[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 491]

The Effect of Wave Length on the Iodine-Sensitized Decomposition of Ethylene Iodide in Carbon Tetrachloride Solution

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The present work was undertaken primarily in order to obtain a partial answer to the question as to what extent iodine atoms are produced by the absorption of radiation by iodine in carbon tetrachloride solution when the radiation is of longer wave length than that of the band convergence of gaseous iodine. The absorption spectrum of gaseous iodine in the visible is continuous for wave lengths below 4989 Å. and shows many fine lines at longer wave lengths. In a well-known paper, Franck[1] has considered absorption in the continuous region to produce dissociation into a normal $({}^2P_{3/2})$ and metastable $({}^2P_{1/2})$ iodine atom, and absorption in the discontinuous to produce electronically excited molecules. These views, aside from their agreement with the dissociation energy of iodine, have received support from experiments[2] showing the disappearance of fluorescence when the wave length of the exciting light is decreased into the continuous; and further support from experiments[3] showing the presence of atomic absorption lines in strongly illuminated iodine vapor. Atomic absorption experiments in the presence of argon[4] showed iodine-atom formation even when the gas was illuminated with wave lengths longer than 5100 Å.; apparently the excited iodine molecules were dissociated by collisions with argon. For iodine in carbon tetrachloride solution, similar information does not exist, but use has been made of photochemical methods.

The decomposition of ethylene iodide in carbon tetrachloride solution has been found to be sensitized to visible radiation by iodine[5] and a chain mechanism has been proposed which is essentially a catalysis of the decomposition by iodine atoms. For this solution reaction, relative values of quantum yields have been measured[6] using both radiation corresponding to the continuum of the gas and radiation corresponding to the region of discontinuous absorption. For the wave length 4358 Å. the quantum yields measured were five to six times as great as those for the wave length 5461 or for the lines at 5770 and 5790. From these facts it was concluded that the excited iodine molecules produced by the absorption of the green or yellow lines, under the conditions of the experiments usually gave up their energy without dissociating.

This conclusion, however, has seemed to us not justified. The reaction in question is one whose rate is proportional to the square root of the intensity of illumination.[5] With a reaction of this type if two experiments were to be made with different wave lengths but with the same concentrations, the same intensities (using einsteins), and substantially complete absorption in each case, then even though the two wave lengths were equally effective in dissociating the absorber, the rates of reaction could be different in the two experiments if the absorption coefficients for the two wave lengths were different; indeed, with properly stirred solutions, the rates should be inversely proportional to the square roots of the absorption coefficients.[7]

The available measurements[8] of the absorption coefficient of iodine in carbon tetrachloride solution show much higher values in the green than in the blue so that, qualitatively, smaller quantum yields in the green than in the blue are to be expected. Unfortunately, however, the published data concerning the quantum yields are insufficiently detailed to permit satisfactory recalculation. We have accordingly attempted to measure the dependence of this reaction rate on the wave length under appropriate conditions, and have measured the absorption coefficients at the temperatures of interest.

Materials.—The carbon tetrachloride was purified by the treatment described by Polissar.[9] The ethylene iodide was prepared as described by Mooney and Ludlam,[10] and contained a small amount of free iodine. A weighed amount was dissolved in a weighed amount of the purified carbon tetrachloride. In most of the experiments the iodine concentration was increased by adding iodine which

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(1) J. Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

(2) Dymond, *Z. Physik*, **34**, 553 (1925).

(3) L. A. Turner and E. W. Samson, *Phys. Rev.*, **37**, 1023 (1931).

(4) L. A. Turner and E. W. Samson, *ibid.*, **37**, 1684 (1931).

(5) Schumacher and Wiig, *Z. physik. Chem.*, **B11**, 45 (1930).

(6) Schumacher and Stieger, *ibid.*, **B12**, 348 (1931).

(7) See A. J. Allmand, *J. Chem. Soc.*, 1557 (1929).

(8) Gillam and Morton, *Proc. Roy. Soc.* (London), **A124**, 604 (1929); Getman, THIS JOURNAL, **50**, 2883 (1928).

(9) Polissar, *ibid.*, **52**, 956 (1930).

