on a Cenco Hydrophil balance. Data obtained on one instrument were in good agreement with those obtained on the other.

The general procedure was that developed by Adam, Askew and Danielli.[12] A 1–2 mg. sample, weighed to 0.005 mg., was dissolved, at room temperature, in carefully purified benzene, and the volume of the solution was adjusted to 25 ml. in a volumetric flask. The solution was placed on the surface by means of a calibrated 1-ml. pipet. The films described by curves I through VIII were spread on distilled water; curves IX, X, and XI concern films which were spread on 0.02 N sodium hydroxide. Each film was studied at room temperature (21–26°).

All of the films studied showed the phenomenon of contraction, and contraction was most pronounced in films of friedelinol and cerin. Films of the acidic substances were very stable but showed some contraction at high pressures. The films reported are equilibrium films.

To check our technique and procedure, data were obtained for films of carefully purified stearic acid. These data agreed very well with those of Adam and co-workers.[13]

Summary

1. Measurements of pressure–area relations of surface films of friedelin and some of its derivatives indicate that the functional group is located near the end of the molecule, certainly not in ring C.

2. A study of surface films of cerin and certain of its derivatives indicates that the hydroxyl and carbonyl groups are not far removed from each other in the molecule.

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[12] Adam, Askew and Danielli, *Biochem. J.*, **29**, 1786 (1935).

[13] N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, New York, N. Y., 1938, page 50.

COLLEGE PARK, MARYLAND RECEIVED APRIL 3, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY, WASHINGTON SQUARE COLLEGE]

The Photolysis of Ethyl Iodide in Various Solvents

BY W. WEST AND J. FITELSON[1]

The photo-decomposition of the lower alkyl iodides is one of the few photo-reactions at present known in which the quantum yield is greater in the liquid state[2a] or in solution[2b] than in the dilute gaseous state. Ethyl iodide, for instance, undergoes photolysis at wave length 2537 Å., with a yield in the liquid state or in hexane solution, of about 0.4 atom of iodine produced per photon absorbed, while in the gaseous state the yield is less than 0.01. The present study is an attempt to secure further experimental information which might aid in understanding the effect of the medium on photo-reactions by observing the photolysis of ethyl iodide in a series of solvents of varied physical and chemical characteristics, namely, hexane, carbon tetrachloride, chloroform, benzene, chlorobenzene, carbon disulfide, ethyl alcohol, diethyl ether, acetic acid, ethyl acetate, methyl iodide and certain mixtures. Most of the experiments were performed at wave lengths embracing the region from about 2800 to 2537 Å., with an energy center at 2610 Å.; hexane solutions were also studied at wave length 2026 Å., and some observations were made at wave length 3130 Å.

Experimental Details.—The apparatus consisted of the normal photochemical set-up of source, quartz lenses, light filters, quartz reaction cell and thermopile–galvanometer system.

Light Sources.—For wave length 2610 Å., a 220-volt mercury arc was used whose light was filtered by 3 cm. of chlorine at one atm., 5 cm. of bromine vapor at a little under its saturation pressure at room temperature and 5 cm. of normal acetic acid, all in separate vessels. The range transmitted was from 2800 to 2537 Å., with an energy center at 2610 Å. For wave length 2026 Å., light from a zinc spark was monochromatized by focal isolation. The absorption of ethyl iodide was such that only the line at 2026 Å. was chemically effective. For wave length 3130 Å., glass vessels were exposed to the full light of the mercury arc. The transmission of the glass and the absorption of the iodide solutions were such as to make most of the actinic action originate in the line at 3130 Å.

Energy measurements were made by the integration method[3] by means of a Moll linear thermopile and Zernicke Zc galvanometer. Calibration was frequently made against Bureau of Standards carbon filament standards. No change in calibration with time occurred.

