[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Effect of High γ-Radiation Dosage on the Organic Yields of Br^{80}, Br^{80m} and Br^{82} Produced by the (n,γ) Reaction in *n*-Propyl Bromide

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Pure liquid *n*-C_3H_7Br subjected to high γ-ray exposures before or during neutron irradiation gives abnormally high organic yields[1] for the $Br^{79}(n,\gamma)$ Br^{80m}(4.4 hr.), $Br^{79}(n,\gamma)Br^{80}$(18 min.), and $Br^{81}(n,\gamma)Br^{82}$(36 hr.) processes. The effect is most pronounced for the 36 hr. species and least for the 18 min. species. It is due to reaction of the HBr or Br_2, formed as a result of the (n,γ) process, with olefin-like species formed from the C_3H_7Br by the γ-radiation.

Introduction

It has been firmly established[2-5] that wide variations of γ-ray intensity and total γ-dose during neutron irradiation do not alter the organic yields obtained from alkyl halides if these variables are within the low ranges which have been used in most studies of the chemical effects of the (n, γ) process. By contrast, we have observed that when pure degassed *n*-C_3H_7Br is irradiated for an hour in a nuclear reactor at a neutron flux of 10^{12} neutrons/cm.²/sec. and a γ-ray intensity of 10^6 r./hr. the organic yield of Br^{82} is 90% rather than the 32% usually observed at relatively low radiation intensities. The work reported below was initiated to determine the maximum γ-dose which could be tolerated by the *n*-C_3H_7Br without causing an increase in the organic yields from the (n, γ) process, and the mechanism by which the organic yields are increased by high γ-dosage.

Experimental

n-Propyl bromide (Eastman Kodak Co. white label) was purified by bubbling a stream of oxygen containing 5% ozone through it for one hour, washing with 3% H_2O_2 solution, shaking with $NaHCO_3$ solution to remove organic acids, and washing with distilled water. The product was then stirred vigorously with concentrated sulfuric acid until fresh portions of the acid did not show color after 12 hours of continuous stirring. It was then washed with $NaHCO_3$ solution and distilled water, dried over anhydrous $MgSO_4$, and fractionated through a 3-foot column packed with glass helices. A 75% center cut of boiling range less than ±0.2° was collected. This method of purification was designed to remove traces of olefinic impurities, which, if present, might react with Br_2 formed by the Szilard–Chalmers reaction to return it to organic combination. The best indication of the success of the purification is that the product gave organic yields in the range of 32-36% at low radiation levels, in agreement with the lowest values obtained following other methods of purification in this laboratory and elsewhere.[3,6]

Neutron irradiations of *n*-C_3H_7Br were made in 16 mm. o.d. Pyrex or quartz tubes placed in holes in a paraffin block about 2 cm. from a hole containing an Sb–Be photoneutron source.[7] Samples to be irradiated in the absence of oxygen were prepared on a vacuum line and sealed off after several cycles of alternate freezing, evacuation, thawing and freezing. The γ-intensity from the source was determined by ferrous sulfate dosimetry[8] to be about 1.6×10^3 r./hr. at the position of the samples at the time of the experiments.

Immediately after neutron irradiation, 1 ml. of 0.1 *M* Br_2 in CCl_4 solution was added to the irradiation vessel as carrier and the inorganic Szilard–Chalmers bromine was extracted with an aqueous solution 0.1 *M* in Na_2SO_3 and 0.1 *M* in NaBr. The organic layer and the aqueous extract were counted separately in solution-type Geiger tubes to determine the organic yields, appropriate corrections being made for density of the counting medium,[9] relative counting efficiencies of the tubes and decay. The three nuclear species, Br^{80m}, Br^{80} and Br^{82} were distinguished by resolution of decay curves.

In some experiments where it was desired to expose an evacuated sample to pure γ-radiation in the absence of neutrons as well as to neutrons, an annular vessel of the type described earlier[10] was sealed to the neutron irradiation tube. With the liquid in the annular vessel it could be subjected to 2×10^5 r./hr. of γ-radiation, from a 40 curie Co^{60} source, following which it could be poured into the tube for neutron irradiation without opening it to the air.

