

agreement with that found on irradiation of *n*-hexane vapor<sup>10</sup> by  $\alpha$ -particles.

### Conclusions

Two fundamentally different processes for labeling by exposure to tritium gas should be considered: first, reactions of recoiling triton particles as in the method of Rowland and Wolfgang<sup>11</sup>; and secondly, reactions between molecules which have been activated by absorption of radiation energy.

Recoil tritons, produced by  $\beta$ -decay of T<sub>2</sub> molecules, can be eliminated as a major source of labeled products. Since 5700 e.v. are absorbed for each triton produced, it is impossible to obtain a "G" value for T incorporation greater than 0.02 from recoil tritons. In addition, the dependence of the observed "G" values on tritium pressure is incompatible with labeling by recoil tritons.

The reactions largely responsible for labeling, then, must occur either between ionized or excited organic molecules and tritium or between tritium atoms or ions and unexcited organic molecules. The results of the present work, particularly those from the experiment with hexane, in which both chemical and radiochemical products were determined, indicate that the former is the favored process.

The one to one correspondence between the carbon skeletons of major labeled and unlabeled products from *n*-hexane implies that the same process or combination of processes is responsible for their formation, and it is difficult to account for the quan-

tity of the chemical products on the basis of H atom reactions. The proportions of hexane and tritium were such that only 0.2% of the energy was absorbed by tritium, and the relative values for the ionization potentials and first excited states of the two molecules are such that transfer of charge and of excitation energy from hexane to tritium molecules is not likely. Assuming that the "G" value of 18<sup>12</sup> for the production of H atoms from H<sub>2</sub> represents an upper limit for production of T atoms, the number of unlabeled molecules produced is more than 100 times the number of T atoms available.

The results suggest strongly, therefore, that the production of excited and ionized organic molecules and their subsequent reactions determine the nature and distribution of the carbon skeletons of labeled and unlabeled products. This conclusion is supported by the striking correspondence between products obtained in previous radiolysis studies of benzene and *n*-hexane with the products reported here.

Since the presence of tritium does not appear to change the nature of the products, the use of tritium as a radiation source may provide a means of identifying products which are undetectable by other methods. This may facilitate the study of compounds which show great radiation stability or permit the use of low dosages to avoid secondary reactions involving initial products.

**Acknowledgment.**—It is a pleasure to acknowledge valuable discussions with Dr. Louis Kaplan of this Laboratory.

(10) V. P. Henri, C. R. Maxwell, W. C. White and D. C. Peterson. *THIS JOURNAL*, **56**, 153 (1952).

(11) F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

(12) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.* **4**, 570 (1936).

## EFFECTS OF PHASE ON REACTIONS INDUCED BY RADIATION IN ORGANIC SYSTEMS

BY T. O. JONES, R. H. LUEBBE, JR., J. R. WILSON AND J. E. WILLARD

*Contribution from the Department of Chemistry of the University of Wisconsin, Madison, Wisconsin*

*Received June 24, 1957*

This paper summarizes some of the data in the literature on the effects of phase on chemical reactions induced in organic systems by light, ionizing radiation and nuclear transformations. It also presents new data which show that: (1) the ratio of HI to I<sub>2</sub> produced in the radiolysis of pure isopropyl iodide with Co<sup>60</sup>  $\gamma$ -rays is about tenfold higher in the solid phase at  $-190^\circ$  than in the liquid at room temperature; (2) the yield of iodine from the radiolysis of isopropyl iodide in either the liquid or solid is dependent on the past history of irradiation of the sample in the other phase; (3) when the spectrum of ethyl iodide glass at  $-190^\circ$  is examined after exposure of the solid to 2537 Å. light, little or no change is observed as a result of the irradiation, but when the glass is then melted and immediately refrozen, an absorption peak appears at 3700 Å.; a similar effect is caused by the self-irradiation of tritiated ethyl iodide glass; (4) the ratio of HI to I<sub>2</sub> produced by the photolysis of ethyl iodide is approximately ten-fold higher in the glass at  $-190^\circ$  than in the liquid at room temperature.

### Introduction

The life history of an atom or molecule activated by radiation may depend critically on whether it is in a gas, a liquid or a solid. In the gas the mean free path and average time between collisions are relatively large. There are no caging effects. Two radicals formed by the dissociation of a molecule have negligible chance of undergoing primary recombination, and they can be prevented from combining with other radicals in the system by the

addition of low concentrations of radical scavengers. In the liquid or solid, however, radicals formed from the same molecule may undergo primary recombination and radicals formed from molecules in adjacent portions of a "spur" may likewise combine with each other before undergoing sufficient diffusion to react with low concentrations of additives. Electrons ejected from molecules in the gas phase by ionizing radiation have no chance of recombining with the parent ion. In a condensed

phase, however, there is a possibility that such neutralization may occur before chemical reaction can take place.<sup>1</sup> Consequently, ion-molecule reactions,<sup>2</sup> which may be very probable in a gas may be of little importance in condensed phases. Molecules in condensed phases are subject to the influence of the surrounding molecules, consequently the available modes of energy transfer and of decomposition may be different. Ionization potentials may be different. As a result of the ordered arrangement of molecules in crystals, radicals which have been produced by radiation may preferentially attack certain portions of adjacent molecules rather than attacking randomly as in the gas or liquid phase.