Determination of Iodine Produced.—This was effected photometrically by means of a Weston Photronic cell, a Leeds and Northrup type P galvanometer of 1000 ω resistance, a 21 candle power automobile lamp lit by a storage battery floated on the line, and the necessary filters, lens and stops arranged so as to permit analysis *in situ* during a run. The filters for violet or red iodine solutions consisted of 8-mm. thicknesses each of saturated

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[1] Present address: U. S. Food and Drug Administration, Federal Security Agency, New York, N. Y.

[2] (a) B. M. Norton, THIS JOURNAL, **56**, 2294 (1934); (b) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

[3] P. A. Leighton and W. G. Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

copper sulfate in water, 5% aqueous sodium chromate containing a drop or two of ammonia, and an aqueous solution of malachite green adjusted by observation with a hand spectroscope to transmit a band about 200 Å. wide, the transmission maximum of this substance falling in the same region as the absorption maxima of violet solutions of iodine. The filters for the brown solutions consisted of the copper sulfate solution and 8-mm. of aqueous crystal violet solution adjusted in concentration to a suitable transmission in the region of absorption of the iodine solutions. A calibration was performed for solutions in each solvent. From master standards determined by titration, calibration standards were prepared by dilution, in the range 1×10^{-5} *N* to 2×10^{-4} *N*, and their transmissions found. It is known that solutions of iodine do not follow Beer's law over large concentration ranges[4] but, with the exception of benzene solutions, those measured in the concentration range of interest to us were found to conform to this law quite strictly.

Filling the Cells.—Vacuum technique was used with the complete avoidance of rubber connections in order to secure practically complete absence of oxygen. The essence of the preparation of the cell for photolysis was evacuation of the vessel containing its solution cooled in liquid air or dry-ice according to the volatility of the solvent, to a pressure of 10^{-3} mm., allowing to warm to room temperature, and repeating the evacuating-warming process several times. The cell was then slipped off the vacuum line after closing a stopcock and placed in its position on the optical bench for irradiation.

Determination of Ethyl Iodide.—Since the method of filling caused changes in the ethyl iodide concentration during the process, a method was devised for the determination of the iodide concentration as at the start of illumination from observations made after the photolysis. The method, based on the procedure of Clark[5] involves the reactions

$$RI + Br_2 = RBr + IBr$$
$$IBr + 2Br_2 + 3H_2O = HIO_3 + 5HBr$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O$$

A convenient volume (10 cc. or less) of the solution of ethyl iodide in hexane (or other solvent) is pipetted into a glass-stoppered flask containing 0.5 cc. of 20% bromine in glacial acetic acid and the mixture shaken frequently for ten minutes. Fifty cc. of water containing 5 cc. of aqueous sodium acetate is added with vigorous shaking for a few minutes. One cc. of 90% formic acid is then added and the flask shaken occasionally until the excess bromine is removed. The hexane and aqueous layers should be colorless. More formic acid is added if necessary. One gram of solid potassium iodide is now added and the liberated iodine titrated with thiosulfate. One-sixth of the iodine found represents the iodine in the alkyl iodide. The method tended to give results about 2% high for concentrations of ethyl iodide below about 10^{-3} *M*: at higher concentrations, the results deviated irregularly from the true by about 0.5%. In the presence of free iodine the procedure was found to give the uncombined and combined iodine, and since in the photo-experiments both free and combined iodine are determined, the original concentration of the alkyl iodide is given by the method.

Temperature Control.—Most of the reactions were carried out at room temperature, but experiments up to 55° in hexane and ethyl alcohol were performed by placing the cell in a heated cube of aluminum provided with holes for the passage of the light. No definite temperature dependence of the quantum yield was observed.

Materials.—All chemicals were carefully purified and dried in all-glass apparatus with particular attention to the removal of possible reactants with iodine, and used not longer than a day after a final purification. For most substances the methods are adequately indicated by the literature citation: in the following summary the wave length figure refers to the cut-off of a 2 cm. layer.