Results

The Effects of Radiation Dosage and of Air on Organic Yields.—Table I and Fig. 1 show the effect of the length of irradiation on the organic yields of each of the three bromine nuclides which can be produced by the (n, γ) reaction when *n*-C_3H_7Br is exposed to the Sb–Be source. The results can be summarized as follows. (1) The organic yields of Br^{80}, Br^{80m} and Br^{82} are essentially equal to each other (*ca.* 34%) for irradiation times up to 4 hr. (6×10^3 r.) either in the presence or absence of air. (2) For irradiations of longer than 16 hr. in the absence of air the organic yields of Br^{82} and Br^{80m} increase, the former faster than the latter, while the value for Br^{80} drops slightly but remains essentially constant out to at least 132 hr. The value for Br^{82} seems to reach a constant value of about 90% after 80 hr. (1.3×10^5 r.) while that for Br^{80m} is 73% and still increasing at 132 hr. (3) The tendency for the organic yield to increase at long irradiations is lessened by the presence of air: for Br^{82} the yield rises to 46% at 80 hr. and remains constant for longer irradiations, for Br^{80m} there is little or no change up to 132 hr., and for Br^{80} the value drops slightly at 16 hr. and thereafter remains constant as in the absence of air.

Nature of the Radiolysis Product Responsible for the Increased Organic Yields.—The results of Table I and Fig. 1 suggest that prolonged exposure

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[1] (a) The "organic yield" is the fraction of the (n, γ) events for which the radioactive bromine atom produced becomes stabilized in organic combination. (b) The literature on this type of reaction is reviewed by J. E. Willard, *Ann. Rev. Nuclear Sci.*, **3**, 193 (1953).

[2] G. Levey and J. E. Willard, THIS JOURNAL, **74**, 6161 (1952).

[3] F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1495 (1953).

[4] J. F. Hornig and J. E. Willard, THIS JOURNAL, **75**, 461 (1953).

[5] W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **22**, 53 (1954).

[6] M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

[7] Obtained from the Oak Ridge National Laboratory (see Oak Ridge National Laboratory Isotopes Catalogue) and irradiated for two months at the Brookhaven National Laboratory. When first received, the source contained about 10 c. of Sb^{124} and gave about 10^7 neutrons per second.

[8] References to the numerous papers dealing with this type of dosimeter are given by E. J. Hart, *Ann. Rev. Phys. Chem.*, **5**, 142 (1954). In calculating the dosages received by the samples used in the present work, we have used the value 15.6 micromoles of Fe^{++} per liter oxidized per 1000 roentgens.

[9] R. S. H. Chiang and J. E. Willard, *Science*, **112**, 81 (1950).

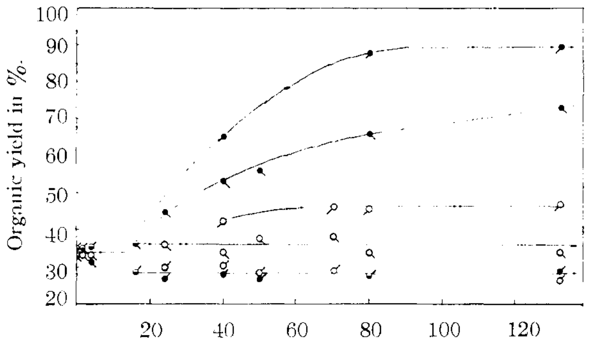
[10] R. F. Firestone and J. E. Willard, *Rev. Sci. Inst.*, **24**, 904 (1953).

TABLE I

ORGANIC YIELDS OF THE RADIATIVE NEUTRON CAPTURE REACTION IN *n*-PROPYL BROMIDE AS A FUNCTION OF THE LENGTH OF IRRADIATION

Length of irradn., hr.	Radiation dosage, roentgens	Organic yield, % In presence of air Br^{82}	Br^{80m}	$Br^{82\,a}$	In degassed liquid Br^{80}	Br^{80m}	$Br^{82\,a}$
0.5	8.0×10^2	36	36		33	32	
1.5	2.4×10^3	34	35		35	34	
4	6.4×10^3	32	36		34	33	
16	2.5×10^4	29	36		29	37	
24	3.8×10^4	30	36		27	45	
40	6.4×10^4	30	34	42	28	53	65
50	8.0×10^4	28	38		27	56	
70	1.1×10^5	29	38				
80	1.3×10^5	28	34	46	27	66	88
132	2.1×10^5	27	34	48	29	73	90

