had been added that it contained 20 to 30% of potassium carbonate at the end of the titration could be titrated with hypobromite, if the atmospheric oxygen was removed from the solution by passing carbon dioxide or nitrogen (free from oxygen) through it. The reaction liquid remains clear and becomes yellow in color after the addition of hypobromite. Yet the attainment of stable potentials is extremely slow and could not be accelerated by changes of temperature or any addition of catalyzers. It is, therefore, of advantage to obtain an idea as to the position of the maximum by a preliminary titration. For the proper titration almost the whole amount of necessary hypobromite is added at once and only the remaining few tenths cc. are used to accomplish the titration. On the whole the procedure is the same as has been described[9] for the much quicker and thereby much more satisfactory titration of cerous salts with ferricyanide. The inflection potential under the given conditions is 0.10 volt against the saturated calomel electrode.

Experiments.—20.00 cc. of *ca.* 0.1 M cerous chloride solution required for a titration 19.13 and 19.13 cc. of 0.1 M ferricyanide. The same quantity of cerous chloride required 19.20, 19.13, 19.04 and 19.09 cc. of the 0.05 M solution of hypobromite.

Summary

1. A new and simple titration of thallous salts with hypobromite has been described. It is very suitable for the standardization of hypobromite solutions by using thallous carbonate or sulfate as standard.

2. Also cerous salts can be titrated with hypobromite in 20 to 30% solution of potassium carbonate from which the atmospheric oxygen has been removed. However, the titration with ferricyanide is to be preferred.

PRAGUE, CZECHOSLOVAKIA RECEIVED JULY 26, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

Photochemical Investigations. II. The Photochemical Decomposition of Ethylene Iodide in Solutions of Carbon Tetrachloride[1]

BY ROBERT E. DERIGHT AND EDWIN O. WIIG

The thermal decomposition of ethylene iodide in solutions of carbon tetrachloride was found by Polissar[2] to consist of two parts, the ordinary and that catalyzed by iodine. Arnold and Kistiakowsky[3] found similar reactions to occur in the gas phase. The iodine photosensitized decomposition in solutions of carbon tetrachloride was found by Schumacher and Wiig[4] to be a chain reaction propagated by iodine atoms. It was thought that an investigation of the decomposition brought about by light absorbed by the ethylene iodide itself might give some insight into the mechanism of the decomposition and the manner in which the iodine is split off the ethylene iodide.

Experimental Details

Preparation and Purification of Materials.—The carbon tetrachloride was purified by the method used by Polissar.[2] Only the middle fraction from the last distillation was retained. The ethylene iodide was prepared from pure ethylene and iodine[5] and purified by recrystallization from dry ether. Attempts to prepare ethylene iodide by bubbling ethylene into concentrated solutions of iodine in carbon tetrachloride gave negligible yields. Uranyl sulfate and oxalic acid were purified in the manner described by Leighton and Forbes.[6]

The decomposition of ethylene iodide was followed by titrating the liberated iodine with $N/200$ solutions of sodium thiosulfate and of iodine. The relative strength of these solutions was checked frequently, the normality of the iodine being determined by titration against potassium permanganate solutions, the titer of which against sodium oxalate remained constant over long periods.

Apparatus and Procedure.—The reaction cell was cylindrically shaped with optically plane windows. The cell, made from fused quartz with fused seams, was 40 mm. in diameter and 35 mm. in length and was filled with 37 cc. of solution by means of a 12-mm. tube located near the rear window. In the experiments with the uranyl sulfate–oxalic acid solutions a stirrer was inserted through this tube. This cell was immersed in a thermostat, provided with a fused quartz window, in which the temperature of the water was regulated to ±0.03°.

The light source was a vertical Uviarc quartz mercury vapor lamp operated on 120 volt d. c. The lamp was rigidly mounted and the voltage carefully controlled so that the intensity was constant over long periods. A large crystalline quartz monochromator (f:1.9) with collimator and exit slits of 1.50 and 1.05 mm., respectively, was adjusted with the aid of a Beck fluorescent spectroscope to give the maximum intensity of light of the wave length desired. In all experiments, except those used to evaluate

---

[1] Presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Polissar, THIS JOURNAL, **52**, 956 (1930).

[3] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[4] Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

[5] Semenoff, Jahresberichte über die Fortschritte der Chemie, 1864, p. 483.