Ethyl and methyl iodides were prepared from the alcohol, red phosphorus and iodine and distilled in nitrogen. Hexane was from petroleum ether,[6] λ 2000 Å. Carbon tetrachloride and chloroform[7] transmitted to λ 2650 and 2450 Å., respectively. Carbon disulfide was c. p. material mechanically shaken with mercury and then mercuric chloride: λ 3800 Å. Benzene was shaken mechanically with concd. sulfuric acid, washed successively with water, sodium hydroxide and water; thiophene free, λ 2800 Å. Ethyl alcohol[6,8] gave λ 2200 Å., ethyl ether,[8] λ 2200 Å., acetic acid,[9] λ 2500 Å. Ethyl acetate was shaken mechanically five times with decreasing volumes of water and dried over potassium carbonate, λ 2500 Å. Chlorobenzene was Kahlbaum product dried over calcium chloride and fractionated, λ 2850 Å.

All of these solvents were tested for possible reactivity with iodine under the experimental conditions. No loss in concentration of a 5×10^{-5} *N* solution of iodine in the various solvents was observed after two hours or more of exposure to the unfiltered light of the mercury arc, provided oxygen was removed from the cell. Without the latter precaution there was loss of iodine in carbon tetrachloride and chloroform solutions.

In connection with the energy measurements, the transmissions of the quartz windows and of the fluorite window covering the thermopile were measured and due corrections were made for loss of light at the windows and for the difference in the transmission of the latter window for the actinic radiation and for the calibrating radiation (mostly infrared).

Results

Table I contains the iodine yields in the photolysis of ethyl iodine in hexane at wave lengths 2610 and 2026 Å.

Table II contains the average values of the quantum yields found in various solvents at wave length 2610 Å. Each value in this table is the average of from two to five experimental values, of the same order of consistency as is illustrated in Table I. In all of the solvents except methyl

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[4] M. Chatelet, *Ann. chim.*, [11] **2**, 5 (1934).

[5] E. P. Clark, *J. Assoc. Official Agr. Chem.*, **17**, 483 (1934).

[6] Castille and Henri, *Bull. Soc. Chim. Biol.*, **6**, 299 (1924).

[7] A. T. Chapman, This Journal, **56**, 818 (1934).

[8] L. Harris, *ibid.*, **55**, 1940 (1933).

[9] W. C. Eichelberger and V. K. LaMer, *ibid.*, **55**, 3633 (1933).

iodide and ethyl alcohol, the concentration of ethyl iodide was 0.36 *M;* in methyl iodide, the yield was determined at five concentrations between 0.006 and 0.16 *M* without showing any trend with concentration; in ethyl alcohol, besides four absolute yields at ethyl iodide concentrations 0.25 and 0.36 *M* whose average is tabulated, comparative experiments down to concentrations of 0.003 *M* ethyl iodide have indicated no dependence of yield on photolyte concentration.

TABLE I

IODINE QUANTUM YIELDS IN PHOTOLYSIS OF ETHYL IODIDE IN HEXANE

EtI moles/l.	Temp., °C.	Exposure, sec. $\times 10^{-3}$	Quanta abs. $\times 10^{-17}$	Iodine atoms produced $\times 10^{-17}$	Φ_I
		At λ 2610 Å.			
0.360	25	7.35	13.85	5.64	0.41
.254	25	7.38	8.50	3.37	.40
.160	25	7.80	13.90	5.64	.41
.090	25	6.99	13.42	5.19	.39
.058	25	6.57	13.41	6.05	.45
.007	25	6.96	9.52	3.27	.34
.003	25	10.29	15.65	6.39	.41
.003	25	7.80	14.62	5.74	.40
.250	55	5.40	27.87	9.59	.35
				Mean	.39
		Mean devn. from mean, ±0.025			
		At λ 2026 Å.			
0.260	25	2.20	19.19	8.44	0.44
.179	25	1.80	18.94	9.95	.53
.027	25	2.02	16.54	8.63	.53
.016	25	1.87	15.53	6.95	.45
.006	25	1.82	12.03	6.06	.50
				Mean	.49
		Mean devn. from mean ±0.036			