[a] The organic yields of Br^{82} are subject to rather large error because of its low specific activity and low counting efficiency. Its organic yields for irradiation times short compared to those shown here were therefore determined on samples irradiated in the Argonne National Laboratory CP3' pile. The pile provides higher neutron fluxes than the Sb–Be source, with a lower ratio of γ-flux to neutron flux. The organic yields of Br^{82} obtained in the short pile irradiations agreed well with the short Sb–Be source irradiation yields of Br^{80} and Br^{80m} shown in the table.



Length of irradiation, hr. (1.6×10^3 r./hr.).

Fig. 1.—Oxygen free: ● Br^{80} (18 min.); ●, Br^{80m}, (4.4 hr.); ● Br^{82}, (36 hr.). Air present: ○ Br^{80}, (18 mm.); ○ Br^{80m}, (4.4 hr.); ○ Br^{82}, (36 hr.).

to the γ-radiation from the Sb–Be source produces an "olefin-like" species which is able to react slowly with the Br_2 or HBr resulting from the (n, γ) process and return it to organic combination, thus increasing the apparent organic yield, the effect being greater the greater the average time the radioactive species in question have existed in the particular solution,[11] and the greater the concentration of the "olefin." As a partial test of this hypothesis the experiments recorded in Table II were carried out.

TABLE II

RESULTS INDICATIVE OF THE TYPE OF IMPURITIES FORMED FROM DEGASSED *n*-PROPYL BROMIDE BY γ-RADIATION

γ-Irradiation, hr. at 2×10^5 r./hr.	Treatment following γ-irradiation and prior to n irradiation	Neutron irradn., hr.	Organic yield, % Br^{80}	Br^{80m}
22	None	5	46	58
20	140 hr. standing under vacuum	4	44	55
20	212 hr. standing under vacuum	5	40	46
16	4180[a] mm. O_2 added and shaken for 2 hr.	11.5	48	60
16	Washed with H_2O and dried with $MgSO_4$	4	46	59
15	Ozonized (15 min.), washed and dried	9	33	38
20	7.5×10^{-3} *M* bromine added and removed immediately, washed and dried	18.5	42	52
31	7.5×10^{-3} *M* bromine added and removed after 12 hr. standing, washed and dried	8	28	32

[a] Oxygen from a large flask of known volume at a known pressure was condensed into the quartz irradiation vessel containing *n*-propyl bromide, with the aid of liquid nitrogen.

Degassed *n*-C_3H_7Br was first exposed to 3×10^6 r. or more of γ-radiation from the Co^{60} source. It was then given the treatment indicated in the second column of Table II, following which it was irradiated with neutrons from the Sb–Be source, and the organic yields of Br^{80} and Br^{80m} were determined. The first three experiments of Table II show that "high" organic yields are obtained when *n*-C_3H_7Br which has received a high γ-dose is subjected to an irradiation with the Sb–Be source which alone (see Table I) would give a "normal" yield. This is consistent with the conclusion that the "high" yields for the long irradiations of Fig. 1 are due to impurities produced in the C_3H_7Br by the γ-radiation from the Sb–Be source. The fact that the solutions of Table II still gave high yields after standing more than 200 hr. between γ-irradiation and neutron irradiation indicates that the compounds responsible are quite stable in the C_3H_7Br environment and are certainly not free radicals. The fourth and fifth experiments of Table II show that they are not destroyed by 2 hr. exposure to 5 atm. pressure of oxygen or by exposure to water. As would be expected of an olefin, they are destroyed by ozonization and by prolonged exposure to Br_2 (experiments 6 and 8 of Table II). The fact that the reaction with Br_2 is slow rather than instantaneous is shown by the experiment 7.