[6] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

the photosensitized reaction, light of λλ303 and 313 mμ was used. Photographs of this light overexposed thirty times showed only traces of longer wave lengths. The light intensity was measured by means of a linear thermopile of the Coblentz type. The thermopile was calibrated after each experiment against a standard lamp which had been compared with Radiation Standard C-67 calibrated by the Bureau of Standards. A resistance pattern of the type described by Leighton and Leighton[7] was used to decrease the deflections of the galvanometer. The solutions of ethylene iodide were prepared by adding weighed amounts to carbon tetrachloride contained in a volumetric flask. These solutions were prepared in artificial light to prevent decomposition and could be stored indefinitely in the dark. The cell was filled, allowed to come to the temperature of the thermostat, and then exposed to the light when the lamp had reached a steady state. At the end of an experiment the cell was cooled to room temperature and two 15-cc. samples pipetted into 100-cc. portions of distilled water. Enough sodium thiosulfate was added to give *ca.* 10 cc. excess. The flask was then shaken thoroughly and slowly back titrated with iodine solution.

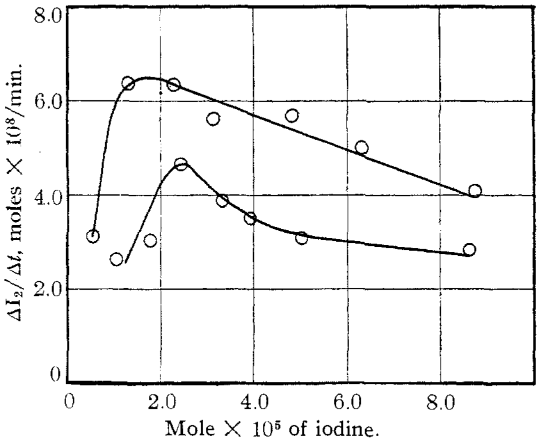

Fig. 1.—The rate of decomposition of ethylene iodide: upper curve, Table I; lower curve, Table II.

Results

Absorption Spectrum.—The absorption spectra of solutions of ethylene iodide in carbon tetrachloride were obtained by photographing the light from impregnated carbon arcs which had passed through the reaction cell filled with solutions containing 0.5, 1.0 and 2.0 g. (1.79, 3.57 and 7.14 × 10^{-3} mole) of ethylene iodide per 50 cc. of carbon tetrachloride. The photographs were made with a large Hilger spectrograph, employing a method described by O'Brien.[8] Absorption was found to begin at a wave length of 360 mμ. The 303 and 313 mμ Hg lines were strongly absorbed. The intensity of this light transmitted by various solutions of ethylene iodide and of iodine was measured with the thermopile. The iodine absorbed weakly in this region. These data were then used to obtain absorption coefficients which could be used to calculate the partition of the light at any time in an experiment.

Rate of Reaction.—A series of experiments was carried out for various lengths of time. The temperature of the thermostat in these experiments was 25°. The data are shown in Table I.

TABLE I

THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE FOR VARIOUS LENGTHS OF TIME

Molarity of ethylene iodide 0.0357

Time, min.	Total I_2 mole × 10^5	ΔI_2 mole × 10^5	$\frac{\Delta I_2 \times 10^8}{\Delta t}$	$\frac{\Sigma \Delta I_2 \times 10^8}{\Sigma \Delta t}$
180	0.57	0.57	3.15	3.15
300	1.33	.76	6.35	4.43
450	2.28	.95	6.33	5.07
600	3.12	.84	5.60	5.20
900	4.82	1.70	5.67	5.36
1200	6.32	1.50	5.00	5.27
1800	8.76	2.44	4.07	4.87

Two similar series of experiments were performed outside the thermostat. The light was first passed through 1 cm. of 0.0055 and 0.0147 molar solutions of iodine in carbon tetrachloride contained in a filter cell. These data are shown in Table II.

TABLE II

THE RATE OF DECOMPOSITION CAUSED BY LIGHT PASSED THROUGH AN IODINE FILTER

Molarity of ethylene iodide 0.0357

I_2 in filter cell, molar	Time, min.	Total I_2 moles × 10^5	ΔI_2 Moles × 10^5	$\frac{\Delta I_2 \times 10^8}{\Delta t}$
0.0357	390	1.03	1.03	2.64
	638	1.78	0.75	3.02
	780	2.44	.66	4.65
	1005	3.31	.87	3.87
	1175	3.91	.60	3.53
	1540	5.03	1.12	3.07
	2805	8.63	3.60	2.85
0.0147	540	1.17	1.17	2.16
	720	1.66	0.49	2.72
	1380	3.91	2.25	3.41

The data from Tables I and II are shown graphically in Fig. 1.