The above differences between the phases may result in differences in the nature and yields of products resulting by a single type of radiation. Neither the mechanisms of radiation chemistry, nor the effects of phase on chemical reactions in general are well enough understood to allow good predictions to be made of the influence of phase on the products of a given reaction formed by radiation.

Recently, a number of investigations have been made of "trapped" free radicals produced in the solid state by ionizing radiation,<sup>3</sup> and light,<sup>4</sup> or produced by discharges in a gas and trapped in the solid state on cold surfaces.<sup>5</sup> However, very few comparisons of reaction rates and ultimate chemical products from activation of a single compound by a single type of radiation in different phases have been reported. Such investigations are important both for a better understanding of radiation chemistry and of phase effects on chemical reactions in general. In the course of other investigations in our laboratory we have occasionally made such comparisons, mostly of an exploratory nature. It is the purpose of this paper to summarize some of these, together with examples from other laboratories, in the hope that such a grouping and interrelation of available information will help to establish a perspective on present knowledge and serve as an aid in the planning of future investigations.

For the purposes of this discussion radiation chemistry will be considered to include not only reactions activated by ionizing radiation but also by visible and ultraviolet light and by nuclear processes. Reviews in these fields include: radiation chemistry,<sup>6</sup> photochemistry<sup>7</sup> and chemical effects of

nuclear transformations.<sup>6a,8</sup> The present paper will not endeavor to include a complete coverage of the literature but will present only selected examples.

### Comparison of Gas Phase and Condensed Phase Reactions

**Caging Effects.**—When a halogen molecule in the gas phase absorbs a quantum of visible light it always dissociates.<sup>7</sup> If, however, the molecule is surrounded by a "cage" of solvent molecules, the atoms may lose their energy to the cage walls and immediately recombine<sup>9</sup> or they may recombine by diffusion after having escaped only a molecular diameter or so from each other.<sup>10</sup> Direct evidence that only about 13% of the iodine atoms escape recombination with the parent partner when iodine solutions in carbon tetrachloride are activated by visible light has been obtained by flash photolysis techniques.<sup>11</sup> Using a very different technique employing a scavenger to react with those atoms which do not recombine, Lampe and Noyes<sup>12</sup> have obtained a similar value. They have also shown that the caging effect decreases with increasing temperature, and that it is lower for hexane and higher for hexachlorobutadiene than for carbon tetrachloride. Also suggestive of the conclusion that caging effectiveness is a sensitive function of molecular weight or size, is the observation that the organic yields of iodine and bromine activated by radiative neutron capture in hydrocarbon solutions increase with increasing chain length of the normal paraffin hydrocarbons.<sup>13</sup>

In planning experiments to determine the effect of density of condensed media on chemical reactions, it is difficult to avoid temperature changes concurrent with the density changes. This difficulty has been avoided in studies of the organic yield of bromine activated by radiative neutron capture in CF<sub>3</sub>Br at different pressures at temperatures above the critical point. The yield seems to show a linear increase with density and no discontinuity with temperature in passing through the critical point<sup>14</sup> at constant density.

Iodine activated by radiative neutron capture in methane enters organic combination as both methyl iodide and ethyl iodide in the liquid phase but only as methyl iodide in the gas phase. It seems probable that the difference is due to the fact that radical fragments are caged in proximity to each other in the liquid phase.<sup>15</sup>

Radioiodine was used by Gevantman and Willard and A. J. Swallow, *Chem. Revs.*, **56**, 471 (1956).

(7) (a) G. K. Rollefson and Milton Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939; (b) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

(8) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953).

(9) J. Franek and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(10) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950).

(11) (a) R. L. Strong and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2098 (1957); (b) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

(12) F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

(13) S. Aditya and J. E. Willard, *ibid.*, **79**, 3367 (1957).

(14) W. E. Rice and J. E. Willard, *ibid.*, **75**, 6156 (1953).

(15) J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

(1) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(2) (a) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *ibid.*, **4**, 479 (1936); (b) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk U. S. S. R.*, **86**, 909 (1952), *C. A.*, **47**, 2590 (1953); (c) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1535 (1955); (d) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956); (e) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **25**, 790 (1956).

(3) (a) W. Gordy and C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956); (b) C. F. Luck and W. Gordy, *ibid.*, **78**, 3240 (1956).

(4) (a) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942); (b) I. Norman and G. Porter, *Proc. Roy. Soc. (London)*, **A230**, 399 (1955); (c) R. G. Sowden and N. Davidson, *J. Am. Chem. Soc.*, **78**, 1291 (1956).

(5) (a) H. P. Broida and J. R. Pellam, *Phys. Rev.*, **95**, 845 (1954); (b) H. P. Broida and C. M. Herzfeld, *ibid.*, **101**, 606 (1956); (c) H. P. Broida and O. S. Lutes, *J. Chem. Phys.*, **24**, 484 (1956); (d) H. P. Broida and A. M. Bass, *Phys. Rev.*, **101**, 1740 (1956); (e) F. O. Rice and C. Grelecki, *J. Am. Chem. Soc.*, **79**, 1880 (1957); (f) J. A. Ghormley, *ibid.*, **79**, 1862 (1957).

