TABLE IV

"SPECIFIC ROTATIONS," Δ/W, OF THE RARE EARTH SOLUTIONS

Praseodymium Chloride ($PrCl_3$)

Molality	$\Delta/W \times 10^6$		
	5086 Å.	5461 Å.	6438 Å.
3.00	−6.02	−5.01	−3.51
2.50	−6.01	−5.01	−3.50
2.00	−6.00	−4.89	−3.48
1.50	−6.01	−5.02	−3.47
1.00	−5.96	−5.04	−3.46
0.50	−5.95	−5.02	−3.44
0.25	−6.09	−4.89	−3.53
Av.	−6.00	−4.98	−3.48

Samarium Chloride ($SmCl_3$)

Molality	$\Delta/W \times 10^5$			
	5086 Å.	5461 Å.	5893 Å.	6438 Å.
3.2644	1.17	0.97	0.84	0.72
3.0	1.21	1.01	.86	.74
2.50	1.22	1.04	.87	.78
2.0	1.26	1.07	.92	.78
1.50	1.30	1.11	.93	.80
1.003	1.30	1.19	.94	.92
0.50	1.57	1.22	.95	..
0.25	0.80	1.21	..	..
Av.	1.29	1.10	.90	.79

Europium Chloride ($EuCl_3$)

Molality	$\Delta/W \times 10^5$				
	4811 Å.	5086 Å.	5461 Å.	5893 Å.	6438 Å.
2.847	0.86	0.78	0.69	0.60	0.56
2.50	.91	.85	.73	.65	.61
2.00	1.00	.90	.78	.71	.65
1.50	1.03	.94	.80	.72	.69
1.0	1.14	.95	.85	.75	.72
0.5	1.05	.98	.90	.80	.54
0.25	0.92	.99	.84	.81	..
Av.	.99	.91	.80	.72	.62

An interesting anomaly appears in the case of the results for europium chloride. Samarium is definitely less paramagnetic than cerium or praseodymium, as shown by the fact that the Bohr magneton number is about 3.6 for praseodymium and 2.5 for cerium, whereas for samarium it is only about 1.5,[11] and the decidedly less magnetic optical rotatory power of samarium might be explained on this basis. In the case of europium, however, the magneton number given by Van Vleck[11] and since recalculated by Schmidt[12] is about 3.4. Therefore, one might expect that europium would have magnetic optical rotatory powers of the order of those of cerium and praseodymium rather than of the order of magnitude of samarium which it does have. We are not able to offer an explanation of this apparent anomaly.

Summary

The magnetic rotations of the aqueous solutions of praseodymium, samarium, and europium chlorides have been measured at 25° for the wave lengths λ4810.5, λ5085.8, λ5460.7, λ5893, λ6362.4, and λ6438.47 Å. except in those cases where absorption interfered.

The refractive index of these aqueous solutions has been reported at 25°.

The Verdet constants have been calculated, those for samarium and europium solutions being positive and those for praseodymium solutions being negative when referred to water.

The specific and molecular rotations have been calculated and the variation of these properties with concentration noted and discussed.

An interesting anomaly has been observed in the comparison of the Verdet constants with the known magnetic moments of these ions.

[11] These data have been taken from Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford, 1932, p. 243.

[12] Th. Schmidt, *Z. Physik*, **108**, 408 (1938).

DURHAM, NEW HAMPSHIRE RECEIVED JULY 19, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Photochemistry of Diiodoacetylene and Tetraiodoethylene

BY JOHN W. TAMBLYN AND GEORGE S. FORBES

The present research represents a further attempt to correlate the mechanisms of photoiodination on either side of the convergence limit of iodine, 499 mμ. Brown[1] states that a continuum in the red, corresponding to production of normal atoms, is not visible below 50°. Bonhoeffer and Harteck[2] hold that this mode of dissociation is of minor importance photochemically. The data of Rabinowitch and Wood,[3] however, might lead to a contrary conclusion. Dickinson and Nies[4] re-evaluated the data of Schumacher and Steiger[5] in terms of the influence of absorbed light intensity. They found the relative efficiencies of quanta corresponding to λλ 578, 546 and 436 mμ to be 0.75, 0.87 and 1.00, respectively. The temperatures were 76.6 and 99°. On the other hand,

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[1] Brown, *Phys. Rev.*, **38**, 1187 (1931).

[2] Bonhoeffer and Harteck, "Grundlagen der Photochemie," Steinkopff, Dresden, 1933, p. 94.

