at high concentrations of acetylene and to the law

$$\frac{-\mathrm{d}(\mathrm{Br_2})}{\mathrm{d}t} = 2I_{\mathrm{abs.}}\frac{k_3}{k_7}(\mathrm{C_2H_2})\frac{k_5(\mathrm{Br_2})}{k_5(\mathrm{Br_2}) + k_6}$$

at low concentrations of acetylene. A mechanism involving Br, Br_3, $C_2H_2Br_3$ and C_2H_2Br as intermediates, and which would lead to the experimentally observed rate law, was suggested.

Measurement of the relative rates at 150 and at 120° showed the influence of temperature to be very small. Using the integrated form of the Arrhenius equation a value of about −1500 calories was calculated for the heat of activation.

BERKELEY, CALIF. RECEIVED JULY 27, 1934

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Quantum Yield in the Photodecomposition of Liquid Ethyl Iodide at 3130, 2654 and 2537 Å.[1]

BY BAYES M. NORTON

The quantum yield in the photodecomposition of liquid ethyl iodide (calculated in terms of the number of atoms of iodine formed per quantum of light energy absorbed) has been measured by Iredale.[2] He used filters to isolate light of wave lengths in the neighborhood of 3660 and 3000 Å., for which he found quantum yields of 1.0 and 1.2, respectively. More recently West and Paul[3] concluded that these yields were too high and reported values, 0.30 and 0.58, for the quantum yields in hexane solutions of several concentrations for wave lengths, isolated by filters, in the neighborhood of 3130 and 2600 Å.

The results given in this paper were obtained with improved technique, and show that the quantum yield for the liquid iodide is 0.315 at 3130 Å., 0.38 at 2654 Å. and 0.41 at 2537 Å.

Materials and Procedures

Ethyl iodide was prepared from ethyl alcohol, iodine and phosphorus according to the directions of Fischer.[4] Also one of the samples used came from the J. T. Baker Chemical Co. Before exposure the iodide was shaken with sodium hydroxide, washed several times with distilled water, dried over calcium chloride and finally freed of oxygen by gentle boiling on a water-bath with a reflux condenser in a current of nitrogen. The reaction cell was connected directly to this system so that it could be flushed with nitrogen before filling.

The cell, which was made of quartz with flat faces of polished quartz fused on, had a capacity of 10 cc. and a depth of 1.5 cm. Stirring was accomplished by a thin glass rod equipped with vanes so that it could be turned by a current of air.

A Hanovia 220-volt advanced research model mercury vapor arc was used as the source of radiation. A quartz lens was used to focus the light on the collimator slit of a D-33 Hilger quartz monochromator. Slit widths of 0.04″ were used in runs A and D of Table II, 0.05″ in runs C, D, F and J of Table III, 0.08″ in runs B and C of Table II and 0.10″ in run E of Table II and in runs A, B, E, G, H and I of Table III. Experiments were thus made with slit widths of either 0.04″ or 0.05″ at all wave lengths used with no appreciable difference in the values of the quantum yields obtained from those using wider slit widths.

The use of the monochromator with a commercial mercury vapor arc meant that the determination of the amount of chemical change by ordinary chemical means of analysis would have necessitated inconveniently long exposures. To overcome this difficulty an optical method of measuring small amounts of iodine was devised. Light from a mazda daylight bulb, filtered by 2.5 cm. of a saturated solution of copper sulfate, entered a thermostat through a window in the wall. The reaction cell was in position behind this and was fixed in a carriage suspended from an overhead track so that it could be run conveniently in and out of the path of light. In back of this there was a copper case with a window through which the light could pass to a thermopile inside. The absorbing solution in the reaction cell and the thermopile were kept at a temperature of 20°.