(6) (a) J. E. Willard, *Ann. Rev. Phys. Chem.*, **6**, 141 (1955); (b) C. J. Hochanadel and S. C. Lind, *ibid.*, **7**, 83 (1956); (c) E. Collinson

liams<sup>16</sup> in the determination of the radical yields from the radiolysis of alkyl iodides in the liquid and vapor phases. They interpret their data to indicate that the ratio of C-C to C-I bond rupture is generally higher for the vapor than for the liquid.

Firestone<sup>17</sup> has made a significant comparison of the radical yields for the radiolysis of gaseous water with that for liquid water. By allowing tritiated water to irradiate itself in the presence of D<sub>2</sub> followed by analysis for HD, he was able to determine the number of hydrogen atoms which exchanged with the deuterium. The *G* value (hydrogen atoms exchanged per 100 e.v. absorbed) found for this gaseous system was about 11 which is some threefold higher than that found by Hart<sup>18</sup> for liquid water, using formic acid as a scavenger for the hydrogen atoms. It is assumed that the differences are due to radical recombinations within the tracks in the condensed system.

**Ion-Molecule Reactions.**—It has been demonstrated by mass spectrometric techniques that many reactions of gaseous ions with molecules have a high probability of occurring on every collision.<sup>2</sup> Concurrently evidence has been accumulating for the occurrence of gas phase reactions, activated by radiative neutron capture and by ionizing radiations, which cannot be explained by "conventional" mechanisms.<sup>15,19</sup> This evidence shows that halogen atoms activated by radiative neutron capture, and also tritium freshly born from the He<sup>3</sup>(n,p)H<sup>3</sup> process, can react with gaseous alkyl halides or hydrocarbons in bimolecular displacement reactions very different from the abstraction reactions normally produced by such atoms. Likewise, ionizing radiations such as beta particles or  $\gamma$ -rays are able to initiate chains in mixtures of methane and HT, producing tritiated hydrocarbons at least as high as hexane. The products of these reactions are very different from those to be expected from radicals attacking molecules, but seem to fit within the framework of what is thus far known about ion-molecule reactions.

In the liquid phase, where caging effects can occur, it is impossible to differentiate experimentally between ion-molecule reactions and reactions which result from a fragmentation of the medium into neutral radicals which then combine to form new species. It is interesting to note, however, that Wolfgang, Eigner and Rowland,<sup>20</sup> using the Li<sup>6</sup>(n, $\alpha$ )H<sup>3</sup> process as a source of tritons in slurries of lithium salts in liquid methane, have observed tritiated products which involve the formation of carbon-carbon bonds up to at least butane. This chain lengthening is similar to that initiated by tritons in gaseous systems.

With the aid of gas chromatography, John E.

(16) L. H. Gevantman and R. R. Williams, *THIS JOURNAL*, **56**, 569 (1952).

(17) R. F. Firestone, *J. Am. Chem. Soc.*, **79**, 5593 (1957).

(18) E. J. Hart, *ibid.*, **76**, 4198 (1954).

(19) (a) G. Levey and J. E. Willard, *J. Chem. Phys.*, **25**, 904 (1956); (b) F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 1055 (1957); (c) R. H. Schuler, *J. Chem. Phys.*, **26**, 425 (1950); (d) A. A. Gordus and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 4609 (1957); (e) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3284 (1957); (f) R. Ahrens, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3285 (1957); (g) M. F. A. E. Sayed and R. Wolfgang, *ibid.*, **79**, 3286 (1957).

(20) R. Wolfgang, J. Eigner and F. S. Rowland, *THIS JOURNAL*, **60**, 1137 (1956).

Quinlan of our laboratory has shown that over fifteen organic chlorides containing Cl<sup>38</sup> are formed when Cl<sup>38</sup> is produced by the Cl<sup>37</sup>(n, $\gamma$ )Cl<sup>38</sup> process in gaseous *n*-propyl chloride. Since these gas phase experiments were done with chlorine scavenger present, the products cannot be due to thermal radical reactions. Ion-molecule reactions seem to be the most plausible explanation at present. The relative amounts of products obtained in the liquid are very similar to the gas, suggesting that the mechanisms of reaction in the two phases may be the same.

Although it has not been demonstrated experimentally that the Cl<sup>38</sup> atoms involved in the above reactions are given a positive charge by the nuclear process, there is reason to believe, by analogy with similar nuclear processes,<sup>8</sup> that they are. If so, the charge is produced by the internal conversion and Auger processes, which may cause electrons to be ejected from the atom with an energy of thousands of electron volts. At such energies the electrons are certain to escape successfully from the coulombic attraction of the parent ion even in condensed phases. There is probably a greater chance for ion-molecule reactions in such a case than when activation is by ionizing radiation, since most of the electrons ejected by the latter have energies of a hundred electron volts or less and so have a greater chance of neutralizing the parent ion before it has an opportunity to react.

