sociation agree with those predicted on the basis of the theory of protection. This illustrates the utility of the theory in obtaining approximate values of the fluidity of compounds for which experimental data are not available.

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The Photo-decomposition of Gaseous Ethyl Iodide and a Comparison of the Photo-change in the Gaseous and Condensed States

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Certain properties of the iodides of the simpler organic radicals suggest the utility of investigating this group of compounds in the study of the photo-behavior of substances. The lower members of the alkyl iodides have a general similarity in absorption spectra, indicating a common type of excitation as the initial process in photo-changes; nevertheless, it is experimentally observed that the efficiency of the light in causing chemical changes varies markedly from member to member of the series, and with the state of aggregation for a given compound, facts which afford opportunity for the accumulation of data from which some understanding of the relation between the net photochemical action and such factors as the constitution of the molecule and its possible degradation products in various environments may ultimately be obtained. Moreover, the possession by the alkyl iodides of at least two different types of absorption in the region of the spectrum readily accessible to not unduly complicated experiment may allow us to correlate photochemical action with the type of excitation supposed to occur in these different regions.

The ultraviolet absorption spectra of the gaseous alkyl iodides have a characteristic continuum with a maximum at about 2500 Å., and methyl and ethyl iodides have a well developed band spectrum of greater intensity than the continuum, beginning near 2000 Å. and extending into the Schumann region.[1] We have found that gaseous vinyl iodide has a similar well-defined band spectrum in the same region, although in this case the region between the end of the first continuum, at 2300 Å., and the band spectrum is occupied by an intense continuous absorption.

The new results reported here are chiefly concerned with the photo-behavior of ethyl iodide in the band region. In the continuum, the quantum yield in the decomposition of liquid ethyl iodide has been found to be about one, at 3100 Å., and to diminish with increasing wave length, although there are indications that the actual values are probably high.[2] Ethyl iodide vapor at 50 mm. is reported by Emschwiller to decompose on exposure to the full light of the mercury arc with a very low yield, not more than one hundredth of that for the decomposition of hydrogen iodide gas.[3] In hexane and in benzene solution the yield is 0.58 at 2610 Å., at 25° in ethyl iodide concentrations from 0.007 to 1.38 moles per liter and 0.3 at 3130 Å.[4] Methyl iodide has a very low yield in the continuum, both in the gaseous state (0.02 at 0° and 141 mm.)[5] and in hexane solution (0.05 at 25° and 1.78 molar).[4]

Experimental

In the region of continuous absorption, the light from a 6-inch Hanovia quartz mercury arc, operating at about 150 volts, was filtered by 5 cm. of bromine vapor at its saturation pressure at 15°, 3 cm. of chlorine at one atmosphere, and 3 cm. of 1 N acetic acid so as to yield the lines between 2800 and 2500 Å. with an energy center at about 2600 Å.

Illumination in the band region was effected by the light of a condensed spark with zinc or aluminum electrodes. The spark gap, an adaptation of that of Wiig and Kistiakowsky,[6] was driven by a 10,000-volt transformer consuming 3.3 kilowatts in the primary, with a 0.04 microfarad oil immersed parallel plate condenser which could be run continuously for four hours as capacity.[7]

Monochromatization of the light was effected by focal isolation by means of quartz lenses, as used by Wiig and Kistiakowsky in their study of the ammonia decomposition.[6] Spectral photographs showed that the zinc spec-

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(1) G. Hertzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930); A. Henrici, *Z. Physik*, **77**, 35 (1932); G. Scheibe, F. Povenz and C. F. Linström, *Z. physik. Chem.*, **B20**, 283 (1933).

(2) T. Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

(3) G. Emschwiller, *Ann. chim.*, **17**, 413 (1932).

(4) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(5) J. R. Bates and R. Spence, THIS JOURNAL, **53**, 1689 (1931).

(6) E. C. Wiig and G. B. Kistiakowsky, *ibid.*, **50**, 1806 (1932).

(7) It may be worth while to remark that in constructing these condensers we found it best not to shellac the thin copper sheeting used as plates to the glass but simply to tie up the bundle of copper and glass plates with string and immerse them in oil. With shellac, air bubbles tend to form between the copper and glass which may eventually lead to breakdown.

trum isolated in this way consisted only of the intense group at 2026–2130 Å., with a complete absence on the plate of longer wave lengths. As only the line at 2026 Å. is appreciably absorbed by gaseous ethyl iodide at the pressures used, the decomposition by light from the zinc spark was effected by practically monochromatic light. With aluminum electrodes, the effective lines were 1990, 1932 and 1862 Å.