TABLE II

QUANTUM YIELDS IN PHOTOLYSIS OF ETHYL IODIDE AT 2610 Å. IN SOLUTION

Solvent	Φ_I	$\Delta\lambda_{I_2}$
Diethyl ether	0.66	680
Ethyl acetate	.60	
Ethyl alcohol	.59	710
Benzene	.43	180
Hexane	.39	0
Chloroform	.38	100
Carbon tetrachloride	.38	0
Acetic acid	.36	490
Methyl iodide	.36	480
Chlorobenzene	.16	131
Carbon disulfide	.15	0
CCl_4 70% and EtOH 30%	.60	

In Table II, $\Delta\lambda_{I_2}$ is the wave length shift in Å., to shorter wave lengths of the maximum absorption of solutions of iodine in the solvent from the normal value in inert solvents.

In each solvent the concentration of the iodine produced in any run was found to increase linearly with the time. This, of course, is simply because only a small fraction of photolyte was decomposed even at the lowest concentrations of iodide so that the intensity of the light absorbed remained practically constant during a run; but it does show that there was no interference by absorption or other action of the molecular iodine produced.

Comparative experiments at wave length 3130 Å. have also established the independence of the iodine yield on ethyl iodide concentration over the concentration range 0.006 *M* in hexane to pure liquid.

The general results of the photolysis of ethyl iodide in the condensed state at present available are summarized as follows: throughout the first region of ultraviolet absorption centered round the maximum about 2600 Å., and at the beginning of the second absorption extending into the Schumann region, at wave length 2026 Å., the quantum yield of iodine is independent of the ethyl iodide concentration from values of a few thousandths molar in hexane to the pure liquid: independent of the intensity, in the first absorption region, over a four and one-half fold variation, in the intensity level corresponding to the absorption of about 4 to 20 × 10^{12} quanta per second per cc., independent of temperature between 25 and 55° in hexane, and ethyl alcohol; but it does depend on wave length and on the nature of the solvent. The value of the yield found in hexane in these experiments at wave length 2610 Å., 0.39, is rather lower than that previously obtained by West and Paul[2] (0.58, uncorrected for window absorption) and is practically identical with Norton's[1] value for the pure liquid (0.41 at 2537 Å. and 0.38 at 2654 Å.).

The previous results of West and Paul in hexane and of Norton in the pure liquid had shown a definite increase in the value of the yield with diminishing wave length. The experiments reported here at wave length 2026 Å. show that this increase continues into the second region of absorption.

Comparing the yields in different solvents, it will be observed that apart from the low values in carbon disulfide and chlorobenzene, they arrange themselves into two groups, one about 0.39 at 2610 Å. in "inert solvents," the other about 0.6 in active solvents, with perhaps the value in benzene occupying an intermediate position. The most outstanding correlation between the value of the yield and the properties of the solvent seems to be a high yield in solvents whose iodine solutions are brown, and a "normal" yield in those whose iodine solutions are violet. In Table I it will be noticed that, with the exception of benzene, wave length displacements of less than between 500 to 600 Å. are associated with normal yields and displacements of about 700 Å., with high yields. It is known that some brown solutions of iodine tend to verge toward the violet type with increase in temperature, but experiments on alcohol solutions gave the same yield at 55° as at 25°. At 55°, however, the solution of iodine obtained was still brown, and the low boiling point of ethyl iodide restricted the temperature rise that could be effected. An experiment also was performed in a solution containing 70% carbon tetrachloride and 30% alcohol by volume (4 molecules of carbon tetrachloride to 3 alcohol) whose iodine solution is a reddish brown about midway between typical violet and typical brown solutions. The yield in this experiment was the same as in pure alcohol.

We have not been able to find any other correlation between the value of the quantum yield and the properties of the solvent; the molecular weight, dielectric properties, viscosity and Trouton constants of the solvents vary irregularly with the yield.