(10) Mooney and Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

had been resublimed from potassium iodide. The free iodine was determined by titration with thiosulfate freshly diluted to 0.00544 *N* and the ethylene iodide concentration calculated.

Apparatus.—A diagram of the experimental arrangements is shown in Fig. 1. The reaction vessel was a Pyrex cylinder 4.0 cm. in diameter and 2.1 cm. in internal length between the plane ends; an accessory bulb provided a free gas space of 25 cc. Since uniformity of concentration of the reactants throughout the solution was desired, the cell was provided with a magnetically operated glass spiral plunger which kept in operation throughout the illumination. The volume of stirrer glass in the light beam was 0.15 cc.; the error in rate caused by its presence is estimated to be 0.8% at most and usually much less. In each experiment the cell was filled with 28.0 cc. of solution (measured at room temperature) and sealed off. It was found imperative to avoid decomposition of carbon tetrachloride during the sealing-off process; this was accomplished, as shown by blank experiments, by sweeping any liquid as well as vapor from the side tube with a stream of air and sealing quickly before more vapor could diffuse into the side tube.

The thermostat was so constructed that the reaction cell could be placed in a small closed air space which was provided with double windows and surrounded by the vapor of boiling liquid except at the ends and top. The reaction cell was heated in the dark to approximately the right temperature; it was then transferred to the thermostat (a dim red room light was used) and was left for twenty minutes before illumination. During illumination stray light was avoided by the use of a cylindrical shield at the window near A and by closing with a black shutter the window near B. After illumination the cell was rapidly cooled to room temperature in the dark. The titration occurred in light; but since the temperature coefficient of the reaction is fairly large (1.6 for 10°) little reaction resulted here.

The light source was a quartz mercury arc; the source was defined by a hole 1.1 cm. in diameter. The light was filtered through 1 cm. of 10% $CuCl_2 \cdot 2H_2O$ solution to remove infra-red and red, and through suitable Corning glass filters to isolate the desired mercury lines. All filter combinations were examined spectroscopically. With the filter for 4358, only this line and its immediate weak neighbors were appreciably transmitted; in particular, the line 4916 and the lines near 4050 and shorter were absent from a plate showing reversal of 4358. The filter for 5461 gave a radiation contaminated by less than 1% of the yellow lines. That for 5770 and 5790 gave a radiation contaminated by less than 0.5% of the green line.

With the aid of the lenses and the 3.5-cm. diaphragm at A, the beam was adjusted so that all of it passed through the reaction solution and remained substantially constant in diameter in so doing. The lens at B threw on the face of a Moll microthermopile an image of the diaphragm A. The thermopile elements were situated at the center of this image whose diameter was 31 mm. The thermostat was mounted on tracks and could be removed entirely from the light beam.

The reaction was followed by measuring the iodine concentration. Before and after illumination, 5 cc. of the reaction mixture at room temperature was pipetted into slightly acidified potassium iodide solution and titrated with thiosulfate.

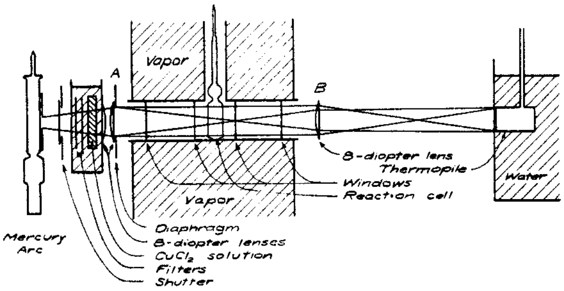

Fig. 1.—Vapor-thermostat and optical arrangements. The thermostat was removable from the light beam for measurement of incident intensity. The window near B was closed by a shutter (not shown) during reaction.