When *n*-C_3H_7Br was irradiated with 3×10^6 r. from the Co^{60} source followed by 4 hr. with the Sb–Be source, both irradiations being in the presence of air, organic yields for Br^{80} and Br^{80m} of 47 and 51%, respectively, were obtained. The γ-dose here was 15-fold higher than the highest of Fig. 1 and it served to raise the organic yields greatly above the "normal" value even though air was present. In marked contrast, a sample subjected to a nearly identical pair of irradiations under a pressure of 5 atm. of O_2 gave an organic yield of 29% for both Br^{80} and Br^{80m}. The sample irradiated in air remained colorless, as do degassed samples, but that

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(11) This average time, $\bar{t}$, for atoms present immediately after a neutron irradiation of duration t may be calculated from the relation $\bar{t} = \frac{1}{\lambda} - t/(e^{\lambda t} - 1)$ where λ is the decay constant. For times of irradiation short compared to the half lives the average times of existence in the solution of atoms of different radioactive species will be essentially the same. For irradiation times which are appreciable compared to the half lives, the time of existence of atoms of long-lived species will be greater than those of short-lived species. This fact has been pointed out by Rowland and Libby[3] and it has been shown to be responsible for the observation that in impure solutions Br^{80m} (4.4 hr.) shows higher organic yields than Br^{80}(18 min.).[12]

(12) J. C. W. Chien and J. E. Willard, THIS JOURNAL, **76**, 4735 (1954).

irradiated under 5 atm. of O_2 became colored with Br_2. The low values of the organic yield would be expected in the presence of Br_2 due to the scavenger effect.[1b] The elevation of the yield by radiation-produced "olefins" is probably prevented by removal of the olefins by Br_2, and by the reaction of oxygen with radicals which may be intermediates in the "olefin" formation processes.

A further conclusive test of the hypothesis that the observed increases in organic yields are due to stable radiolysis products was made as follows. A sample of purified degassed n-C_3H_7Br was irradiated for three hours with the Sb–Be source. It was then mixed with an identical sample which had been exposed to 4×10^6 r. from the Co^{60} source. After standing for 5 hr. in darkness the mixture gave an organic yield of 50% whereas the sample exposed to the Sb–Be source alone would have given 32–35% if not mixed with the sample which had received the high γ-dose.

Discussion

Reaction in the Absence of Air.—The observations reported above seem to indicate that the inorganic bromine (Br_2 and/or HBr) formed as a result of the (n, γ) process is stable in pure n-C_3H_7Br but can reenter organic combination by reaction with olefins formed by the γ-ray induced radiolysis of C_3H_7Br. The process may be represented by the equation inorganic bromine + olefin $\rightarrow$ organic bromide. The probability that a given radiobromine atom which has entered combination as Br_2 or HBr following the (n, γ) process will enter organic combination before it decays and before the solution is analyzed depends on the concentration of the olefin (which increases with increasing time of irradiation) and on the average time of existence[11] of the radiobromine in the solution. The fact that both of these values are very low during the first hours of irradiation accounts for the equal and constant organic yields of all three nuclear species during this period (Table I and Fig. 1), while the increase in the values for Br^{82}(36 hr.) and Br^{80m}(4.4 hr.) which begins between 4 and 16 hr. is due to the increase in both the olefin concentration and the average time of existence of the radioactive species in the system.

The average time which the Br^{80m}(4.4 hr.) atoms have existed in solutions which have just completed a 16 hr. irradiation is 4.9 hr. Figure 1 shows that the organic yield curve for this species is just starting to rise at this point. At the same point, the average time of existence of Br^{80}(18 min.) atoms has reached its limiting value of 0.43 hr., which does not change for longer irradiations. Since its existence time is *ca.* 0.1 that of the Br^{80m} at the point where the yield of Br^{80m} begins to rise, it may be reasoned that the yield of Br^{80}(18 min.) would begin to rise at a 10-fold higher "olefin" concentration, *i.e.*, at 160 hr. or 2.6×10^5 r. Consistent with this conclusion, the data of Table II show several examples of "high" organic yields of Br^{80}(18 min.) for irradiations greater than 2.6×10^5 r.