[3] Rabinowitch and Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

[4] Dickinson and Nies, THIS JOURNAL, **57**, 2382 (1935).

[5] Schumacher and Steiger, *Z. physik. Chem.*, **B12**, 348 (1931).

Forbes and Nelson[6] found that light of λ 644 mμ was much less efficient than light of λ 436 mμ in promoting iodination of *cis*-butene in chloroform. Quanta corresponding to λ 644 mμ are still substantially greater than the minimum requisite for production of normal atoms. Rollefson[7] has ably discussed the issues involved in this situation.

Diiodoacetylene represents a type of compound not yet investigated with the above stated problem in mind. The thermal addition of iodine takes place slowly in carbon disulfide[8] and rapidly in boiling toluene.[9] We found that the photochemical reaction proceeds smoothly in visible light, at 0°, without important thermal reaction. We varied light intensity, and concentrations, measured quantum yields and temperature coefficients, and set up rate equations valid for the different spectral regions.

Materials.—Diiodoacetylene was prepared according to Dehn[10] with the additional precaution that the acetylene was washed with lead acetate to remove hydrogen sulfide.[11] The product was twice recrystallized from petroleum ether. After storage at 0° in the dark for a period of nine months, no change in appearance or in melting point could be detected.

Tetraiodoethylene was prepared following the directions of Datta and Prosad,[12] also by boiling diiodoacetylene in toluene with purified iodine. The product was in each case recrystallized twice in toluene distilled from sodium.

Hexane, from Eastman Kodak Co., was shaken with portions of concentrated sulfuric acid until one remained colorless for several hours. Three or four treatments with fuming acid followed over a period of one to two days. A final washing with alkaline permanganate preceded distillation. Our criterion of purity was 99% transmission of light of λ254 mμ in a 5-mm. layer. The product, which boiled over the range 64 to 69°, was evidently a mixture of hydrocarbons, but it did not react thermally with iodine, nor photochemically even in light of λ254 mμ.

Apparatus and Method.—The quartz reaction cell previously used by Forbes and Nelson[6] had plane parallel faces 5 × 2 cm. in area and 1 cm. apart. It was surmounted by a quartz cylinder with a ground-in hollow Pyrex stopper through which passed sealed-in tubes for ingress and egress of nitrogen. For removal of oxygen, which retards many halogenation reactions, the best method found was to bubble nitrogen (said to be 99.93% pure) through the reaction mixture at dry-ice temperature, for an hour at the rate of two bubbles per second. After this, the solution was warmed to 0° and shaken to redissolve precipitated iodine. The following relative reaction rates were observed at 0° and in constant red light after an hour's treatment with the following mixtures of nitrogen and oxygen, respectively:

p_{O_2} (atm.)	0.0000[b]	0.0007[a]	0.028	0.21	0.995[c]
Rate, R	9.3	9.5	1.92	1.55	0.78

[a] Tank nitrogen. [b] Nitrogen treated with hot copper. [c] Tank oxygen.

In addition, R was found to be 3.9 in a solution prepared in air, frozen at liquid air temperature, pumped out, melted, again frozen, and so on, three times in all. Willard and Daniels[13] repeated such a cycle six or seven times before their reaction rates reached maximum values. Unless otherwise specified, all solutions mentioned below were freed from oxygen by tank nitrogen as described above.

The reaction cell[6] was lowered into an air thermostat[6] with a double quartz window to avoid condensation of moisture. Temperature was held at 0 ± 1° by a regulated current of chilled air. Whenever a prism monochromator was not employed, a light-filter cell one inch thick was in contact with the thermostat window. The solution was shaken as often as seemed desirable.

Since the quantum yields varied with incident light flux, the divergent beam from the exit slit of a monochromator, having a wide range of intensity over its cross section, would have been unsuitable in certain experiments. A tungsten lamp was employed with its U-shaped filament parallel to the cell window. Thanks to an efficient voltage regulator, the readings of an ammeter in series were constant within 3%. Known relative light intensities were realized by use of the inverse square law, valid within 1% except perhaps at the highest point of Graph II, Fig. 1.

Analytical.—Immediately after photolysis the solution was analyzed in dim light. Grease was carefully removed from the mouth of the cell, and the mixture was transferred to a flask containing 1 g. of potassium iodide in 5 cc. of water. The cell was rinsed into the flask with a little more potassium iodide solution, after which the iodine was titrated, while shaking, with 0.01 N thiosulfate. The thermal reaction, never more than 3% of the whole, was subtracted. The speed of this reaction was not measurably altered by packing the cell with quartz fragments, glass beads or glass wool.