Discussion

Transparent Solvents.—Two essential problems arise in understanding the action of transparent solvents in the photolysis of ethyl iodide; their general action in raising the iodine yields from a few thousandths in the gaseous state to some tenths, and the action of certain "active" solvents in raising the value above that observed in inert solvents.

For concreteness in discussion, the primary photo-process in the photolysis of gaseous ethyl iodide in the first region of absorption is assumed to be equivalent to a dissociation to ethyl radicals and iodine atoms, followed by a series of changes, of which the fastest is recombination of radicals and atoms, and including relatively slow bimolecular associations of iodine atoms and ethyl radicals.[10]

There is a great deal of evidence that the low over-all yield in the gaseous photolysis of ethyl and methyl iodides is not due to chemical inefficiency in the primary absorption process. The effect of silver[10] and mercury surfaces in increasing many-fold the rate of the gaseous photodecomposition, the very considerable increase in yield caused by the addition of inert gas at high pressure,[10] the relatively high yield in the gaseous photoöxidation of the lower alkyl iodides[11] all indicate an efficient primary disruption, and the low observed yield must be attributed to the recombination of alkyl radical and iodine atom.

In general, solvents could influence such a photo-reaction by affecting (a) the primary process, by changing the energy levels, with or without change of the essential mechanism, or (b) by affecting the secondary processes.

There are no indications here that the solvents used have large influences on the energy levels of ethyl iodide; its absorption spectrum in hexane and in alcohol is not markedly different in position and intensity from the gaseous spectrum,[12] and the existence of minimum boiling points of mixtures of ethyl iodide with hexane, ethyl acetate and ethyl alcohol[13] points to the absence of strong solute–solvent interaction.

The process of primary recombination in solution,[14] however, does present the possibility of a fundamental change of mechanism from that in the gaseous state. During the recombination, there must be an interval over which the combining radicals behave as an electronically excited quasi-molecule, and bimolecular reactions of these with normal photolyte molecules could change the mechanism from one involving free radicals to one between practically saturated molecules. The scheme of such a mechanism is

$$\begin{aligned} \mathrm{EtI} + h\nu &= \mathrm{Et\ldots I} && k_1 \\ \mathrm{Et\ldots I} &= \mathrm{EtI} && k_2 \text{ (deactivation)} \\ \mathrm{Et\ldots I} + \mathrm{EtI} &= \mathrm{I_2} + \mathrm{Et_2} && k_3 \end{aligned}$$

where Et...I represents the quasi-molecule. On the assumption that the rate of production of quasi-molecules is proportional to the intensity of the light absorbed, the equation of the quantum yield is $\Phi_{\mathrm{I}} = k_1[\mathrm{EtI}]/[(k_2/k_3) + [\mathrm{EtI}]]$. If deactivation is negligible the yield becomes independent of the concentration of iodide. The experimental fact of a yield independent of con-

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[10] W. West and L. Schlessinger, THIS JOURNAL, **60**, 961 (1938).

[11] J. R. Bates and R. Spence, *ibid.*, **53**, 1689 (1931); L. T. Jones and J. R. Bates, *ibid.*, **56**, 2285 (1934).

[12] G. Scheibe, *Ber.*, **58**, 586 (1925).

[13] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 320.

[14] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

centration to values as low as 0.003 M is consistent with a ratio of k_2/k_3 not above 0.001. The consequences of the assumption of this ratio can be approximately, but very probably essentially correctly, seen by applying simple gas-kinetic collision theory to estimate the frequency of encounters between a quasi-molecule and a normal molecule of ethyl iodide. The highest probability of reaction between quasi- and normal molecules occurs when every collision between them is effective; the maximum probability of reaction of a given quasi-molecule at an ethyl iodide concentration of 0.003 M would be about 10^9 to 10^{10} per sec.; the maximum probability of deactivation would then be about 10^6 to 10^7 per second, corresponding to a minimum average life before deactivation of about 10^{-6} to 10^{-7} sec. It is scarcely conceivable that the quasi-molecule could survive this period without deactivation by collision or fluorescence (which latter cannot be observed), and we can dismiss the hypothesis that the action of the solvent is to change the free radical mechanism to one of the type just discussed.