The fact that the curve for the organic yield of Br^{82}(36 hr.) rises more rapidly than that for Br^{80m} is probably due to the fact that the average existence time of Br^{82} in the solution changes much more rapidly with time of irradiation, in this time range, than does that of Br^{80m} (*i.e.*, from 7.6 hr. at 16 hr. of irradiation to 30 hr. at 80 hr. of irradiation as compared to a change from 4.9 hr. to 6.4 hr. for the Br^{80m}).

In terms of the explanations given here, the organic yields of Br^{80}, Br^{80m} and Br^{82} would all increase to the same maximum value after sufficiently long irradiation, *i.e.*, after a sufficiently high "olefin" concentration is built up. If HBr and Br_2 are both able to react with the "olefins" this value would be 100%. If, however, HBr does not react and its yield from the (n, γ) process is, say, 10%, the observed organic yield would be observed to increase to 90% for long irradiations. The reasoning here is probably oversimplified since there is reason to believe that non-radioactive HBr is produced from the n-C_3H_7Br by γ-radiation at a considerably faster rate than radiobromine as HBr and Br_2 is produced by the (n, γ) reaction. The rate of this radiolysis is currently under investigation in our laboratory.

Reaction in Presence of Air.—It has been noted above that visible amounts of Br_2 are produced when n-C_3H_7Br is subjected to γ-irradiation in the presence of 5 atm. of O_2. The same Br_2 producing process must occur to a lesser extent when irradiation occurs in air (0.2 atm. O_2). A plausible explanation of the fact that prolonged irradiation does not increase the organic yields in the presence of air to the extent that it does in degassed n-C_3H_7Br is that sufficient bromine is produced so that the fraction of the total bromine in the system which enters organic combination by reaction with "olefin" per unit time is much smaller than in the absence of oxygen. A second contributing factor may be a decrease in the rate of olefin production, as a result of reaction of O_2 with radicals which are precursors of the olefins in the radiolysis mechanism. Quantitative consideration of the relative importance of different possible contributing causes is precluded by such factors as the fact that the solutions were not stirred to maintain oxygen equilibrium, by the simultaneous radiolytic production of HBr, and by the unknown fate of the oxygenated products formed.

Decrease in Br^{80}(18 min.) Organic Yield.—The decrease in the Br^{80}(18 min.) organic yield for times of irradiation of 16 hr. and longer, as compared to short irradiations (Fig. 1), can best be ascribed to a difference in the organic yields of the Br^{79}(n, γ)Br^{80}(18 min.) process and the Br^{80m}(4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80}(18 min.) process since the 18 min. activity produced by the latter is indistinguishable from that produced by the former. Following neutron irradiations of a few minutes duration the 18 min. activity produced by the isomeric transition is negligible (about 2% at 18 min.) compared to that produced by the (n, γ) process, but increases to about 25% of the total for irradiations long enough to give saturation with respect to Br^{80m}. If the organic yield of the isomeric transition is 20% as compared to 32% for the (n, γ) process, this would lead to 29% as the average organic yield of Br^{80} for irradiations sufficiently long to achieve saturation. On the basis of this same assumption, the observed

Br^{80} organic yield after 3 hr. irradiation should be indistinguishable from that for the (n, γ) process, in accord with previous observations.[12]

Expected Effects of γ-Dose in Other Systems.—In systems where radiolysis does not produce a substance which can react with the radioactive inorganic compounds produced by the (n, γ) process no increase in organic yield would be expected as a result of increased γ-dosage. The (n, γ) reaction on organic chlorides seems to produce 10% of the radiochlorine as Cl_2 and 70% as HCl.[13] The latter reacts very slowly with olefins, hence the radiolytic production of olefins might increase the usual organic yield of 20% to a maximum of 30%. Organic iodides liberate free iodine when exposed to high γ-dosage. This would serve to reduce organic yields of the (n, γ) reaction because of the scavenger effect.[2] It is to be expected that some compounds, including some bromides other than n-C_3H_7Br may show higher sensitivity of their organic yields to γ irradiation than does the latter.