Influence of Light Intensity.—To minimize undesirable thermal reactions, experiments were conducted at 0°. In Series I a 200-watt bulb was used. A ferric thiocyanate filter transmitted light, λ ≧ 600 mμ, according to visual observations with a Hilger wave-length spectrometer. No change in the absorption limit could be detected after exposure. In Series II, a 500-watt bulb was used behind a Corning filter H R Signal Red, λ ≧ 610 mμ. In Series III, blue light, λ ≦ 480 mμ, was transmitted by a cuprammonium sulfate filter. Exposure times varied from a few minutes to an hour. In Fig. 1, $\log_{10} R$ (reaction

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(6) Forbes and Nelson, This Journal, **59**, 693 (1937).

(7) Rollefson, "The Photochemistry of the Halogens," Hermann et Cie., Paris, 1938, esp. pp. 5–9 and 48–49.

(8) Maguenne and Taine, *Z. allgem. österr. Apoth.-Ver.*, **31**, 810 (1893).

(9) Biltz, *Ber.*, **30**, 1202 (1897).

(10) Dehn, This Journal, **33**, 1598 (1911).

(11) Biltz and Küppers, *Ber.*, **37**, 4415 (1904).

(12) Datta and Prosad, This Journal, **39**, 451 (1917).

(13) Willard and Daniels, *ibid.*, **57**, 2240 (1935).

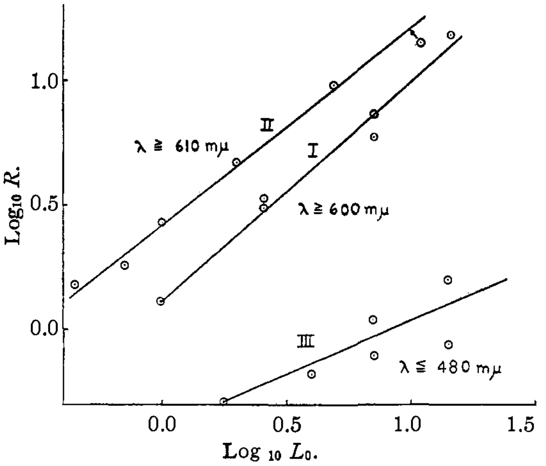

Fig. 1.—Influence of light intensity L_0 on reaction rate, R. The values of R on line II were multiplied by ten before plotting.

rate) is plotted against log L_0 (incident light flux), both in arbitrary units. As filter II had a relatively low transmission, and lamp distances were greater, all values of R_{II} were multiplied by ten before plotting. Drawing the best straight lines, $\Delta \log R_{\text{I}} = 0.90\ \Delta \log L_0$; $\Delta \log R_{\text{II}} = 0.78\ \Delta \log L_0$; and $\Delta \log R_{\text{III}} = 0.40 \log L_0$. Giving Series II slightly more weight than Series I, we wrote $R_{\text{red}} = k_{\text{red}}\ L_0^{0.8}$ and $R_{\text{blue}} = k_{\text{blue}}\ L^{0.4}$. An additional series, IV, was carried out with a dichromate filter, λ ≧ 530 mμ. Although the results are open to objection because air was not removed, it appears reasonable that $R_{\text{yellow}} = k_{\text{yellow}}\ L^{0.65}$; that is, the exponent lies between 0.8 and 0.4.

Influence of Diiodoacetylene Concentration.—This was varied from 8×10^{-4} to $8 \times 10^{-2}\ M$, and no visible light was absorbed. Lamp I with filters I and III was employed. Figure 2 gives the experimental data in comparison with curves plotted from the equations

$$R_{\text{red}} = \frac{[C_2I_2]}{0.038 + 4.0[C_2I_2]} \text{ and } R_{\text{blue}} = \frac{[C_2I_2]}{0.108 + 28[C_2I_2]}$$

which suffice to predict these data within experimental error.