A Moll micro-thermopile and a low-resistance high-sensitivity Leeds and Northrup galvanometer were used to measure the energy. The thermopile was used as a linear pile, with a slit width of 1.25 mm., and integration of the energy in the beam effected by moving the surface over the whole beam by means of accurate micrometer screws furnishing horizontal and vertical motion.

The thermopile–galvanometer system was calibrated by means of a carbon filament lamp standardized by the Bureau of Standards. Owing to slight changes in the galvanometer sensitivity the calibration changed irregularly a few times over the series of experiments by a few per cent. Another carbon filament lamp was therefore placed on the working bench so that at the beginning and end of each run the calibration could be checked and if necessary, a new calibration made.

Filling the Cells.—The cells used for the gas reaction were of quartz, 5 cm. long, with plane parallel windows 4 cm. in diameter. In experiments at low pressures, the quartz cell was 50 cm. long and 6 cm. in diameter. The liquid was examined in a quartz cell 2 mm. thick and 16 mm. in diameter.

As photo-oxidation of ethyl iodide readily takes place, great precautions were taken to avoid the presence of traces of oxygen in the reaction cell. This was connected to a high vacuum line provided with a McLeod gage, a Hyvac pump and a charcoal–liquid air absorption vessel. Diffusion of mercury vapor from the gages to the reaction cell was prevented by a gold leaf trap. Ethyl iodide vapor, introduced into the reaction cell at the pressure desired for the experiment, was frozen by liquid air into a side tube attached to the cell, which was sealed off from the vacuum line and placed in a stand on the optical bench for exposure to radiation. At the completion of an experiment the iodine produced was frozen into the side tube by liquid air, the side tube cut off, rinsed several times with a solution of potassium iodide and the iodine solution titrated with *N*/200 thiosulfate with starch indicator, by means of a microburet graduated in hundredth of a cc.

During exposure, the reaction vessel was placed in an air thermostat provided with quartz windows, a fan for stirring and a temperature regulator of the Beaver type.[8]

Deposition of iodine on the cell windows during a run was prevented by maintaining the cell at a higher temperature than the side arm, which projected from the thermostat.

The energy measurements were made as follows. The reaction vessel charged with ethyl iodide frozen in the side tube by means of liquid air, was placed in position in the optical bench and the total radiant energy passing through the empty cell integrated. The thermopile was then placed behind the center of the cell, the deflection noted, the ethyl iodide vapor allowed to fill the cell, and the deflection again noted. These two readings give, except for some minor corrections which we have neglected, the fraction of light absorbed by the iodide, permitting the computation of the total deflection which would have been obtained by integration in the presence of the iodide. The deflections for the empty and full cell have now to be corrected for loss of light at the rear windows of the cell and thermostat and the difference between the corrected deflections is a measure of the energy absorbed by the iodide. These losses were ascertained by separate determinations of the transmission of the various windows to the wave lengths in question.

We proved the substantial adequacy of our arrangement by measuring the quantum yield for the decomposition of gaseous hydrogen iodide, for which Warburg's classical experiments give the value 2. The method of experiment was exactly the same as in the experiments with ethyl iodide with the substitution of hydrogen iodide gas. Although the results we obtained were consistently high (2.6) we do not feel justified, without further investigation, in correcting our results by multiplying by 2/2.6, as the experimental conditions do not exactly reproduce Warburg's in that our method is a static one; and in any case the yields we have obtained for the alkyl iodides are so small that it is unlikely that they can lead to serious errors in interpretation even if the correction has ultimately to be made.

Results

The Continuum.—Twelve hours exposure of ethyl iodide vapor at 90 mm. and 25° to the filtered light of the mercury arc gave no measurable amount of iodine, nor did three hours at 100°, in agreement with Emschwiller's observation.