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[13] J. C. W. Chien and J. E. Willard, THIS JOURNAL, **75**, 6160 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Exchange of Isotopic Chlorine between HCl and the Series CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl[1,2]

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CH_3Cl exchanges chlorine with HCl in the gas state in Pyrex vessels at a rate $R = 1.4 \times 10^9 e^{-43,600/RT}$ [CH_3Cl] moles liter^{-1} sec.$^{-1}$ at a surface–volume ratio of 7.4 cm.$^{-1}$. For the exchange between CH_2FCl and HCl the rate is $R = 1.4 \times 10^9 e^{-47,100/RT}$ [CH_2FCl] moles liter^{-1} sec.$^{-1}$ at surface/volume = 7.4 cm.$^{-1}$. These two reaction rates are directly proportional to the surface–volume ratio and depend strongly on the condition of the surface. CHF_2Cl exchanges chlorine with HCl at a rate $R = 9 \times 10^4 e^{-30,200/RT}$ [CHF_2Cl]$^{1/2}$[HCl]$^{1/2}$ moles liter^{-1} sec.$^{-1}$ in a reaction which is independent of the surface area or condition. The CF_3Cl–HCl exchange rate is much slower.

The progressive substitution of fluorine atoms in an organic molecule has been shown to effect a marked change in the structural parameters of that molecule.[3,4] There is also a good deal of qualitative information regarding the effect of such substitution on chemical activity, but little quantitative work of this nature is available. It was decided, therefore, to make a comprehensive study of a chemical reaction involving a series of compounds containing progressively larger numbers of fluorine atoms. It was hoped that the rates and mechanisms of such a reaction might enable the effect of the fluorines on the reactivity of the molecules to be understood.

An isotopic exchange reaction seemed to offer many advantages since the products would not be chemically different from the reactants and interpretation of the results might be simpler. The reaction chosen was the exchange of chlorine between HCl and the individual members of the series CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl in the gas phase.

While this work was in progress, Peri and Daniels[5] reported the results of an investigation of the exchange of radioactive bromine between C_2H_5Br and Br_2, HBr and DBr. They observed the same rate law as is reported here for chlorine exchange in the CH_3Cl–HCl and CH_2FCl–HCl systems.

Experimental Procedures

Materials.—All of the organic chlorides were dried by passing them several times through a tube filled with P_2O_5, non-condensable impurities were removed by repeatedly freezing *in vacuo*, and the compounds were then fractionally distilled. Absence of foreign lines in the mass spectra of the purified materials was used as the criterion of purity.

The HCl used was generated by dropping C.p. hydrochloric acid solution into C.p. sulfuric acid. After concentration of the heavier isotope by thermal diffusion, the gas was passed through P_2O_5, repeatedly frozen *in vacuo*, and fractionally distilled.

Isotopic Separation.—A thermal diffusion column was constructed to separate the chlorine isotopes. This has been described in detail elsewhere.[1] The HCl used in this work varied from 40.9 to 68.2% Cl^{37}, compared with the normal concentration of 24.6% Cl^{37}.

Isotopic Analysis.—Isotopic analyses were performed on a model 21-201 Consolidated-Nier mass spectrometer. Chlorine isotopic ratios could be determined directly in the organic chlorides without separating them from their mixtures with HCl. The Cl^{37}/Cl^{35} ratio was read from the peaks corresponding to the undissociated molecules in the cases of CH_3Cl and CH_2FCl. For CHF_2Cl and CF_3Cl it was more practical to use the CHFCl and CF_2Cl peaks, respectively.

The chlorine isotopic ratio could not be read directly in the HCl molecule because of an intense memory effect for this compound that was observed in the mass spectrometer. When successive samples with different Cl^{37}/Cl^{35} ratios were analyzed, the ratio obtained for the second sample would initially be close to that of the first sample, drifting slowly over a period of many hours toward the correct value for the new sample. HCl was apparently absorbed on the walls of the instrument in such a way that it could not be pumped off in any reasonable time, but could be rapidly displaced by or undergo chlorine exchange with additional HCl in the gas phase. An effort to analyze the HCl after

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[1] Abstracted from the dissertation of J. E. B. submitted in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, Summer, 1952. More complete details of this investigation may be obtained from the dissertation filed in the library of the University of Michigan.

[2] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

[3] L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

[4] L. O. Brockway and C. G. Thornton, paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

[5] J. B. Peri and F. Daniels, THIS JOURNAL, **72**, 424 (1950).