Iodine concentration could not be varied widely, because saturation was reached at $10^{-2}\ M$, and light transmission became excessive below $1.5 \times 10^{-3}\ M$. The solutions were made up determinate at 25° and a correction applied for the contraction to 0°. A mercury lamp[14] operated under atmospheric pressure, and the radiations λλ 578, 546 and 436 mμ were isolated by a monochromator having a large prism of extra dense

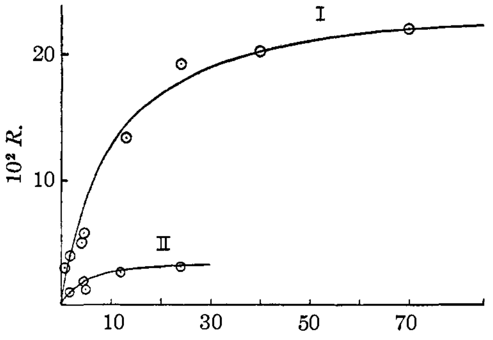

Fig. 2.—Influence of diiodoacetylene concentration on reaction rate, R. On Curve I, λ ≧ 600 mμ, and on Curve II, λ ≦ 480 mμ.

flint glass. Red light was similarly isolated from a constant spark[15] between cadmium bars. L_0 was measured radiometrically by the method of integration.[16] The extinction coefficients of iodine in hexane at 0° were obtained by interpolation of data by Groh and Papp[17] which we also checked at several points. Absorbed light energy was referred to average iodine concentration and average absorption in every case. The quantum yield ϕ is the ratio of m the number of iodine molecules reacting photochemically to q the number of quanta absorbed by iodine per second. Figure 3 summarizes these experiments. The temperature was

TABLE I

IODINE CONCENTRATIONS AND QUANTUM YIELDS

λ, mμ	Time, sec.	$q \times 10^{-15}$	$m \times 10^{-18}$	ϕ	$[I_2] \times 10^3$	$\phi/[I_2]$
644	870	2.9	2.3	0.9	4.6	0.20
578	1230	3.5	1.5	.35	1.32	.27
578	900	4.2	2.7	.71	2.67	.27
578	750	4.6	4.9	1.4	4.41	.32
578	600	5.0	3.7	1.2	4.55	.26
578	660	5.0	3.6	1.1	4.57	.24
578	750	3.7	4.7	1.7	9.40	.18
						.25
546	1500	4.0	7.8	1.3	4.98	.26
546	900	3.7	4.6	1.4	4.98	.28
						.27
436	1200	0.46	0.65	1.2	1.42	.85
436	900	.95	1.80	2.1	2.77	.76
436	1420	.99	6.4	4.6	4.23	1.1
436	810	1.03	6.5	6.2	4.24	1.5
436	740	1.27	3.7	4.0	4.54	0.88
436	810	1.15	3.7	4.0	4.55	.88
436	540	1.33	3.3	4.6	4.59	1.0
436	750	1.28	4.3	4.5	9.44	0.48
						0.92

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[14] Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

[15] Brackett and Forbes, *ibid.*, **53**, 3973 (1931).

[16] W. G. Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

[17] Groh and Papp, *Z. physik. Chem.*, **149**, 153 (1930).

0°, and initial [C_2I_2] was uniformly 0.005. Although measurements at λ 436 mμ were unexpectedly discordant, no trend in $\phi/[I_2]$ is anywhere apparent.

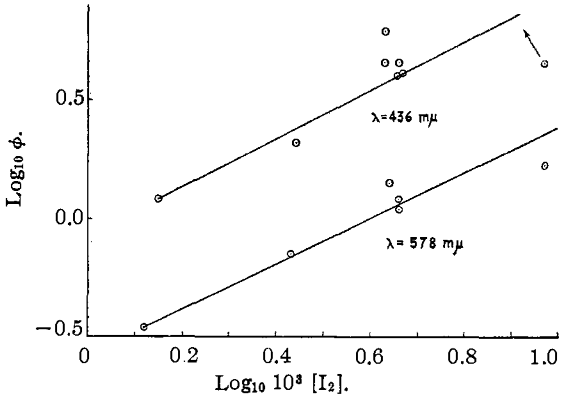

Fig. 3.—Influence of iodine concentration on quantum yield, ϕ.

Evidently $\phi/[I_2]$ increases slowly with decreasing wave length as the convergence limit is approached, and becomes considerably greater after this has been passed.

The ten-degree temperature coefficient Z of the photochemical reaction was found from eleven measurements at −32, 0 and 25°, behind the ferric thiocyanate and cuprammonium sulfate filters. The relative fractions of L_0 absorbed at each temperature were estimated by interpolation of data by Groh and Papp[17] on iodine at −53° and at room temperature. In red light $Z = 1.11$ between −32 and 0°, $Z = 1.22$ between 0 and 25°. In blue light both the corresponding values of Z were 1.18. Within experimental error all these values of Z can be considered identical.