It is to be expected that bromine and iodine may exhibit greater contrast than chlorine between the products formed in gaseous and liquid hydrogenous material. Bromine and iodine atoms require an appreciable activation energy for reaction with carbon-hydrogen bonds. Consequently those which become neutralized and thermalized without reacting can live long enough to encounter thermalized free radicals which they may have formed in losing the energy from the nuclear activation. Chlorine atoms, on the other hand, may be expected to abstract hydrogen and become stabilized as HCl without having opportunity to diffuse as thermal atoms.

**Temperature Effects.**—When reactions are induced by radiation, the activating energy is introduced to the system from outside and dissipated in large increments by the excitation and ionization process. Since these increments are, in general, large compared to chemical bond energies, it is common to think of the reactions as being temperature independent, *i.e.*, all "hot" processes. This is true of the primary acts, but may not be true for the subsequent reaction steps. If the molecular fragments are born with kinetic or vibrational energy higher than the average thermal energy of the medium, they may undergo "hot" reactions with the medium to form stable products, without evidence of temperature dependence. If the fragments become thermalized before reacting, their fate will depend upon the rate constants for various competing reactions, and may be temperature-sensitive. Even radical recombination steps, which have very low activation energy, may show a temperature dependence if diffusion is a determining factor. As examples, the *G* value for the production of iodine from liquid ethyl iodide is inde-

pendent of temperature from 100 to  $-78^{\circ}$ ,<sup>21</sup> whereas the  $G$  values for the production of bromine from bromotrichloromethane<sup>22</sup> reveal two temperature sensitive steps, one sensitive to low concentrations of bromine and the other independent of bromine concentration. The apparent activation energies are about 3 kcal. per mole suggesting that they may be associated with the escape of bromine atoms and  $\text{CCl}_3$  radicals from the parent cage.

Bromotrichloromethane shows the same bromine-insensitive temperature dependence in the solid phase from its freezing point at  $5^{\circ}$  down to  $-78^{\circ}$  as it shows in the liquid phase. Ethyl iodide, which shows no temperature dependence in the liquid phase, shows a decrease in  $G$  value in the crystalline phase in going from  $-120^{\circ}$  to liquid air temperatures, as do also methyl iodide and isobutyl iodide.<sup>21</sup>

Observations on the organic yields of halogens activated by neutron capture show that, within experimental error, there is no change between room temperature and  $-78^{\circ}$  for either ethyl iodide or ethyl bromide.<sup>23</sup> Limited data<sup>24</sup> indicate a small negative temperature coefficient for the organic yield of  $\text{Br}^{80}$  from both the  $(n,\gamma)$  process and the isomeric transition process in liquid  $\text{CCl}_3\text{Br}$ , but little or no temperature coefficient for  $\text{Cl}^{38}$  in liquid  $\text{CCl}_4$ . In the solid state the organic yield of  $\text{Br}^{80}$  from the  $(n,\gamma)$  process in  $\text{CCl}_3\text{Br}$  increases from 58% at  $-6^{\circ}$  to 72% at  $-80^{\circ}$  and the corresponding yield for the isomeric transition process increases from 70 to 86% over the same temperature range. The organic yields of  $\text{Cl}^{38}$  from the  $(n,\gamma)$  process are 51% in solid  $\text{CCl}_4$  at  $-37^{\circ}$  and 75% at  $-80^{\circ}$ . These changes in yield with temperature may be related to the same basic causes that are responsible for the positive temperature coefficient of the radiolysis of  $\text{CCl}_3\text{Br}$  cited above. By contrast to these observations, Fox and Libby<sup>25</sup> have found that the organic yields of the propyl bromides do not increase with decrease in temperature in the solid phase.

The above observations of the influence of temperature on  $G$  values and organic yields are currently waiting for a good correlating hypothesis.

### Comparison of Liquid Phase and Solid Phase Reactions

**Organic Yields of the  $(n,\gamma)$  Reaction in Liquid and Solid Alkyl Halides.**—A halogen atom which undergoes radiative neutron capture may be given a recoil energy of 1,000 kcal. per mole or more and at the same time acquire a high positive charge.<sup>8</sup> Experiments show that this activation makes it possible for the atom to re-enter organic combination in many different ways, *e.g.*, at least 20 different radiobromine compounds are formed when *n*-propyl bromide is irradiated with neutrons.<sup>26</sup> The

elementary reaction steps which may account for these products include: (1) combination of the tagged atom with a radical it has formed in losing its energy. This may occur either at the site where the radical was formed or after both the radical and the tagged atom have diffused in thermal equilibrium with the medium; (2) reaction of the tagged neutral atom with a neutral molecule by a high energy process; (3) reaction of the tagged halogen as a positive ion.

Each of the above types of reaction step may conceivably produce either inorganic or organic binding of the tagged atom. How may one predict the effect of a change from the liquid to the solid phase on the gross organic yield? The answer to this question is not yet known.