TABLE I

C_2H_5I, mm.	Temp., °C.	Quanta absorbed $\times 10^{-18}$	Iodine atoms produced $\times 10^{-18}$	Yield
		λ 2026		
95	30	12.12	1.55	0.128
88	30	17.60	2.03	.115
90	30	12.90	1.24	.096
87	30	12.38	1.06	.086
90	30	10.75	0.914	.085
90	40	5.09	.473	.093
90	40	12.15	.912	.075
90	37	4.46	.567	.127
90	39	5.88	.669	.114
90	41	12.38	.989	.080
45	40	4.73	.543	.115
			Mean	.101
0.1	30	2.02	.073	.036
.1	25	1.74	.053	.031
.1	25	3.53	.068	.020
			Mean	.029
Liquid	25	11.20	2.35	.21
Liquid	25	9.4	2.56	.27
			Mean	.24
		λ 1962		
95	30	1.50	0.127	.085
95	30	1.13	.080	.071
			Mean	.078

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[8] D. J. Beaver and J. J. Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

The Band Region.—Our results here are given in Table I.

Summary of Results

In the continuum at about 2600 Å. the yield is very low in the photo-decomposition of gaseous ethyl iodide, a result to be compared with a similar low yield for gaseous methyl iodide.[5] On the other hand, in hexane solution, even at concentrations comparable to that of the gas at 90 mm., ethyl iodide decomposes in this region with a yield of 0.6,[4] and the pure liquid seems to behave in much the same way.

At the beginning of the band region at 2026 Å., at 90 mm. and 30° the yield has the value of about 0.1, is not influenced by a 10° temperature change, and is the same at 45 mm. as at 90 mm. At a pressure of 0.1 mm., however, the yield is definitely lower than at the higher pressures. The liquid decomposes in this region with a definitely greater yield than the gas, but it does not attain the value exhibited by the liquid or solution in the continuum. At 1962 Å. the yield in the gas is substantially the same as at 2026 Å., although the low precision caused by the relatively low intensity of the aluminum lines would obscure small differences.

There is thus a complete reversal in the relative photo-behaviors of the various fluid states of aggregation of ethyl iodide in the two spectral regions, from very low yields in the gas and much higher yields in the liquid and dissolved states, independent of concentration, in the continuum, to appreciable gaseous yields in the band region, falling at low pressure, and liquid yields somewhat higher, but not more than half their values in the continuum.

Discussion

(1) **The Continuum.**—In the continuous region in the gas phase, there is little doubt that the primary photochemical process is dissociation of the molecule with the production of a free ethyl radical and an iodine atom endowed with a large amount of kinetic energy. There would then be the possibility of interaction such as

$$C_2H_5 + C_2H_5I = C_4H_{10} + I \qquad (1)$$

$$C_2H_5 + I = C_2H_5I \qquad (2)$$

$$C_2H_5 + C_2H_5 = C_4H_{10} \text{ or } C_2H_6 + C_2H_4 \qquad (3) \text{ and } (4)$$

$$I + I + M = I_2 + M \qquad (5)$$

and, after the reaction has proceeded for some time

$$C_2H_5 + I_2 = C_2H_5I + I \qquad (6)$$

The low yield shows that reactions (1), (3) and (4) are infrequent compared with the recombination (2), for which the collision efficiency seems high. In particular, the collision efficiency for reaction (1) must be quite low, and processes (3) and (4) are slow compared with (2). These conclusions are in complete agreement with those of R. A. Ogg, who has studied the thermal reaction of ethyl iodide with hydrogen iodide;[9] and of course, it has been known since the experiments of Paneth and Hofeditz on ethyl radicals from organo-metallic compounds that (3) and (4) were slow in the gaseous phase.[10]

In considering the mechanism of the process in the dissolved or liquid state, we have first to notice that ethyl iodide vapor at 90 mm., for which the yield is very small, has a concentration of 0.005 mole per liter, which is of the same order as the most dilute solution which has been examined, 0.007 molar, for which the yield at 2610 Å. is 0.6. The mere presence of the hexane molecules has increased the amount of decomposition of ethyl iodide by something of the order of one hundred fold. Also, passage from this dilute solution to the pure liquid iodide does not increase the yield. This behavior of ethyl iodide may be contrasted with that of hydrogen iodide, which in dilute hexane solution decomposes with a yield distinctly lower than in the gas, slowly rising toward the value for the gas as the concentration increases;[11] or with that of ammonia, which Ogg, Leighton and Bergstrom found not to suffer permanent decomposition in the liquid state.[12]

If the primary process in solution or the liquid is a dissociation, as for the gas, one might attempt to explain the increase in yield in the condensed state as due to the increased probability of the secondary reaction $C_2H_5 + C_2H_5I = C_4H_{10} + I$, but this explanation seems to be inconsistent with the fact that the yield is as great at 0.007 *N* as at 200 times that value. We should then be compelled to seek for some effect by which the solvent could either prevent recombination of the radical and the iodine atom, or facilitate the reactions (3), (4) and (5) which would compete with the yield-lowering recombination. As (5) re-

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(9) R. A. Ogg, THIS JOURNAL, **56**, 532 (1934).