It is apparent that in every case, despite changes in intensity and passage of the light beam through solutions of iodine, the rate increased to a maximum and then fell slowly. These facts preclude the possibility that the increase was due to absorption by the iodine of light of longer wave

---

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

(8) O'Brien, *Bull. Am. Phys. Soc.*, Feb. 10 (1932).

length. The increase was much larger than the experimental error.

Effect of Concentration.—The effect of varying the initial concentrations of ethylene iodide, iodine and ethylene in experiments performed outside the thermostat is shown in the following tables.

TABLE III

THE EFFECT OF THE INITIAL CONCENTRATION OF ETHYLENE IODIDE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

$C_2H_4I_2$ molar	Time, min.	Total I_2 moles × 10^5	ΔI_2 moles × 10^5	$\frac{\Delta I_2 \times 10^3}{\Delta t}$
	300	1.24	1.24	4.13
0.0357	600	2.89	1.65	5.50
	945	5.50	2.61	7.57
	300	1.28	1.28	4.27
0.0714	603	2.86	1.58	5.21
	936	5.47	2.61	7.84
	300	1.23	1.23	4.10
0.143	660	3.14	1.91	5.31
	960	6.03	2.89	9.63

TABLE IV

THE EFFECT OF THE INITIAL CONCENTRATION OF IODINE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Time, min.	Mole × 10^5 iodine added initially	Total mole × 10^5 dec.	Mole × 10^7 dec. per min.
600	0	3.12	0.520
620	0.87	3.09	.498
600	2.72	2.75	.458
603	3.26	2.62	.436
600	4.17	2.56	.427
607	7.52	2.46	.405
600	10.78	2.40	.400

TABLE V

THE EFFECT OF ETHYLENE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Ethylene added	Time, min.	Total mole × 10^5 dec.	Mole × 10^7 dec. per min.
Yes	615	2.94	0.478
Yes	660	3.30	.500
No	600	2.89	.482

These data show that increasing the concentration of the ethylene iodide appears to increase the rate of decomposition slightly. Small initial concentrations of ethylene had no measurable effect on the rate while increasing amounts of iodine caused successively larger decreases in the rate of decomposition.

Effect of Intensity.—The light absorbed was varied thirty fold. These results are shown in Table VI. The rate of decomposition was approximately proportional to the energy absorbed throughout the range investigated.

TABLE VI

THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE FOR VARIOUS LIGHT INTENSITIES ABSORBED

Molarity of ethylene iodide, 0.0357

Reaction ratio	1.71	1.74	2.01	1.91	1.93
Intensity	1.83	1.83	1.91	1.91	1.91
Moles decompd.	1.03	1.87	1.35	2.23	2.36
Reaction ratio	2.32	2.50	2.10	28.7	28.5
Intensity ratio	2.38	2.38	2.38	28.4	28.4
Moles decompd.	1.17	1.66	3.91	0.44	0.43

Effect of Temperature.—Measurements of the rates of decomposition at 20 and 30° showed only very slight effects of temperature so that some of the preceding experiments, as already indicated, were not carried out in the thermostat. Raising the temperature to 50°, however, resulted in a measurable increase in the rate as shown in the following table.

TABLE VII

THE EFFECT OF TEMPERATURE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Temp., °C.	Time, min.	Total mole × 10^5 dec.	Mole × 10^7 dec. per min.
25	720	3.64	0.506
50	615	3.75	.610
50	618	3.71	.601

Using these data and additional data at 25° from Table I, the ratios of the times necessary for equal amounts of decomposition were determined. The decomposition which occurred in 615 minutes at 50° required 694 minutes at 25° or a ratio of 1.13. The corresponding temperature coefficient for 10° is 1.05. It is to be noted that the thermal reaction which is responsible for this temperature coefficient accounts for only a part of the total reaction.