The experimental data indicate that sometimes this yield increases, as in the case of the propyl bromides,<sup>25,27</sup> carbon tetrachloride, bromotrichloromethane, dibromodichloromethane,<sup>24</sup> the alkyl chlorides<sup>28</sup> and some of the alkyl iodides.<sup>29</sup> In the case of ethyl iodide, isobutyl iodide and *sec*-butyl iodide, however, the change from the liquid to the solid state seems to have little or no effect on the organic yield. Among the compounds which show an increase in yield on solidification the magnitude of the effect is much greater for some than for others as indicated in the data of Table I.

De Maine, Maddock and Taugbol<sup>29b</sup> have observed that the organic yield of bromine from solid  $\text{C}_6\text{Br}_6$  irradiated with neutrons at room temperature is a function of the time and temperature at which the solid stands before being dissolved for analysis. Further experiments should be made to determine whether such annealing effects in solid organic compounds are common for reactions activated by nuclear processes or ionizing radiation. Most studies of such compounds have involved melting prior to analysis, rather than dissolving, thus precluding observation of an annealing effect.

The effect of solidification on the yield of individual tagged products has been examined in a few cases. The ratio of tagged  $\text{CCl}_3\text{Br}$ ,  $\text{CCl}_2\text{Br}_2$  and higher boiling species produced by the neutron irradiation of  $\text{CCl}_3\text{Br}$  at room temperature is essentially the same as this ratio for the irradiation in the solid phase at  $-80^{\circ}$ .<sup>24</sup> By contrast, the relative amounts of products from ethyl iodide are considerably changed by freezing, although the increases and decreases compensate for each other in such a way as to leave the gross organic yield essentially unchanged.<sup>29</sup> The organic yield of tagged methyl iodide from the neutron irradiation of methyl iodide decreases from 48 to 44% in going from the liquid phase at room temperature to the solid at liquid air temperatures, whereas the yield of methylene iodide increases from 8 to 18% for the same change of conditions.<sup>29</sup> Fox and Libby<sup>25</sup>

(21) E. O. Hornig and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2429 (1957).

(22) R. F. Firestone and J. E. Willard, Abstracts, Am. Chem. Soc., Paper No. 53 (127th meeting, Cincinnati, Ohio, April 1954, Division of Physical and Inorganic Chemistry).

(23) J. R. Roy, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3278 (1954).

(24) S. Goldhaber, R. S. H. Chiang and J. Willard, *ibid.*, **73**, 2271 (1951).

(25) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

(26) J. B. Evans and J. E. Willard, *J. Am. Chem. Soc.*, **78**, 2908 (1956).

(27) (a) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1495 (1953); (b) R. H. Schuler and C. E. McCauley, *J. Am. Chem. Soc.*, **79**, 821 (1957).

(28) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 6160 (1953).

(29) (a) G. Levey and J. E. Willard, *ibid.*, **74**, 6181 (1952); (b) M. M. De Maine, A. G. Maddock and K. Taugbol, *Disc. Faraday Soc.*, **23**, 211 (1957).

TABLE I  
EFFECT OF CHANGE FROM LIQUID TO SOLID PHASE ON GROSS ORGANIC YIELDS OF HALOGENS  
ACTIVATED BY THE  $(n, \gamma)$  PROCESS IN ORGANIC HALIDES

Alkyl group	Chloride <sup>b</sup>		Organic yields, % <sup>a</sup>		Bromide	
	Liq.	Solid	Liq. Iodide <sup>c</sup>	Solid	Liq.	Solid
Methyl			56	65		
Methylene			62	70		
Ethyl	23	62	41	43		
<i>n</i> -Propyl	23	62	41	54	34	87 <sup>d</sup>
Isopropyl					38	77 <sup>e</sup>
<i>n</i> -Butyl	21	35	27	46	24	81 <sup>f</sup>
Isobutyl	23	33	40	60		
<i>sec</i> -Butyl	22	32	43	39		
Isoamyl	22	32	27	25		
<i>sec</i> -Amyl	22	38				
Others <sup>g</sup>	CCl <sub>2</sub> Br	51(50°)	81(-80°)	CCl <sub>2</sub> Br	40	72
	CCl <sub>4</sub>	43	75(-80°)	CCl <sub>2</sub> Br <sub>2</sub>	40	75(0°)
				CBr <sub>4</sub>	88(100°)	93(25°)

<sup>a</sup> The organic yields in the liquid phase are for irradiations at room temperature, and those in the solid phase are for irradiations at liquid air temperature, except where other temperatures are indicated. <sup>b</sup> Reference 28. <sup>c</sup> Reference 29. <sup>d</sup> Data of Fox and Libby.<sup>26</sup> <sup>e</sup> Data of Schuler and McCauley.<sup>27b</sup> <sup>f</sup> Reference 24.

have shown that the ratios of the yields in the solid phase to those in the liquid phase for six products of the neutron irradiation of the propyl bromide vary from unity to 9.4.

From the observations cited above it may be concluded that the magnitude of phase effects for reactions activated by the  $(n, \gamma)$  process in alkyl halides varies greatly from one compound to another even within an homologous series. Among the possible causes of this are differences in density changes, differences in the orientation of the molecules in the crystals, and differences in the types of solid obtained, *i.e.*, glass or crystal.