(10) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(11) E. Warburg and W. Rump, *Z. Physik*, **47**, 305 (1928).

(12) R. A. Ogg, P. A. Leighton and F. W. Bergstrom, THIS JOURNAL, **55**, 1754 (1933). We had made this observation independently on liquid ammonia and take this opportunity to record our confirmation of the result.

quires a triple collision, there is a certain possibility that this effect of the solvent does occur to some extent. It is also possible to imagine mechanisms whereby some protective action of hexane molecules prevents ready recombination of radical and iodine atom, making the solvent act as an acceptor for one of the products, but such schemes are *ad hoc*, and seem intrinsically not very plausible.

But it is also possible that the primary photochemical act in solution is *not* a dissociation. Franck and Rabinowitch have pointed out how in the condensed state a molecule excited to a state in which there is repulsion between the nuclei and which in the gaseous state would lead to dissociation, may not dissociate owing to the constraints imposed by the solvent environment.[13] We shall suppose that the excitation of the ethyl iodide molecule which accompanies the absorption of light is of the same nature in the gaseous and condensed states, so that, as a result of absorption, a molecule is raised from the lower potential energy curve to the upper repulsive one. It now begins to traverse this curve in the direction of increasing nuclear separation, but before this has increased sufficiently for the molecule to dissociate, there is a high probability of collision with a solvent molecule, and, hemmed in by the barrier of solvent molecules, the excited ethyl iodide molecule may oscillate on a portion of the repulsive curve as an entity having the properties of a molecule rather than of a radical and an atom. In due course the molecule loses its energy of excitation, either by energy transfer or by spontaneous return to the normal state. The time of oscillation over the portion of the repulsion curve will be comparable to that of a molecular oscillation, *i. e.*, about 10^{-13} sec. for a C–I vibration, a time comparable to the average period elapsing between collisions of an ethyl iodide molecule and solvent molecules as calculated from the expression $Z = 3\pi\eta\sigma/2m$, where Z is the number of collisions per second experienced by a solute molecule of mass m and diameter σ in a solvent of viscosity η. For the average time between such collisions with ethyl iodide molecules and hexane molecules, the value 3.3×10^{-13} sec. is obtained, so that there would be a rather high probability of the occurrence of the mechanism described above.

There is thus the possibility of understanding the difference in the behavior toward light in the continuum shown by ethyl iodide in the gaseous and condensed states in terms of a difference in mechanism which is neither *ad hoc* nor intrinsically unplausible, if the reaction takes place on collision between a molecule, excited in this way, and a normal molecule, as exemplified in the simplest formulation, $C_2H_5I^* + C_2H_5I = C_4H_{10} + I_2$. If the average life of the excited molecule is long compared with the time between collisions with normal molecules, *i. e.*, if the probability of energy transfer to solvent molecules is small, an increase in concentration of the normal molecules will not increase the yield after a certain concentration, which may be quite low, has been attained. At the lowest concentration at which values of the yield are available in solution, the simple gas kinetic expression for collision frequency gives the value 2×10^{-9} sec. as the average time between collisions of ethyl iodide molecules, and according to this mechanism, the period of persistence of the excited quasi-molecule must be greater than this value; this may be compared with the mean life of an excited atom or ordinary excited molecule, 10^{-7} to 10^{-8} sec. Only when the concentration of the ethyl iodide in solution is reduced to a value at which the mean time between collisions is of the same order as the mean life of the excited molecule will the yield begin to fall, and this may well be below 0.007 molar.

(2) **The Band Region at 2000 Å.**—Although the far ultraviolet absorption spectra of the alkyl iodides do not yet appear to have been examined under adequate dispersion, their general features have been elucidated.[1] The bands are associated with transitions to a group of stable electronic states in which the equilibrium distances between the nuclei do not differ greatly from those in the ground state, so that the most intense band is for a $0 \longleftarrow 0$ transition. Frequency intervals of about 460 cm.$^{-1}$ and 1100 cm.$^{-1}$ have been attributed to parallel C–I and parallel C–H vibrations (the latter probably connected with the group CH_3), respectively, in the upper state. The intense band with a sharp head at 2010 Å. is apparently the $0 \longleftarrow 0$ transition for the system[14] and it, along with a much fainter band at 2023 Å., originating in the $1 \longleftarrow 0$

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[13] J. Franck and R. Rabinowitch, *Trans. Faraday Soc.*, **30**, 125 (1934).