As comparison standards for this optical method solutions of iodine in ethyl iodide were prepared gravimetrically and diluted with more ethyl iodide until there were present in the cell from 1.5×10^{-6} to 9.5×10^{-6} g. atoms of iodine. The percentage absorption for these amounts ranged from 20 to 60. The absorption values plotted as ordinates against the log of the iodine concentrations as abscissas gave a straight line except for a small decrease in slope at the lower values. By making absorption measurements at intervals on ethyl iodide that was undergoing photolysis and comparing with the graph, it was possible to obtain a number of values for the amount of iodine formed.

The radiometric measurements were made by the integration method[5,6,7] developed by Forbes and his co-

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(1) From the Dissertation presented to the Graduate School of Yale University by the author in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1934.

(2) Iredale, *J. Phys. Chem.*, **33**, 290 (1927).

(3) West and Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(4) Fischer, "Introduction to the Preparation of Organic Compounds," translated by R. V. Stanford, D. Van Nostrand Co., New York, 1928.

(5) Villars, THIS JOURNAL, **49**, 326 (1927).

(6) Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

(7) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932)

workers. Thermopile settings 1 mm. apart were used. The thermopile was a linear vacuum pile of the Coblentz type made by the Eppley Laboratories. A Leeds and Northrop d'Arsonval galvanometer (No. 2285-x) was connected directly to this. The thermopile–galvanometer system was frequently calibrated with Bureau of Standards radiation standard C-105 and less often, as a check against deterioration, with C-155. The agreement between the two standards was always within 1% with a final, maximum deviation corresponding to C-105 with an intensity 0.8% less than C-155. The factors given by Leighton and Leighton[7] were used in correcting for the reflections at the thermopile window of the standard lamp radiation and of the radiation of the experimental wave length.

Reflection losses at the front wall of the reaction cell were calculated from the square root of the over-all transmission of the cell after correcting for absorption by 1.5 cm. of water. The values found for the transmission of the front wall were 0.945 at 3660 Å. and 0.94 at the other wave lengths used.

The amount of energy absorbed by the reacting substance was calculated as a sum of terms because, for reasons of convenience, the runs usually consisted of a number of exposures of about four hours' duration. During this length of time the energy output of the arc, although not operated on a completely isolated generator, but, however, on one within the laboratory, varied only 1 or 2%. In fact in some of the preliminary measurements in which the decompositions of uranium oxalate solutions were used to measure the amount of energy, a variation of only 3% was observed for a series of exposures over a period of several weeks.

Preliminary Measurements

Table I summarizes some preliminary measurements made during the development of the optical method of determining the iodine concentration. Light of the wave lengths in the neighborhood of 3000 Å. was obtained by using a filter solution made from 0.125 g. of auramine[8] (Eastman Kodak Co.) diluted to 1 liter with distilled water. A fresh portion of this was used for every experimental run.

The amount of energy was measured by means of the actinometer solution[6] of uranium oxalate. Both this solution and the ethyl iodide absorbed completely the ultraviolet light transmitted by the auramine. The runs were carried out with the reaction cell in a thermostat with the cell containing the filter solution fixed in the wall as a window.

Comparisons of the rate of decomposition of the uranium oxalate solution in consecutive runs at 5 and 58° showed it to have a 10° temperature coefficient of 1.032 ± 0.015. By comparing with a run made at 22°, the 10° coefficient was found to be 1.033 for 5–22°, and 1.030 for 22–58°.

In the runs at 4 and 28° of Table I, the amount of iodine formed was measured by titration with approximately $N/50$ sodium thiosulfate solution. In the remainder the amount of iodine was measured by means of its light absorption. In principle the procedure in every case was the same as that described above which referred to the final arrangement adopted for the quantum yield determinations made using the monochromator. In the first measurements a standard curve was constructed for absorption by the iodine solution of the visible light transmitted by the auramine filter, and the analytical determinations were made without moving the cell. The photolysis was stopped during these by cutting out the ultraviolet light with a glass plate. The runs at the various temperatures also necessitated modifications to overcome changes in absorption.