**Yields of Iodine and Hydrogen Iodide from the Radiolysis of Alkyl Iodides.**—Of four alkyl iodides tested,<sup>21</sup> three (CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I and *i*-C<sub>3</sub>H<sub>7</sub>I) have *G* values for the production of iodine with  $\gamma$ -rays which are at least fourfold lower in the crystalline state at  $-190^\circ$  than in the liquid at room temperature. The *G* value for the fourth (*i*-C<sub>4</sub>H<sub>9</sub>I) is only 25% lower in the crystals at  $-190^\circ$  than the initial *G* value in the liquid.

Of particular interest is the fact that the *G* values for crystalline ethyl iodide and isobutyl iodide are both lower than the corresponding values for the glassy forms at the same temperature. The difference between the crystalline and glassy forms may be due to the fact that in the oriented structure of the crystals hot radicals or atoms have a greater probability of hitting one part of a molecule than another; or they may be due to the differences in caging effects in the two media.

The observations noted in the preceding paragraphs have led us to a further exploration of the radiolysis of solid alkyl iodides, which has revealed that: (1) the *G* values in both the solid and liquid phase vary with the previous history of irradiation of the sample in the other phase; (2) the ratio of HI to I<sub>2</sub><sup>30</sup> produced in the irradiation of pure crys-

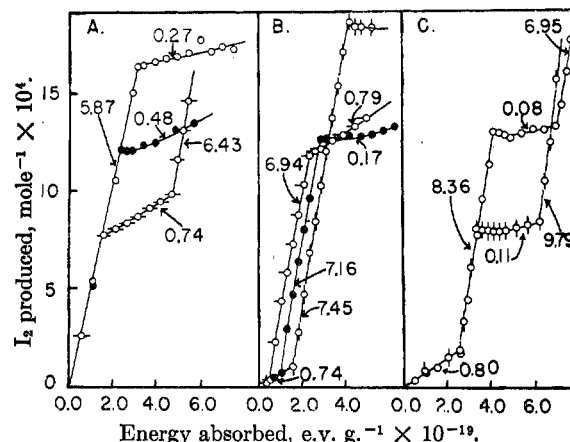


Fig. 1.—The effect of change of phase on  $G_{I_2}$  in the radiolysis of isopropyl iodide. (See text for further explanation of the figure.)

talline isopropyl iodide at  $-190^\circ$  is 10 as compared to a ratio of 1 for the pure liquid. The first of these phenomena is illustrated by Fig. 1 in which the concentration of iodine produced by radiolysis with Co<sup>60</sup>  $\gamma$ -rays is plotted as a function of energy input for samples of purified degassed isopropyl iodide irradiated as a liquid at room temperature, and as a solid at  $-190^\circ$ . The irradiations and analyses were done as described previously.<sup>21, 31a</sup> The numbers on the face of the graphs are average *G* values for the portion of the graphs indicated. Successive points of a single type represent successive readings on a single sample. The steep portions (*G* values greater than 5) were obtained from liquid phase irradiations and the more nearly horizontal portions (*G* values less than 1) from solid phase irradiations. The data indicate that, for the conditions of these experiments: (1) the *G* value for irradiation in the solid phase decreases with increasing length of prior irradiation as a

method of analyzing for HI in alkyl iodides was developed by R. J. Hanrahan of our laboratory.

(31a) R. J. Hanrahan and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2434 (1957).

(30) The HI was determined by admitting oxygen to the irradiated liquid and determining the increase in I<sub>2</sub> concentration which occurred as a result of oxidation of HI. After several hours of standing with oxygen, with intermittent shaking, the iodine concentration remained constant. It was determined spectrophotometrically. This

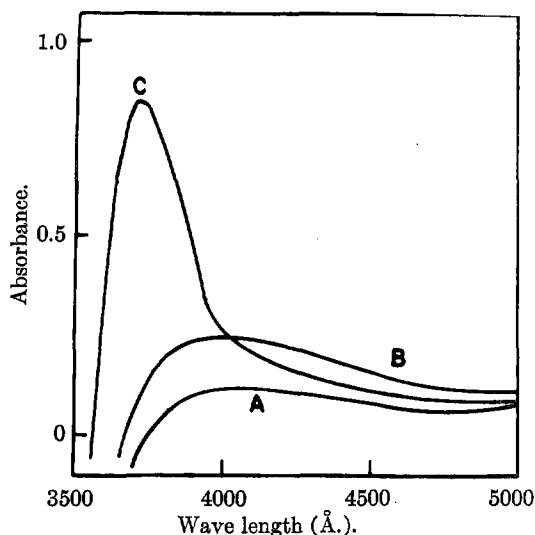


Fig. 2.—Spectrum of ethyl iodide (glass) at  $-190^{\circ}$ : curve A, before photolysis; curve B, after 15 minute photolysis; curve C, after melting and re-freezing.

liquid; (2) the  $G$  value for irradiation in the liquid phase increases with length of prior irradiation as a solid; (3) the iodine concentration may actually decrease for irradiations in the solid following prolonged irradiation in the liquid. Experiments have been performed (Fig. 1) in which irradiations of a single sample have been carried out first in the liquid phase, then in the crystalline phase, and then again in the liquid. The  $G$  value for the second liquid phase irradiation was higher than the value obtained for the first liquid irradiation in two such experiments, while in a third experiment the value was lower.