The simplest free radical mechanism in solution would be

$$\begin{aligned}
\mathrm{EtI} + h\nu &= \mathrm{Et}^* + \mathrm{I}^* && (1)\ k_1 \\
\mathrm{Et}^* + \mathrm{I}^* &= \mathrm{EtI} && (2)\ k_2 \text{ (primary recombination)} \\
\mathrm{I}^* &= \mathrm{I} && (3)\ k_3 \\
\mathrm{Et}^* &= \mathrm{Et} && (3a)\ k_3 \\
\mathrm{I} + \mathrm{I}(+\mathrm{S}) &= \mathrm{I}_2 && (4)\ k_4 \\
\mathrm{Et} + \mathrm{Et}\ (+\mathrm{S}) &= \mathrm{Et}_2 && (5)\ k_5 \\
\mathrm{Et} + \mathrm{I}\ (+\mathrm{S}) &= \mathrm{EtI} && (6)\ k_6 \text{ (secondary recombination)}
\end{aligned}$$

An ethyl iodide molecule, in its "cage" of solvent molecules, absorbs a photon and is dissociated into Et* and I*, where the asterisks indicate that the radicals, if unable to escape from the cage, may undergo primary recombination, in reaction (2). Conservation of momentum at collision indicates that only the heavy iodine atom will escape with appreciable probability,[15] rendering the ethyl radical likewise incapable of primary recombination (Reactions 3 and 3a). The most likely subsequent reactions are the associations 4, 5 and 6, of which the first two tend to increase the yield and the other to decrease it. If the rate of the primary reaction is proportional to the intensity of the light absorbed, the iodine yield becomes

$$\Phi_{\mathrm{I}} = \frac{k_1}{(1 + k_2/k_3)(1 + k_6/\sqrt{k_4k_5})}$$

independent of the iodide concentration, and, assuming k_1 equals 1, reduced from the value unity by the primary and secondary recombinations indicated in the two denominator terms. The essential action of the solvent must therefore be one of partially preventing recombination by facilitating the yield increasing reactions, as by making nearly every encounter between two iodine atoms lead to association. The absence of an appreciable temperature coefficient in the over-all reactions is then the consequence of the small energies of activation of the association reactions.

A reasonable explanation of the high yields in "active" solvents is the formation of complexes between these solvents and iodine atoms, whose disruption in the reaction S...I + Et = S + EtI would require an energy of activation greater than that for the reaction with free iodine atoms. The correlation between the yields and the color of molecular iodine solutions demands a stability of the atom complexes roughly parallel to that of the molecular complexes with active solvents, whose stability seems to be the greater, the greater the displacement of the visible absorption band from its position in a violet solution.[16] Rabinowitch and Wood also have proposed the formation of complexes such as $C_6H_5{\cdot}I$ as an explanation of the diminished transmission of intensely illuminated iodine solutions in benzene, alcohol and water.[17]

Absorbing Solvents.—The low yields in carbon disulfide and in chlorobenzene have a ready explanation in the "inner filter" action of the solvent. Carbon disulfide itself undergoes photochange, while the energy absorbed by chlorobenzene is apparently degraded thermally without being transferred to the iodide. Chlorobenzene is in this respect quite different from benzene, which likewise absorbs strongly the bulk of the incident radiation, but transfers the energy to the iodide in a sensitization process. We hope to discuss the photosensitizing properties of aromatic hydrocarbons and their derivatives in detail in a later communication.

Carbon tetrachloride, acetic acid, and ethyl acetate have also some absorption in the photolytic region, but their absorption coefficients are so low compared with that of ethyl iodide that they are in these experiments photo-chemically practically transparent.

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(15) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

(16) O. J. Walker, *ibid.*, **31**, 1932 (1935).