Absorption Coefficients.—The absorption coefficients of iodine solutions at various wave lengths were determined by measuring: (1) the transmission τ_0 of the thermostat with the reaction cell in place and containing only carbon tetrachloride; (2) the transmission τ of the thermostat with a known iodine solution in the cell. The coefficients α' were then calculated from the equation

$$\alpha' = \frac{1}{(I_2)l} \log_e \frac{\tau_0}{\tau}$$

where (I_2) is the concentration of iodine in moles per kilogram of solution, and l is the inside thickness of the cell (2.1 cm.). These and the coefficients α, calculated with concentrations in moles per cc., are given in Table I.[11] Although these absorption coefficients were determined in pure carbon tetrachloride solution, the small effect of non-polar solvents on the molal absorption coefficients of the halogens makes it unlikely that the values are unsuitable for use in solutions containing mol fractions of ethylene iodide of 0.01 or less.

Treatment of Reaction Rate Data.—From the work of Schumacher and Wiig,[5] we have taken the local rate of photochemical reaction in any illuminated element of the solution to be given by

$$d(I_2)/dt = k(I_{abs.})^{1/2}\ (C_2H_4I_2) \qquad (1)$$

where $(I_{abs.})$ is the local rate of absorption of radiation in einsteins $\times$ cc.$^{-1}$ $\times$ sec.$^{-1}$. This assumption receives *a posteriori* justification in the present work. The average rate in a solution of

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[11] The thermal expansion of the solution was assumed equal to that for pure carbon tetrachloride. The density of carbon tetrachloride was taken as 1.59 g./cc. at 22°; 1.48 at 76.6°; and 1.45 at 99°.

TABLE I

ABSORPTION COEFFICIENTS OF IODINE IN CARBON TETRACHLORIDE SOLUTION

	4358 Å.		5461 Å.		5770 and 5790 Å.	
T., °C.	(I_2) (moles/kg.) $\times 10^4$	α'	(I_2) (moles/kg.) $\times 10^4$	α'	(I_2) (moles/kg.) $\times 10^4$	α'
22	8.94	242	0.70	2620	3.05	1050
	12.00	239	1.50	2520	4.27	1040
	15.45	248	2.56	2570	7.48	1010
	16.45	240	3.00	2510		
	Mean α'	242	Mean α'	2560	Mean α'	1030
	Mean α	1.52×10^5	Mean α	1.60×10^6	Mean α	6.49×10^5
76.6	11.90	250	1.08	2450	3.05	1170
	17.00	248	1.54	2430	4.27	1170
	23.75	247	2.15	2380	7.48	1160
	Mean α'	248	Mean α'	2420	Mean α'	1170
	Mean α	1.68×10^5	Mean α	1.64×10^6	Mean α	7.32×10^5
99	7.72	247	0.70	2420		
	9.84	250	0.90	2460		
	10.45	245	1.40	2412		
	19.85	248	1.80	2420		
	Mean α'	247	Mean α'	2430		
	Mean α	1.70×10^5	Mean α	1.68×10^6		

volume v and thickness l illuminated by a parallel beam of cross-section a, is then given by

$$\frac{d(I_2)}{dt} = \frac{2kI_0^{1/2}(C_2H_4I_2)\ a}{\alpha^{1/2}(I_2)^{1/2}\ v}\,(1 - \sqrt{\tau}) \qquad (2)$$

Here I_0 is the intensity of radiation incident on the solution in einsteins × cm.$^{-2}$ × sec.$^{-1}$; and τ is the transmission $e^{-\alpha(I_2)l}$ of the solution. In obtaining (2) it is assumed that: (a) the concentrations of the reactants are maintained uniform throughout the solution; (b) Beer's law applies; (c) the rate in one element of solution is unaffected by the intensity prevailing in neighboring elements.

With constant incident intensity, values of the specific rate constant k may be obtained from equation (2)

$$k = \frac{\alpha^{1/2}\ v}{2I_0^{1/2}\ a\,\Delta t}\int_{c_1}^{c_2}\frac{(I_2)^{1/2}\ d(I_2)}{(1 - \sqrt{\tau})\ (C_2H_4I_2)} \qquad (3)$$

where Δt is the time of illumination and c_1 and c_2 are the values of (I_2) just before and after illumination. We have calculated the specific rate constant in arbitrary units k_a using the equation

$$k_a = \frac{1}{\lambda^{1/2}\ G^{1/2}\alpha'\Delta t}\int_{y_1}^{y_2}\frac{y^{1/2}\ dy}{(1 - e^{-y/2})\left(S - \frac{y}{\alpha' l}\right)} \qquad (4)$$

In equation (4), $G^{1/2}$ is the mean of the square roots of the corrected galvanometer deflections, λ is the wave length (used to obtain proportionality to einsteins), y is equal to $\alpha'(I_2)l$ and S is the total concentration of iodine (free and combined). Since the value of the integrand may be calculated for any stated value of y, we have approximated the integral using Simpson's rule;[12] this is convenient since the integrand often remains fairly constant over a considerable range of values of y.