It is known that  $G_{I_2}$  for liquid alkyl iodides increases with increasing  $HI/I_2$  ratio.<sup>31</sup> Since our data show that the production ratio of  $HI/I_2$  in solid isopropyl iodide is 10 as compared to 1 in the liquid, the increase in  $G_{I_2}$  following solid phase irradiation is to be expected. The decrease in  $G_{I_2}$  solid following liquid phase irradiations suggests that in the solid phase, as in the liquid, iodine and  $HI$  compete for radicals. It is not possible to say whether this occurs at liquid air temperatures, or while the sample is being warmed and liquefied for analysis. The smooth curves given by the experimental points obtained from the solid phase determinations suggest that, if the reaction is complete in the solid phase, the substances which compete for the radicals must distribute themselves in the solid in a reproducible manner in successive re-freezings of the solvent. These phenomena are now being investigated with the aid of electron spin resonance, added  $HI$ , and  $I_2$  scavengers, and gas chromatographic characterization of all of the products. Milman has very recently shown<sup>31b</sup> that the organic yield of bromine from the  $(n, \gamma)$  activation of  $C_2H_5Br$  decreases with increased bromine concentration in a manner similar to that observed for the liquid system. This demonstrates that it may be possible to use scavenger techniques<sup>8</sup> for investigating "thermal" radical processes in the solid state, as they have been used in the liquid.

(31b) M. Milman, *J. Am. Chem. Soc.*, **79**, 5581 (1957).

**Yields of Iodine and Hydrogen Iodide from the Photolysis of Ethyl Iodide.**—Current work in our laboratory indicates that the ratio of  $HI/I_2$  produced in the photolysis of ethyl iodide glass at  $-190^{\circ}$ , using 2537 Å. light, is about 5 as compared to 0.5 in the liquid at room temperature.<sup>32</sup> The ratio 0.5 for the liquid phase is similar to that indicated by results of Bunbury, Williams and Hamill.<sup>34</sup> The total quantum yield for equivalents of  $HI$  plus  $I_2$  in the glass is about 0.8 of that in the liquid. The fact that the  $HI/I_2$  ratio is higher for the solid than the liquid is analogous to the result noted above for the radiolysis of isopropyl iodide. As in the latter case, experiments designed to determine the cause of the increase are in progress.

**Spectral Changes Following the Photolysis and Radiolysis of Ethyl Iodide Glass.**—In exploratory investigations designed to look for spectral evidence of trapped reaction intermediates produced by 2537 Å. light in ethyl iodide glass at liquid air temperature, we have used a cryostat<sup>33</sup> which allowed the spectrum of the glass to be observed with a Cary recording spectrophotometer. An end-window Hanovia SC 2537 lamp was used. After a typical irradiation of the glass there was very little change in the spectrum, although a very thin layer of intense iodine color on the cell face which faced the light beam could be seen. When the sample of irradiated ethyl iodide was melted and immediately refrozen, however, the glassy sample gave a pronounced absorption peak at 3700 Å. The spectrum at room temperature did not show this peak. That iodine production during the above photolysis in the glass was slight was indicated by the absence of appreciable absorption at 4800 Å. Typical spectra observed in these experiments are shown in Fig. 2. The apparent negative absorption at the low wave length end of the scale of Fig. 2 is a result of the fact that the compensator cell contained ethyl iodide at room temperature, and of the fact that the absorbance of ethyl iodide is lower at  $-190^{\circ}$  than at  $25^{\circ}$ .

When iodine was added to the ethyl iodide before photolysis, the peak at 3700 Å. could not be observed because of the masking of that region of the spectrum by the iodine-ethyl iodide absorption.<sup>35</sup> Another peak appeared, however, at 3975 Å. As with the first peak, this did not appear in the irradiated glass but could be observed after melting and refreezing of this glass. Whereas the 3700 Å. peak could be observed in liquid ethyl iodide at  $-100^{\circ}$ ,

(32) These determinations were made using Beckman-type quartz cells which could be maintained at  $-190^{\circ}$  in a cryostat<sup>33</sup> while irradiating with 2537 Å. light. The ethyl iodide was Eastman white label, further purified by passage through alumina and distillation through a Todd column. It was degassed and distilled through phosphorus pentoxide, under vacuum, before sealing off in the reaction cells. With quartz cells which had been scrupulously cleaned, and flamed to remove bloom from the faces, it was usually possible to obtain a clear uncracked glass by rapid freezing of the pure ethyl iodide. In a number of cells which gave crystals rather than a glass when first sealed off, glass formation became possible after the liquid had stood for a few days in the cell. The concentrations of iodine and  $HI$  were determined spectrophotometrically.

(33) T. O. Jones and J. E. Willard, *Rev. Sci. Instr.*, **27**, 1037 (1956).

(34) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 6228 (1956).

(35) D. E. Schuler and R. H. Schuler, *ibid.*, **76**, 3092 (1954).

the 3975 Å. peak disappeared at this temperature.