To exclude the possibility of side reactions, a solution of average composition, free from oxygen, was exposed to red light until 5.23×10^{19} molecules of iodine had reacted. The hexane, together with the unchanged diiodoacetylene, was evaporated off. The residue, at constant weight, was 0.0450 g., *i. e.*, the weight of 5.16×10^{19} molecules of tetraiodoethylene. The melting point was 188° both before and after addition of a known sample of tetraiodoethylene. Apparently, therefore, the only important over-all reaction is $C_2I_2 + I_2 = C_2I_4$.

Experiments without removal of oxygen were performed at 0° and at 25° in purified hexane and in absolute ethanol. Both initial concentrations were 0.005 M. The only reaction product detected was tetraiodoethylene. In Table II, d is the extreme variation in ϕ_{air} within the group of experiments considered. In the last column, ϕ refers to experiments in solutions with the same initial concentrations but with oxygen removed. The second and third of these were performed at 0° but have been referred to 25° through multiplication by $(1.18)^{2.5}$.

TABLE II

QUANTUM YIELDS, OXYGEN NOT REMOVED

λ, mμ	Solvent	t	Expts.	d	ϕ_{air}	ϕ
644	C_6H_{14}	0°	2	0.02	0.16	0.9
546	C_6H_{14}	25°	8	.07	.25	1.95
436	C_6H_{14}	25°	5	.22	.62	6.8
436	C_2H_5OH	25°	2	.01	.15	
366	C_2H_5OH	25°	2	.04	.17	

The retarding effect of oxygen, in hexane solutions at least, seems to increase with decreasing wave length. The solvation of iodine in ethanol may well be responsible for the lower quantum yields there. Berthoud and Mosset,[18] likewise, found triiodide ions only one-fifth as effective as iodine molecules for iodination of allyl alcohol.

Photolysis of tetraiodoethylene was studied in hexane using an argon-filled mercury resonance lamp. About 83% of the total radiation was of wave length 254 mμ according to measurements by Leighton and Leighton.[19] Radiant flux was measured by actinometry with uranyl oxalate; the transmission of which for other wave lengths was much like that of tetraiodoethylene. Absorption of light by the iodine and diiodoacetylene formed by photolysis was shown to be negligible.

In absence of oxygen, two distinct reactions were observed: first a rapid liberation of 85% of the iodine corresponding to the equation $C_2I_4 = C_2I_2 + I_2$, then a (much slower) photolysis of diiodoacetylene, during which a characteristic odor different from that of diiodoacetylene was noticeable. In one experiment not carried to the second stage, liberated iodine was titrated; hexane and diiodoacetylene were evaporated off. The original weight of tetraiodoacetylene minus the weight of the residue corresponded within one milligram to the weight of iodine found by titration. Two other experiments (oxygen removed) gave ϕ = molecules of I_2 produced/quanta absorbed by C_2I_4 = 0.77 and 0.79. Parallel experiments without removal of oxygen gave ϕ = 0.81, 0.80 and 1.00 in hexane, also ϕ = 0.50, 0.57 and 0.58 in ethanol.

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[18] Berthoud and Mosset, *J. chim. phys.*, **33**, 287 (1936).

[19] Leighton and Leighton, *J. Chem. Education*, **12**, 139 (1935).

Photolysis of Diiodoacetylene in Hexane.—In absence of oxygen ($\lambda = 254$ mμ), two reaction stages were observed. At the start iodine appeared very slowly and the solution became somewhat milky. Later, but before the diiodoacetylene had been largely decomposed, iodine was released more rapidly. The milkiness tended to disappear, and a brownish deposit formed upon the cell window. Only about 55% of the original combined iodine could be liberated as such by light. The brown deposit evolved iodine when dried and heated, or when treated with alcohol or with potassium iodide solution. When the exposed solution was evaporated after extraction of iodine, a pale yellow oil remained having the odor already noted in the second stage of the photolysis of tetraiodoethylene. This oil turned brown upon exposure to air. If the photolysis was conducted in hexane or ethyl alcohol without exclusion of air, the liberation of iodine began at once. No milkiness or brown deposit was observed at any time, but carbon dioxide was detected when oxygen was bubbled first through the irradiated solution and then through barium hydroxide.

Attempts at photoiodination of tetraiodoethylene were unsuccessful in benzene, carbon disulfide, hexane and ethanol. Red, orange and white light was employed in succession, and temperatures ranged from −40 to 25°.

