly made cells. However, after a few long bombardments the fresh metal surfaces were covered and in such cells the HCN remained in the gas phase.

It is interesting to compare this work with that of Winkler, *et al.*,<sup>3-5</sup> in which reactions of active nitrogen with organic molecules were studied. In the case of hydrocarbons and organic halides these authors report that HCN and ClCN are the sole products. In their case, only thermal nitrogen atoms were involved, whereas in the present case the recoiling nitrogen starts out at high energies. In view of the identity of the products it is probable that in both cases one is dealing primarily with reactions of thermal nitrogen atoms. The sequence of events in the hot atom case is probably the following. At the time of its formation the N<sup>13</sup> is in the form of a positively charged ion; as it recoils it produces ions, free radicals, etc., contributing to the observed radiation damage products which are produced mainly by the bombarding deuterons. When the ion slows down, it neutralizes and becomes a nitrogen atom which on thermalization reacts to form the observed products.

It is interesting to note that just as in Winkler's case no significant amount of ammonia was found. A trace of activity was found with ammonia carrier

(3) B. Dunford, H. G. V. Evans and C. A. Winkler, *Can. J. Chem.*, **34**, 1074 (1956).

(4) H. G. V. Evans, G. R. Freeman and C. A. Winkler, *ibid.*, **34**, 1271 (1956).

(5) S. E. Sobering and C. A. Winkler, *ibid.*, **36**, 1223 (1958).

on distilling a basic aqueous solution of  $\text{NH}_4\text{Cl}$  and  $\text{KCN}$  containing the radioactive hot atom products. However, no peak corresponding to radioactive  $\text{NH}_3$  was found in the gas chroma-

tograms; consequently it was concluded that the small amount of activity found probably was due to small amounts of nitrogen gas being carried over into the distillate.

[CONTRIBUTION NO. 2545 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

## Some Iodine Atom Recombination Rates by Flash Photolysis<sup>1</sup>

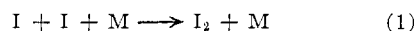
BY ROLF ENGLEMAN, JR.,<sup>2</sup> AND NORMAN R. DAVIDSON<sup>3</sup>

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The rate constants of the homogeneous gas-phase iodine atom recombination have been measured by flash photolysis in the presence of several third body gases. Hydrogen, helium, benzene and methyl iodide have been studied as third body gases at several temperatures between 323 and 548°K., and their third order rate constants are  $1.41 \times 10^9 (298/T)^{0.80}$ ,  $4.93 \times 10^9 (298/T)^{1.48}$ ,  $1.00 \times 10^{11} (298/T)^{2.83}$  and  $1.50 \times 10^{11} (298/T)^{3.24}$  moles<sup>-2</sup> sec.<sup>-1</sup>, respectively. Ethyl iodide, hydrogen iodide and carbon monoxide were used at 323°K. and yielded  $2.38 \times 10^{11}$ ,  $2.81 \times 10^{10}$  and  $5.42 \times 10^9$  moles<sup>-2</sup> sec.<sup>-1</sup>, respectively. Limited experiments were made with nitric oxide as a third body gas. The recombination rate was apparently too fast to measure with this apparatus, but an apparent lower limit of  $4.8 \times 10^{14}$  moles<sup>-2</sup> sec.<sup>-1</sup> was established.

The homogeneous gas-phase iodine atom recombination in the presence of a third body gas has been studied by several methods and many investigators. Some of the earliest measurements were made by Rabinowitch and Wood<sup>4</sup> using a photostationary state method. Shock tube measurements have been used to study the rate of iodine dissociation in the presence of a third body gas at high temperatures (1000–1600°K.).<sup>5</sup>

The flash photolysis technique has been applied to iodine atom recombination by numerous investigators,<sup>6–13</sup> and this paper is a continuation of earlier measurements in this Laboratory.<sup>8,12</sup> The over-all simple recombination reaction and rate equation are



$$-d[\text{I}]/dt = 2k(\text{M}, T)[\text{I}]^2[\text{M}] \quad (2)$$

where M is the third body gas. The third order rate constant,  $k(\text{M}, T)$ , specifies the third body gas and the temperature, and it will be given here in units of l.<sup>2</sup> moles<sup>-2</sup> sec.<sup>-1</sup>. The extensive measurements of Russell and Simons<sup>7</sup> give the rate constant for recombination in helium as much larger than predicted by the "intermediate complex" treatment of Bunker and Davidson.<sup>14</sup> Their measurements

give relatively large rate constants for recombination in benzene and ethyl iodide, presumably due to complex formation with iodine atoms. In an attempt to clarify and confirm these results, helium, hydrogen, benzene and methyl iodide have been used as third body gases at various temperatures. In addition, limited measurements were made at a single temperature on recombination in ethyl iodide, hydrogen iodide, carbon monoxide and nitric oxide. The experiments recently reported by Porter and Smith<sup>13</sup> were directed towards the study of essentially the same questions that interest us.

### Experimental

The apparatus used in this study was essentially that described by Bunker and Davidson.<sup>12</sup> The measurements with helium and hydrogen were made with a Dumont 304-H oscilloscope as described previously. The other measurements were made with a Tektronix 535 oscilloscope with a 53/54D amplifier plug in unit. The sweep of the Tektronix oscilloscope was triggered manually to give a base line from which to measure deflections. At a preselected point on the sweep, the oscilloscope generates a delayed trigger pulse which causes a 2D21 thyratron to discharge and generate a 200 volt pulse. This pulse is applied to the control grid of a 5C22 hydrogen thyratron and the resulting breakdown allows a 4 $\mu$ f condenser bank to discharge through the flash lamp. A high voltage power supply was used to charge the condenser bank to between 10 and 16 kv., depending on the flash intensity desired.

**Materials.**—Reagent grade iodine crystals were used after at least one sublimation. Linde argon (99.9%), Linde hydrogen (99.9%) and Ohio Chemical Company helium (99.9%) were used directly after passage through a Dry Ice or liquid nitrogen trap. Matheson C.P. carbon monoxide was used without further purification. Baker and Adamson reagent benzene was used after freezing and degassing. A freshly opened bottle of Matheson C.P. methyl iodide was degassed by pumping and freezing and was stored in the dark over a piece of copper wire. The methyl iodide remained almost colorless throughout the experiments. Matheson C.P. ethyl iodide was used after a similar treatment.

Matheson C.P. nitric oxide was purified as described by Huffman.<sup>15</sup> Condensed nitric oxide was twice distilled from a methylpentane-bath at about  $-150^\circ$  to a liquid nitrogen bath. This process changed the nitric oxide from a multi-colored solid to a very light blue liquid or a light blue ice-like solid. This solid was stored at liquid nitrogen temperature.

(1) (a) This work was supported by the Office of Naval Research. (b) Further experimental details may be found in the Ph.D. thesis submitted by R. E. to the California Institute of Technology, 1959.

(2) Los Alamos Scientific Laboratories, Los Alamos, New Mexico.

(3) To whom inquiries concerning this paper should be addressed.

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(15) R. E. Huffman and N. Davidson, *ibid.*, **81**, 2312 (1959).