Evaluation of the Photosensitized Reaction.—Since Schumacher and Wiig[4] found the iodine photosensitized decomposition of ethylene iodide to be a chain reaction and since iodine, a product of the photodecomposition, absorbs slightly light of the wave lengths used here, experiments were carried out to determine whether the acceleration observed could be accounted for by a sensitized reaction. The yield at λλ436 and 465 mμ, where ethylene iodide does not absorb and iodine absorbs strongly, was determined under our experimental conditions. Assuming the same quantum efficiency at the shorter wave lengths and calculating the partition of light of these wave lengths between iodine and ethylene iodide, the maximum possible effect of the photosensitized reaction was found to be less than 2–3% of the observed increase in rate at any time.

Determination of the Quantum Yield.—The quantum measurements were made outside the thermostat but the variation of room temperature was less than ±1°. The lamp voltage was carefully controlled and the intensity measured frequently as described previously. The experiments with the uranyl sulfate–oxalic acid actinometer were carried out under identical conditions. Assuming a quantum yield[6] of 0.561 at $\lambda 313$ mμ the following transmission factors for the rear window of the cell and optical system were obtained: 1.480, 1.481, 1.490 and 1.511, or an average of 1.490. The results of the quantum measurements are given in Table VIII.

TABLE VIII

THE DETERMINATION OF THE QUANTUM YIELD FOR THE DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Time, min.	Mole $\times 10^5$ dec.	Molecules $\times 10^{19}$ dec.	Quanta $\times 10^{19}$ absorbed	Quantum yield
600	1.29	0.78	1.10	0.71
600	1.35	.82	1.11	.74
900	2.00	1.21	1.62	.75
900	2.23	1.35	1.67	.81
960	2.36	1.43	1.77	.81

Discussion

The mechanism of the photochemical decomposition of ethylene iodide is probably given by the equations

$$C_2H_4I_2 + h\nu \longrightarrow C_2H_4I + I \qquad (1)$$
$$C_2H_4I_2 + I \rightleftharpoons C_2H_4I + I_2 \qquad (2) \text{ and } (3)$$
$$C_2H_4I \rightleftharpoons C_2H_4 + I \qquad (4) \text{ and } (5)$$
$$I + I \longrightarrow I_2 \qquad (6)$$

Light of the wave lengths used supplies more than enough energy to break the carbon–iodine bond so that reaction (1) is possible. The remaining equations have been suggested previously in connection with the formation,[9] thermal decomposition[3,9] and the photosensitized decomposition[4] of ethylene iodide. Some calculations by Narayanmurti[10] based on the mechanism for the last-mentioned reaction indicate that the theoretical and observed rates are in excellent agreement. Reactions analogous to (2) through (5) have been suggested in connection with the photosensitized decomposition of dibromotetrachloroethane.[11] With reasonable simplifying assumptions these reactions lead to the rate equation

$$-d(C_2H_4I_2)/dt = I_{\text{abs.}}/[1 + (k_3/k_4)\,(I_2)]$$

This is in agreement with the experimental results except that it does not account for the increase in the decomposition rate observed when only small amounts of iodine have been formed. The initial increase in rate might be due either to a decrease in the concentration of an inhibitor or to some unknown reaction involving perhaps C_2H_4I or I_3. The carbon tetrachloride was carefully purified but air was not removed or excluded from the reaction mixture. That oxygen may have an inhibiting effect has been found in somewhat similar reactions.[12] The amount of iodine formed at the maximum (Fig. 1) is less than the solubility of oxygen in carbon tetrachloride, so that inhibition by oxygen is a possibility. Unfortunately no experiments were performed to test this.

In the early stages of an experiment reaction (3) would be of no importance because of the low iodine molecule concentration. As the concentration of iodine builds up, however, reaction (3) will predominate over (2), since their energies of activation are 1.8 and 11.8 cal., respectively.[13] This explains the retarding effect of iodine.

The quantum yield experiments give an average value of 0.76 but the measurements include the period in which the reaction rate is rising. If the yield is calculated for the period of six-hundred to nine-hundred minutes in Table VIII, a value of 0.86 is obtained. The light intensities employed in the experiments in Table I may be estimated quite readily. The quantum yields corresponding to those energies are 0.54 at the beginning, 1.10 at the maximum and 0.70 at the end of the measurements. The value to be assigned to the quantum efficiency of the primary process depends upon the interpretation of the initial increase in reaction rate.