TABLE II

SPECIFIC RATE-CONSTANT DETERMINATIONS

$(C_2H_4I_2)_0$ (moles/kg.) $\times 10^3$	$(I_2)_0$ (moles/kg.) $\times 10^3$	$(I_2)_f$ (moles/kg.) $\times 10^3$	$G^{1/2}$ cm$^{1/2}$	Δt min.	τ_0	τ_f	$k_a \times 10^6$
Wave length 4358 Å., temperature 76.6°							
33.1	0.81	1.59	2.28	225.5	0.66	0.44	4.37
66.2	1.02	2.15	1.31	270.5	.59	.33	4.12
66.2	1.02	3.25	2.54	245.5	.59	.18	3.82
66.2	1.08	1.97	2.51	116.3	.57	.36	4.04
66.2	1.08	2.19	2.66	241.0	.57	.32	2.27[a]
66.2	1.10	2.28	2.75	138.5	.57	.30	4.01
58.7	2.48	3.09	3.19	61.0	.27	.20	4.01
58.7	2.50	3.82	3.11	128.0	.27	.14	4.16
							Mean 4.08
Wave length 5461 Å., temperature 76.6°							
58.7	0.357	1.38	5.29	60.0	0.16	0.0_392	3.75[b]
58.7	.360	1.63	4.50	90.0	.16	$.0_326$	3.78
58.7	.258	1.72	3.98	116.5	.27	$.0_316$	3.87
58.7	.357	1.78	5.19	90.0	.16	$.0_312$	3.78
58.7	.258	1.94	4.47	125.5	.27	$.0_454$	3.78
33.1	.81	2.09	3.42	252.0	.016	$.0_324$	3.66
66.2	1.02	2.65	2.26	257.5	$.0_256$	$.0_515$	3.73
66.2	1.02	2.82	3.95	154.0	$.0_256$	$.0_66$	4.04
							Mean 3.80
Wave length 5770 and 5790 Å, temperature 76.6°							
60.8	0.440	1.40	3.12	91.5	0.34	0.033	3.48
60.8	.445	1.65	2.66	132.5	.34	.018	3.55
60.8	.445	2.01	2.73	183.5	.34	.0074	3.29
66.2	.870	2.73	2.90	186.0	.12	.00125	3.49
66.2	1.49	3.71	3.54	181.5	.026	$.0_311$	3.88
							Mean 3.54
Wave length 4358 Å., temperature 99°							
58.7	0.068	0.89	2.58	60.0	0.97	0.67	14.6
58.7	1.72	3.33	2.70	60.0	.41	.18	13.2
58.7	1.72	3.56	3.09	60.0	.41	.16	13.2
							Mean 13.7
Wave length 5461 Å., temperature 99°							
58.7	0.068	1.25	4.36	30.0	0.71	0.0018	10.9
58.7	.068	1.77	2.77	30.0	.71	$.0_312$	11.9
58.7	.068	1.49	3.70	40.0	.71	$.0_353$	10.7
58.7	.428	1.99	3.88	45.0	.12	$.0_442$	11.6
58.7	.428	2.15	4.36	45.0	.12	$.0_419$	11.6
							Mean 11.3

[a] Not included in the mean. [b] Stirrer not operated.

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[12] See, for example, E. B. Wilson, "Advanced Calculus," 1912, Ginn and Co., Boston, p. 77.