TABLE I

THE QUANTUM YIELD OF ETHYL IODIDE IN LIGHT TRANSMITTED BY THE AURAMINE FILTER (~ 3000 Å.)

Temp., °C.	Number of runs	G. atoms of iodine formed × 10⁶	Analytical detns.[a]	Einsteins absorbed × 10⁶	Av. quantum yield	Av. devn.
4	1	30.8	1[b]	108.6	0.28	
7	3	5.0–14.0	7	18.7–45.7	.30	0.01
22	2	2.15–17.5	14	6.9–59.4	.30	.01
25	2	18.5–19.0	2	70.2	.265	.005
28	3	17.1–30.1	3[b]	72.5–108.6	.27	.01
31	1	8.9–17.5	3	27.6–59.3	.31	.01
45	1	12.7–19.0	2	36.8–70.2	.28	01
50	1	3.9–7.6	2	13.8–27.6	.28	

[a] *E. g.*, in one of the runs at 22°, 12 analytical determinations by light absorption measurements showed 2.15, 3.5, 3.8, 5.8, 6.45, 7.0, 8.6, 10.35, 10.75, 14.0, 16.6, 17.5 (all $\times 10^{-6}$) g. atoms of iodine to be present after 6.9, 12.4, 13.8, 20.7, 24.15, 24.8, 30.4, 34.5, 38.0, 46.0, 55.2, 59.4 (all $\times 10^{-6}$) Einsteins had been absorbed, respectively, as calculated from the rate of energy input measured with the uranium oxalate actinometer.

[b] Made by titration with $N/50$ sodium thiosulfate solution.

Within the experimental error, a temperature coefficient of unity was found over the range studied.

In Table II are shown the results of some measurements made on the decomposition of the uranium oxalate actinometer as a cross-check on the apparatus when the monochromator and the thermopile–galvanometer system were used. Since a chemical method of analysis (similar to that described by Leighton and Forbes)[6] was used, the exposures were inconveniently long, up to sixty hours; but they do serve to show through substantial agreement with the standard results[6] that there were no sources of error of serious magnitude in the apparatus employed.

TABLE II

QUANTUM YIELDS OF THE URANIUM OXALATE ACTINOMETER

Run	Moles of oxalate decomposed × 10⁵	% decomposed	Å.	Einsteins absorbed × 10⁵	Quantum yield	Yield[6] by Leighton and Forbes
A	0.78	1.6	3660	1.73	0.45	
B	3.11	6.2	3660	6.21	.50	0.492
C	2.15	4.3	3660	4.30	.50	
D	1.66	3.3	3130	2.89	.57	.561
E	4.28	8.6	2537	7.10	.60	.603

Experimental Results

Table III shows the results obtained with the monochromator for liquid ethyl iodide. The durations of the runs were from eight to twenty-two hours. The quantum

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[8] See Bowen, *J. Chem. Soc.*, **134**, 2236 (1932), for an improved way of using this substance as a filter.

yields, computed from the averages of the several runs, are 0.315 at 3130 Å., 0.38 at 2654 Å. and 0.41 at 2537 Å.

TABLE III

QUANTUM YIELDS OF ETHYL IODIDE AT 3130, 2654 AND 2537 Å.

Run	G. atoms[a] of iodine $\times 10^6$	Analytical detns.	Einsteins absorbed $\times 10^6$	Number of integrations	Average[b] quantum yield	Av. devn. from mean of run
			3130 Å.			
A	5.0–6.3	3	16.75–19.5	12	0.315	0.003
B	3.4–6.9	8	10.8–22.6	2	.305	.008
C	3.2–4.7	5	9.0–14.6	6	.33	.006
D	1.6–6.5	10	5.6–18.9	4	.32	.01
					.315	
			2654 Å.			
E	3.5–6.0	6	8.6–15.6	2	.39	.006
F	1.5	1	4.1	7	.37	
					.38	
			2537 Å.			
G	2.7–4.8	5	6.3–12.1	6	.415	.014
H	3.8–5.9	4	10 0–15.5	6	.38	.005
I	2.3–6.3	8	5.7–16.5	6	.41	013
J	3.4–4.1	2	7.6–9.7	7	.43	.013
					.41	

[a] The values in this column show the amounts of iodine obtained in the first and last analytical determinations of the run; the number of Einsteins absorbed up to the time of these are shown in the fourth column.