The value of the quantum yield for the primary photo-process is of interest in connection with theories of photochemical reactions in solution. In a recent paper, Franck and Rabinowitsch[14] discuss the photochemistry of reactions in solution. They compare reactions in solution with the bet-

---

[9] Shumacher, THIS JOURNAL, **32**, 3132 (1930).

[10] Narayanmurti, *J. Ind. Chem. Soc.*, **12**, 173 (1935).

[11] Carrico and Dickinson, THIS JOURNAL, **57**, 1343 (1935).

[12] Dickinson and Leermakers, *ibid.*, **54**, 3852 (1932); Chapman, *ibid.*, **56**, 818 (1934); Bauer and Daniels, *ibid.*, **56**, 2014 (1934).

[13] Sherman and Sun, *ibid.*, **56**, 1096 (1934).

[14] Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 129 (1934).

ter known gas reactions and point out three effects which are of importance in the former. (1) There is a certain time lag between the absorption of light and the decomposition of the molecule. The large number of collisions with solvent molecules makes deactivation possible during this interval. (2) Similarly, since all collisions of reaction products would be triple collisions, secondary recombination would be enhanced. (3) If the decomposition yields atoms or radicals these would lose their excess kinetic energy by collision before going much more than the length of a molecular diameter and if they were still close together they would undergo primary recombination. All of these effects would decrease the quantum yield but the third would be of greatest importance. Hence, they conclude that for all reactions involving atoms or radicals the primary quantum yield should be definitely less than one. Furthermore, light of shorter wave length should cause the decomposition products to leave with greater kinetic energy; they should travel further before losing their kinetic energy and primary recombination would be decreased. Thus light of shorter wave length should produce a greater quantum yield. The photodecomposition of ethylene iodide would seem to proceed by atoms and radicals. If the low yield at the beginning of an experiment is not due to inhibition, then the present results would tend to substantiate the theory of Franck and Rabinowitsch.

Without citing any evidence, Emschwiller[15] states that when solutions of ethylene iodide are exposed to polychromatic ultraviolet light the primary decomposition products are ethylene and iodine. Such a simple mechanism cannot account for the retardation of the reaction rate observed in our experiments, since union of ethylene and iodine proceeds too slowly at room temperatures. The mechanism suggested here follows from related studies on the decomposition of ethylene iodide. With polychromatic light the ethylene iodide photodecomposition is quite likely complicated by the iodine photosensitized decomposition, which would increase the difficulty of interpreting the results.

The study of the photodecomposition of the halogen addition products of ethylene is being continued in this Laboratory. It is also planned to extend the investigations to the gaseous reactions.

Summary

The apparent quantum yield for the photodecomposition of ethylene iodide in carbon tetrachloride solutions by light of wave lengths 303 and 313 mμ was found to be 0.76. This includes both the photo- and any subsequent thermal reactions. A mechanism involving a primary dissociation into C_2H_4I and atomic iodine has been suggested. The rate equation based on this mechanism is in agreement with the data obtained. A further study of this reaction should be of interest in connection with the Franck and Rabinowitsch theory of photochemical reactions in solution.

ROCHESTER, NEW YORK RECEIVED AUGUST 12, 1935

---

[15] Emschwiller, *Compt. rend.*, **199**, 854 (1934).

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Paraffins with Aromatic Hydrocarbons (Destructive Alkylation)[1]

BY ARISTID V. GROSSE AND V. N. IPATIEFF

We have recently described the catalytic reaction of saturated hydrocarbons with olefins.[2] We have also found that paraffins can react with aromatic hydrocarbons in the presence of catalysts under mild conditions. The reaction consists in the splitting of the paraffin into a lower molecular weight paraffin and an olefin "in statu nascendi," which immediately alkylates the aromatic hydrocarbon. The general reaction proceeds according to the equation

$$\underset{\text{Paraffin}}{C_{(m+n)}H_{z(m+n)+2}} + \underset{\text{Aromatic hydrocarbon}}{C_xH_{2x-6}} \xrightarrow{\text{Catalyst}} \underset{\text{Lower molecular paraffin}}{C_nH_{2n+2}} + \underset{\text{Alkyl-aromatic hydrocarbon}}{C_xH_{2x-5}\cdot C_mH_{2m+}}$$

---

[1] Presented before the Organic Division of the 90th meeting of the American Chemical Society at San Francisco on August 21, 1935.

[2] V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1616 (1935).