The results of the measurements and calculations of k_a are given in Table II. The measurements at 76.6° are more extensive than those at 99° and are more reliable because of smaller uncertainty arising from thermal reaction. Since the mechanisms of the thermal and photochemical reactions are probably not independent, it is doubtful whether the results would be improved by subtraction of the thermal from the combined rates; at 76.6° thermal reaction would amount to 0.5 to 3% of the combined reaction in the present experiments, and at 99° from 3 to 10%. No correction for thermal contribution to the reaction during illumination has been applied; but for the experiments at 99° the initial iodine concentrations have been corrected (by separate blank experiments) for thermal reaction previous to the beginning of illumination. At the close of illumination the solution was quickly cooled. The results show that at either temperature there is only a small decrease of k_a with increasing wave length.

Discussion.—It is possible to draw conclusions from the comparative constancy of k_a with wave length without making detailed representations as to the complete mechanism of the reaction. This may be especially important since the possible effect of oxygen has not been investigated, and air was present in these experiments. Since it is probable that blue light dissociates iodine molecules, and since the empirical rate expression is of the same form for all visible wave lengths investigated, we may assume simply that light brings about reaction through dissociation of iodine molecules, either directly or on collision subsequent to absorption; and, further, that at a point in a solution of given composition the local rate of reaction is dependent only on the rate at which iodine atoms are produced by light regardless of the wave length that produces them. This rate of production of iodine atoms by light is $2\beta(I_{\text{abs.}})$ where β is the fraction of the absorbed quanta which result in dissociation (and may depend on λ). From the empirical result $\mathrm{d}(\mathrm{I}_2)/\mathrm{d}t = k(I_{\text{abs.}})^{1/2} f(c\ldots)$, where $f(c\ldots)$ depends only on the composition but where k may depend on the wave length, it may readily be shown that $\mathrm{d}(I_2)/\mathrm{d}t = \beta^{1/2}(I_{\text{abs.}})^{1/2}k'f(c\ldots)$ where k' is independent of the wave length.

For two different wave lengths it is evident that $\beta_1/\beta_2 = k_1^2/k_2^2$. The data of Table II give the result that at 76.6°, $\beta_{5461}/\beta_{4358} = 0.87$ and $\beta_{5780}/\beta_{4358} = 0.75$. On the assumptions made it appears, then, that wave lengths corresponding to discontinuous absorption in gaseous iodine are little less effective than those corresponding to continuous absorption in producing dissociation in carbon tetrachloride solution.

Absolute Values of the Rate Constants.—Although not essential to the examination of wave length effect, we have made an approximate determination of the absolute value of the k of equation 1 using equation 3. For this purpose, the units employed throughout were moles, einsteins, centimeters and seconds. The determination involved: (a) calibration of the thermopile against a Bureau of Standards carbon filament lamp; (b) corrections for reflection at various windows (multiple reflections were ignored); (c) examination, with the aid of the thermopile, of the distribution of intensity across the beam at the position of the cell and at the diaphragm A; (d) determination of the relative galvanometer deflections with the thermopile in the position shown and with it at the center of A. From this calibration it was found that the effective value of $aI_0^{1/2}$ in ergs$^{1/2}$ × cm. × sec.$^{-1/2}$ was given by 87.1 $G^{1/2}$. These values of k, expressed in einsteins$^{-1/2}$ × cm.$^{3/2}$ × sec.$^{-1/2}$ are: at 76.6°, 0.42 for 4358, 0.39 for 5461, 0.37 for 5780; and at 99°, 1.4 for 4358, and 1.2 for 5461 Å. The radiation measurements and corrections should be good to 20% or better.

Quantum yields, calculated as moles of iodine formed per quantum absorbed in the whole experiment, are, of course, quite variable. The first two experiments of Table II, for example, give the values 2.9 and 8.8, respectively, while the twelfth gives 0.96.

Summary

The dependence on wave length of the rate of iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution has been reexamined. In view of the lack of proportionality between rate and intensity, absorption coefficients have been measured and special attention has been given to the distribution of intensity through the solutions. The wave lengths used were 4358, 5461, and 5770 and 5790 Å.; for these three radiations the relative values of the rate-constant at 76.6° have been found to be 1:0.931:0.867. The results indicate that light corresponding to continuous absorption in gaseous iodine is slightly

more effective in bringing about dissociation of iodine in the solution than light corresponding to the discontinuous absorption, but that the difference is not large. Absolute values of the empirical specific rate constant have been measured.