[b] This is the average of a number of quantum yields equal to the number of determinations shown in the third column.

Discussion

The quantum yield at 3130 Å. is in substantial agreement with the value 0.30 reported by West and Paul for the decomposition in hexane solution. At the shorter wave lengths, however, the increase in quantum yield is considerably less. Further work is being undertaken to determine whether this is an effect produced by the difference in the medium (hexane or ethyl iodide) surrounding the light-absorbing molecule, or is due to factors not accounted for in the experimental procedure.

One possible explanation of the difference between the quantum yield in the decomposition of the liquid ethyl iodide and its hexane solution at the shorter wave length may lie in the higher amount of absorption per unit path length in pure ethyl iodide than in its solution in hexane. *If* free radicals are produced, a higher concentration of them in a small region of the reaction vessel (near the window through which the light enters the cell) will cause a slight lowering of the quantum yield. Since the absorption coefficient increases with decrease in wave length, this effect will cause a deviation of the type noted.

The result of approximately unity found by Iredale[2] appears to be accounted for by the presence of oxygen. In hexane solution, West and Paul[3] found a yield of two in the presence of excess oxygen. The author obtained a similar increase in the rate of the reaction for ethyl iodide when measurements[9] were carried out on a number of alkyl iodides in solutions of petroleum ether in polychromatic light with and without removing oxygen.

Furthermore, from the standpoint of the views of Franck and Rabinowitsch[10] concerning the mechanism of photochemical reactions in liquid systems, a quantum yield of unity would be unlikely unless one of the primary products of the decomposition were a molecule, or unless there were a reaction with the solvent. In other cases the quantum yield would be diminished due to the loss of energy by the activated molecule by a collision of the second kind with conversion under proper conditions of the electronic excitation energy into vibrational energy, or by primary recombination of the dissociated radicals and atoms (C_2H_5 and I in this case) to form the original molecules after collision with a third body before the products have reached a statistical distribution in the liquid. This mechanism would account for the increase in quantum yield in the ethyl iodide decomposition observed with decrease in wave length as the absorption of a quantum of greater excess energy would cause the parts to separate more violently, and thus have less chance of primary recombination. In these results the increase in quantum yield is of approximately the same degree as the increase in the energy content of the quanta absorbed. The quantum yield would also be affected by the intensity, temperature and concentration, but these effects, although probably existing, were too small to be realized experimentally.

The author wishes to acknowledge his thanks to Professor H. S. Harned, who supervised this investigation, and to Mr. E. J. Bowen, under whom the study of the photochemistry of the alkyl iodides was begun.

Summary

The quantum yield in the photodecomposition of liquid ethyl iodide at 20° was found to be

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(9) Thesis for B.Sc. degree, Oxford University, 1929.

(10) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

0.315 at 3130 Å., 0.38 at 2654 Å. and 0.41 at 2537 Å.

A technique using a commercial mercury vapor arc and a quartz monochromator was employed. As a cross-check on the apparatus quantum yield measurements were made on the decomposition of the uranium oxalate actinometer with results in good agreement with the standard results of Leighton and Forbes.

To overcome the difficulty of low intensities at the slit of the monochromator, a special optical procedure for measuring the small amounts of iodine produced was devised.