(17) B. Rabinowitch and W. C. Wood, *ibid.*, **32**, 816 (1936).

Special interest seems to be attached to the results in methyl iodide solution in which most of the photons must have been captured by the solvent. Liquid methyl iodide was here found to show an iodine yield of 0.07 at wave length 2610 Å.; the introduction of 0.006 *M* ethyl iodide increased the yield to 0.36, independent of the ethyl iodide concentration above 0.006 *M*, as if the ethyl iodide decomposed in a nearly transparent solvent. The arguments already advanced show that in methyl iodide the primary process is an efficient dissociation; the low yield in the liquid must be due to primary associations effective at nearly every collision. In liquid ethyl iodide and in solutions of ethyl iodide, on the other hand, the first primary collision of the disrupted fragments is apparently not chemically effective, and there is a greater chance of escape from the cage and for the intervention of solvent influences as described. In spite, however, of the strong primary recombination of methyl radical and iodine atoms, the energy absorbed is not dissipated and can be communicated to a foreign molecule, as ethyl iodide, in a photosensitization process.

Summary

The quantum yield in the photolysis of ethyl iodide in solution is independent of concentration of photolyte in hexane, alcohol, and methyl iodide from values of a few thousandths molar to the pure liquid, independent of temperature in the range 20 to 55°, increases with decreasing wave length between 3130 and 2026 Å., and depends on the solvent.

Incidental to these experiments, a method for the determination of alkyl iodides in organic solvents has been devised, based on the procedure of E. P. Clark.

The "normal" yield in solution, about 0.39 at wave length 2610 Å., many times larger than in the gas, is exhibited in hexane and other transparent solvents whose iodine solutions are violet. In solvents whose iodine solutions are brown, the yield is higher.

Solvents which themselves absorb the actinic radiation in this reaction may give normal iodine yields, by sensitizing the decomposition of the alkyl iodide; benzene (and other aromatic hydrocarbons not reported here) and methyl iodide are good sensitizers; chlorobenzene and carbon disulfide, poor.

The general action of solvents in increasing the yield over the gas value is interpreted as an effect of facilitating atomic iodine association relatively to the recombination of ethyl radicals with iodine atoms; and the effect of active solvents is correlated with the proposed formation of complexes of atomic iodine with the molecules of these substances, whose stability is roughly parallel to that of the molecular complexes which confer the brown color to solutions of iodine.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, AND FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

The Tetra Alkyl Methylene Immonium Salts

BY HAROLD G. REIBER[1] AND T. D. STEWART

An earlier communication[2] gives the evidence for the occurrence of nitrogen substituted methylene immonium salts in relatively strong acid solutions. These were prepared from the corresponding amino ethers.

$$H_2C(NR_2)OR' + H^+ \longrightarrow H_2C{=}N^+R_2 + HOR'$$

The higher derivatives, substituted upon carbon, have been reported in the case of cyclic structures.[3,4] The preparation of the phenyl and the ethyl cyclopropyl ketimines from cyclopropyl cyanide and a Grignard reagent have been reported by Cloke.[5] He also obtained the hydrochlorides of these free bases. It is also possible to prepare tetra alkyl methylene immonium salts from the corresponding amino nitriles and silver nitrate.

$$R_2C(NR_2)CN + AgNO_3 \longrightarrow R_2C{=}N^+R_2 + NO_3^- + AgCN$$

We have isolated a number of these salts with a reasonable degree of purity, proved their structure by hydrolysis to the corresponding amine and ketone, and studied some of their reactions.

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[1] College of Agriculture, University of California, Davis, Calif.

[2] Stewart and Bradley, THIS JOURNAL, **54**, 4172 (1932).

[3] Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899).

[4] Aston, THIS JOURNAL, **52**, 5254 (1930); **53**, 1448, 4298 (1931).

[5] Cloke, *ibid.*, **51**, 1174 (1929); **62**, 117 (1940).