PASADENA, CALIFORNIA RECEIVED AUGUST 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Determination of the Zirconium–Hafnium Ratio[1]

BY GRANT WERNIMONT[2] AND THOMAS DE VRIES

The optical rotation of solutions containing potassium tartrate along with various amounts of zirconium or hafnium oxychloride has been studied by de Boer and Emmens.[3] They found that the effect of zirconium was somewhat less than that of hafnium and suggested that the polariscope might be used for determining zirconium–hafnium ratios. This paper describes such a procedure in which the fluorides were used.

Experimental

The rotation measurements were made with a Schmidt and Haensch No. 52b, Lippich type polarimeter using sodium D light from a monochromator.

Three samples of zirconium oxide were prepared (one by the method of Drophy and Davy[4] to remove completely small amounts of hafnium) from C. P. zirconium salts which were shown to contain no iron or titanium.

Measurement of Rotation Change.—To measure the rotation change, zirconium oxide samples were weighed into platinum crucibles, dissolved in 5 ml. of 50% hydrofluoric acid, evaporated to dryness on the steam-bath and the residues taken up with a little water. The solutions were transferred to volumetric flasks, 10 ml. of approximately 20% tartaric acid solution (about 14 millimoles) and 10 ml. of six normal potassium hydroxide were added along with sufficient water to make 50 ml. of solution. Blank solutions containing no zirconium were also prepared.

The rotations of the solutions and blank were determined in 2-dm. tubes, the differences being taken as the rotation change. When the weight of zirconium oxide was plotted against rotation change, a straight line resulted (Fig. 1). The equation for this is $\Delta\alpha_{\mathrm{Zr}} = 5.37W_{\mathrm{Zr}}$ where W_{Zr} is the grams of ZrO_2 and $\Delta\alpha_{\mathrm{Zr}}$ is the corresponding rotation change in degrees. Twenty-six points ranging from 0.1017 to 1.002 g. of oxide were used to fit the equation. The maximum deviation of calculated rotation change from the observed value was 0.09° and the average of all deviations was 0.04°.

When less than 0.3 g. of ZrO_2 was present in solution, these results are in good agreement with those of de Boer and Emmens but when more than this amount of zirconium was present, the values found by de Boer and Emmens were less than those found in this investigation.

As the molecular ratio of tartrate to zirconium approached or became greater than two to one, the observed values were less than the calculated values. Therefore care must be taken that the ratio of tartrate to zirconium (and hafnium) is greater than two to one in the final solutions.

Hafnium salts, free from zirconium, were not available in this Laboratory; hence it was necessary to use the values of de Boer and Emmens for the rotation of hafnium tartrate solutions. Their results give a straight line (Fig. 1) and were fitted to the equation $\Delta\alpha_{\mathrm{Hf}} = 1.16W_{\mathrm{Hf}}$.

Calculation of Zirconium–Hafnium Ratios.—A convenient method of evaluating the ratio of hafnium to zirconium was devised by using the linear equations to derive a general expression for the relation between mole ratio, rotation change and weight of zirconium–hafnium oxide present in solution. The following equation was obtained

$$\frac{N_{\mathrm{Hf}}}{N_{\mathrm{Zr}}} = 0.5851 \times \frac{5.37W - \Delta\alpha}{\Delta\alpha - 1.16W}$$

where W is the grams of mixed oxides present in 50 ml. of test solution and $\Delta\alpha$ is the corresponding rotation change measured in a 2-dm. tube using sodium D light.

Preparation of Zirconium–Hafnium Oxide Samples for Analysis.—Two oxide samples were prepared from two fractions of a series of

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[1] Abstracted from a thesis submitted by Grant Wernimont to the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] Present address, Eastman Kodak Company, Rochester, N. Y.

[3] De Boer and Emmens, *Rec. trav. chim.*, **49**, 955 (1930).

[4] Drophy and Davy, *Phys. Rev.*, **25**, 882 (1925).