NEW HAVEN, CONN. RECEIVED JULY 28, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Heats of Solution and Heats of Reaction in Liquid Ammonia. III

BY CHARLES A. KRAUS AND FREDERIC C. SCHMIDT

In the earlier papers of this series,[1] a liquid ammonia calorimeter was described and results of measurements of heats of solution and heats of reaction were presented. In the present paper, we present further results by the same method in which both the apparatus and the procedure have been improved.

I. Experimental Details

To save space, only the changes in apparatus and procedure over those of the earlier papers will be described. These consist essentially of the following.

(1) The substance whose heat of solution or reaction was to be measured was sealed in a fragile, glass bulb which was crushed under the liquid when thermal equilibrium was established in the calorimeter.

(2) The spring, from which the stirrer was suspended, was fitted closely into the surrounding tube so as to provide sufficient friction to damp out the natural vibrations of the stirrer system.

(3) In the case of substances that dissolve with absorption of heat, ammonia was introduced into the calorimeter through a needle valve at such a rate as to maintain the temperature of the calorimeter as nearly constant as possible. An ammonium nitrate solution of ammonia, in a weighed bulb, served as source of ammonia. Several hundred cc. of ammonia vapor were withdrawn from the bulb into a chamber over mercury, the pressure being suitably adjusted by means of a leveling bulb, and the ammonia was allowed to pass into the calorimeter through the needle valve. Ammonia remaining in the chamber on completion of the experiment was reabsorbed in the ammonium nitrate tube, which was then weighed back.

(4) In order to prevent oscillations of pressure due to the pumping action of the glass-encased armature of the stirrer system, a by-pass was provided for the ammonia vapor between the two ends of the armature.

Temperatures were read by means of a copper–constantan thermocouple (0.0385 m. v./deg.) similar to that of Kraus and Prescott. Temperature readings were taken at intervals of one-half minute from the moment of breaking the bulb until temperature equilibrium was reëstablished. In the case of processes accompanied by the evolution of heat, the pressures were maintained constant according to the method described by Kraus and Prescott. The pressures were read on a mercury manometer by means of a cathetometer.

It is essential to remove liquid adhering to the walls of the calorimeter above the liquid surface, particularly in the case of endothermic processes. This was accomplished by attaching a 100-cc. flask to the system and allowing ammonia vapor to expand into this flask, thus reducing the pressure momentarily. The weight of ammonia in the calorimeter was corrected for the ammonia withdrawn in this process. The amount of ammonia vaporized was determined by titrating the solution in the absorption flask. All measurements were at the boiling point of ammonia, −33°.

Constants and Corrections.—The calorimeter constant was determined experimentally and found to be 7.73 cal./deg. at 25°. Allowing for the change of the specific heat of silica and glass, due to temperature, this reduces to 6.73 cal./deg. at the boiling point of liquid ammonia. Uncertainties in this value do not affect the precision of the results since the temperature changes involved are small. The radiation constant of the calorimeter was determined and found to be 0.481 cal./deg./min., which value agrees with that obtained by Kraus and Ridderhof for the same calorimeter. The pressure equivalent of the calorimeter was found to be 0.00608 g./cm. of mercury. This is the amount of ammonia required to change the pressure in the apparatus one cm. under conditions of use. The amount of ammonia employed in the calorimeter was 26.57 g., which was corrected for ammonia vaporized or condensed during a measurement.

The following constants of ammonia were employed: specific heat,[2] 1.067 cal./deg.; heat of vaporization,[3] 327.1 cal./g.

The time–temperature curves were plotted in all cases and the mean radiation temperature was obtained by dividing the area under the curve by the time.

II. Results

The data for solutions of sodium, potassium and acetamide are given in Table I, of lithium, sodium

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[1] Kraus and Ridderhof, THIS JOURNAL, **56**, 79 (1934); Kraus and Prescott, *ibid.*, **56**, 86 (1934).

[2] Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 313, issued Dec. 13, 1917; THIS JOURNAL, **40**, 1 (1918).

[3] Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 315, issued Dec. 21, 1917; THIS JOURNAL, **40**, 14 (1918).