[14] In referring to vibrational transitions we shall use the convention that the upper state is written to the left.

transition of a perpendicular vibration of about 290 cm. is responsible for the absorption of the zinc line at 2026 Å. The excited molecule resulting from the absorption of this line is therefore in its lowest vibrational state, and a direct dissociation cannot occur; moreover, though the resolution employed has been quite inadequate to demonstrate rotational structure, the sharpness of the head indicates that predissociation does not occur, and only by undergoing collisions can the molecule decompose in this state. There is also a probability of a transition, either spontaneously, or after collision, to the repulsive electronic state between the ground state and the stable excited state, with consequent dissociation of the molecule.

We therefore attribute the large increase in yield which takes place in proceeding from the continuum to the band spectrum to a change from a mechanism which involves production of free radicals and atoms and subsequent recombination, to one in which an electronically excited molecule collides with a normal, in much the same way as was described in the discussion of the process in solution. Some production of free radicals and atoms by transition to the repulsive state is not excluded in the gaseous state, and this may account partly for the fact that the yield in the gas in the band region is lower than in correspondingly dilute hexane solution in the continuum. At sufficiently low pressures, when the time between collisions of the excited ethyl iodide and normal molecules becomes comparable with the mean life of the excited molecule, the yield should begin to fall. For a mean life of 10^{-7} sec., this pressure is about 1.4 mm., and the experimental fact that the yield at 0.1 mm. is only about one-third of that at 45 or 90 mm. is in accord with this interpretation. Moreover, the state of affairs in the liquid and the gas is not materially different in the band region, with the result that there is no striking difference between the yields in the two cases.

In the experiments in which illumination was from the aluminum spark the effective lines were 1990, 1933 and 1862 Å. The first falls near a diffuse band at 1992 Å., a member of a group interpreted by Scheibe, Povenz and Linström as belonging to a parallel C–I vibration for which it would be the 1 ⟵ 0 transition,[1] the second near a band at 1935 Å. of uncertain significance, and 1862 Å. on a band at 1864 Å. which is the 4 ⟵ 0 transition of the parallel C–I vibration. Our experiments do not allow us to determine the effect of absorption in these bands separately, but simultaneous excitation of all these transitions leads to a result not greatly different from that of illuminating in the 0 ⟵ 0 band.

We have been unable to clinch our argument that the photo-change in the band region involves principally excited molecules by failing to observe this band group as fluorescence. Long exposures were made at various pressures of ethyl iodide in an apparatus which, when containing iodine vapor, allowed dense spectral photographs of the iodine fluorescence, excited by the focally isolated aluminum group 1990 Å., etc., to be made in thirty minutes, without a suggestion of ethyl iodide fluorescence appearing. Nevertheless, the photochemical results, along with the appearance of the spectra, seem to us to indicate a high probability of our suggested mechanism, and we attribute the difficulty of observing fluorescence to intense self-quenching of ethyl iodide.

Summary

1. The quantum yield in the photo-decomposition of ethyl iodide, in terms of the number of iodine atoms produced per quantum absorbed, is very low (of the order of 0.01 or less), at wave lengths in the continuous spectrum, about 2600 Å., increases to about 0.1 at 2026 Å., in the band spectrum, at about 90 mm. pressure, and is distinctly lower in this region at 0.1 mm. pressure. In the continuous region, liquid ethyl iodide and its solution in hexane have much higher quantum yields than the gas (about 0.6) whereas at 2026 Å. the yield in the liquid is about 0.24. A 10° increase in temperature does not appreciably change the yield at 2026 Å.

2. Primary dissociation and recombination seems a likely mechanism for the gaseous photoreaction in the continuum, and interaction between optically excited molecules and normal molecules, the predominating reaction responsible for the decomposition in the short wave region. A feasible explanation of the large difference in yield between the gaseous state and dilute hexane solution at 2600 Å. is afforded by the application of the principle of Franck and Rabinowitch by which primary dissociation is repressed in the condensed state, so that reaction takes place between excited quasi-molecules and normal molecules.

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