In order to determine whether radiolysis produced the same spectral changes as photolysis, tritiated ethyl iodide with a specific activity of 0.5 curies per milliliter was allowed to stand as the glass at  $-190^{\circ}$ . Its spectrum could not be taken before melting since the self-irradiated glass always cracked after about one-half hour. When, after 41 hours as the glass, it was melted and refrozen, its spectrum showed a peak at 3975 Å. with a maximum absorbance of 0.5.

The nature of the species causing these peaks is not fully known. However, when hydrogen iodide was added to a cell containing pure ethyl iodide, a peak was observed at 3700 Å. exhibiting identical behavior to that produced by the photolysis of pure ethyl iodide. The peak at 3975 Å. was observed when both hydrogen iodide and iodine were added to ethyl iodide. Neither of these peaks appear in the spectrum of the liquid at room temperature. It appears, therefore, that a complex between hydrogen iodide and ethyl iodide and one between hydrogen iodide, iodine and ethyl iodide are formed at low temperatures. The fact that this complex does not appear in the spectrum of the glass after the photolysis of ethyl iodide, until the glass has been melted and refrozen, suggests that either hydrogen iodide is not produced in molecular form in the glass, but is formed when the glass is melted, or that the activation energy for the formation of the complex is high enough to prevent its formation at  $-190^{\circ}$ .

**Other Comparisons of Liquid and Solid Phase Yields.**—Norman and Porter<sup>4b</sup> have produced a number of "frozen in" free radicals by the photolysis of the parent compounds in rigid glasses of 3-methylpentane and also of ether-isopentane-ethanol-(EPA). In the course of these studies they have observed that the quantum yield of iodine production from ethyl iodide, by 2537 Å. light in the solid glasses at  $-196^{\circ}$  is 0.5 of that in the liquid at  $20^{\circ}$ . They report that the iodine color was not visible until the glass had been warmed. This observation suggests the presence of "trapped" atoms.

The probability of dissociation in rigid media seems to depend on the size of the radical fragments. For instance, a spectrum assigned to the benzyl radical has been reported<sup>4b</sup> to have been produced in the photolysis of toluene, benzyl chloride, benzyl alcohol and benzylamine in EPA and hydrocarbon glasses. This spectrum was not produced, however, in similar solutions of diphenylmethane or dibenzyl. In addition, acetophenone and diphenylmercury have a negligible quantum yield for photodissociation in isopentane-3-methylpentane glasses compared to the liquid solution.<sup>4c</sup> Additional references to related work are given in the references<sup>3-5</sup> cited above.

**Acknowledgments.**—This work was supported in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation and in part by the Atomic Energy Commission. It also was aided by a fellowship provided by the Standard Oil Foundation.

## RADIATION CHEMISTRY OF ORGANIC COMPOUNDS. II. *n*-HEXANE

By H. A. DEWHURST

General Electric Research Laboratory, Schenectady, N. Y.

Received June 24, 1957

The formation of gas and liquid products in the 800 kvp. electron radiolysis of *n*-hexane liquid has been studied as a function of the energy absorbed, temperature and the presence of solutes. The hydrogen yield decreased with temperature to a limiting value in the solid state. The same limiting yield was attained in the presence of solutes. The yield of unsaturated product, mainly *trans*-vinylene was independent of temperature but was found, in some cases, to decrease in the presence of solutes, notably oxygen and iodine. The yield of intermediate and dimer product was found to depend on temperature as well as the solute present. The results are discussed in terms of ion-molecule, radical and so-called molecular processes.

### 1. Introduction

The nature of the products formed in the radiolysis of *n*-alkane liquids was reported in a previous paper.<sup>1</sup> The diversity of product formation indicated that extensive C-H and C-C bond rupture had occurred. Apart from end effects and physical state the small hydrocarbon molecules are useful as model compounds for long chain hydrocarbon polymers such as polyethylene. A better understanding of the formation of non-volatile products in model compounds could be useful for the elucidation of processes which occur in polymers.

Previous studies<sup>2</sup> with *n*-hexane were concerned mainly with the gaseous products. Henri and co-

workers<sup>3</sup> examined the  $\alpha$ -particle decomposition of *n*-hexane in the gas phase. The authors worked at very high conversions (40%) and found that 73% of the reacted *n*-hexane was in a non-volatile liquid. Recently Krenz<sup>4</sup> has studied the  $\gamma$ -ray decomposition of *n*-hexane liquid. He showed that anthracene ( $10^{-3} M$ ) had no measurable effect upon the gas yields but caused a diminution in the yield of unsaturated products.

The radiolysis of *n*-hexane liquid was examined in order to evaluate the processes responsible for product formation. Gas-liquid partition chromatography was used to examine the formation of intermediate and dimer product under a variety of experimental conditions.

(1) H. A. Dewhurst, A.C.S. Miami Meeting, April 1957; *THIS JOURNAL*, **61**, 1466 (1957).

(2) C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

(3) V. P. Henri, C. R. Maxwell, W. C. White and D. C. Peterson, *THIS JOURNAL*, **56**, 153 (1952).

(4) F. H. Krenz, *Nature*, **176**, 1113 (1955).