Reaction Mechanism in Blue Light.—A complete rate expression for addition of iodine to diiodoacetylene in blue light follows from the experiments described above, in which L_0, $[I_2]$, and $[C_2I_2]$ were varied one at a time. A suitable correction for incomplete absorption of incident light was made in each separate experiment.

$$-\left[\frac{\mathrm{d}[I_2]}{\mathrm{d}t}\right]_{\text{over-all}} = k_{\text{blue}}\, L_0^{0.4}\, [I_2]^{1.0} \frac{[C_2I_2]}{a_{\text{blue}} + b_{\text{blue}}[C_2I_2]}$$

Schumacher and Wiig,[15] for the iodine-sensitized decomposition of ethylene iodide, found a ten-degree temperature coefficient Z of 1.57, corresponding to an activation energy E of 11.8 kcal. per mole which they assigned to a reaction analogous to the reverse of equation (3) above. Since ΔH for this step should be nearly zero,[20] E should be nearly the same in both directions. We found for the iodination of diiodoacetylene $Z = 1.18$, corresponding to $E = 2.5$ kcal./mole. Then unless the formation of tetraiodoacetylene at λ 436 mμ proceeds mainly by way of the less probable step (5), E_3 must be much smaller than that of the analogous reaction for ethylene iodide. For the over-all dark reaction we found $Z = 3$, approximately, representing $E = 20$ cal./mole. By an argument similar to that of Polissar,[21] this should be equal to half the heat of dissociation of iodine (18 kcal./mole) plus E_3, which predicts $E_3 = 2$ kcal./mole in agreement with the over-all activation for the photochemical reaction calculated above.

Reaction Mechanism in Red Light.—The exponent of L_0 in red light is 0.8, in orange light between 0.7 and 0.6, and in blue light 0.4. This progression indicates either a continuous change in one particular mechanism or in the relative efficiencies of two mechanisms, as the convergence limit is passed. Several imaginable explanations are all open to well-recognized objections.

Direct addition to diiodoacetylene, of an excited iodine molecule is improbable in view of the observed dependence of ϕ upon $[I_2]$. Ogg[20] has argued against the addition, in a single act, of any halogen to an ethylenic linkage. Moreover, a chain mechanism initiated by molecules excited by red light cannot be seriously proposed, since about a thousand collisions with solvent molecules will on the average precede one with diiodoacetylene. As an exercise, we worked out a reaction scheme in harmony with our experimental results and plausible except for this fundamental objection. The same objection would impair any scheme assuming that the excited iodine atoms formed in blue light are more effective in starting chains than normal iodine atoms formed, exclusively, in red light.

Primary formation of halogen atoms need not in itself preclude linear dependence of reaction rate upon L_0. Booher and Rollefson[22] showed this for the photobromination of acetylene by omitting from their reaction scheme all steps involving reaction between two radicals. By analogous treatment of our reaction scheme proposed above for blue light, the results in red light could be made to appear reasonable, but those in blue light would then in turn become anomalous.

A remaining possibility, that atoms produced by a quantum of red light, less energetic at first than those produced by one of blue light, might recombine more rapidly in presence of third bodies, and thus lead to lower quantum yields, cannot be tested by the data of the present paper.

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[20] Ogg, THIS JOURNAL, **58**, 607 (1936).

[21] Polissar, *ibid.*, **52**, 956 (1930).

[22] Booher and Rollefson, *ibid.*, **56**, 2288 (1934).

The Measure of Spectral Efficiencies.—Allmand,[23] also Dickinson and Nies,[4] have pointed out that when R is not proportional to $L_0{}^{1.0}$, ϕ_λ is no longer, in any simple sense, a measure of spectral efficiency, unless the variation of extinction coefficient is negligible over the spectral range considered. Usually there is considerable variation, and then a less simple but still practicable measure of efficiencies is found[4] in the specific rate constant k^* provided that a uniform rate expression is valid throughout the spectral region in question. The constant k^* may be obtained by an integration from front to back of the reaction mixture, of the rate expression taken as valid at any point in the light path. But when, as in the iodination of diiodoacetylene, the rate expression varies with wave length, the situation becomes more complex than that encountered by Dickinson and Nies. Consider a solution in which iodine is the only absorbent. In any layer of thickness dl perpendicular to the monochromatic light beam and l cm. behind the cell window, let L_l be the quanta per sec. absorbed per cc. Let L_0 represent quanta per second passing the cell window, as usual, and k_{I_2} the extinction coefficient of iodine for λ, the wave length employed.

$$L_l = -\frac{\mathrm{d}L}{\mathrm{d}l} = -\frac{\mathrm{d}(L_0 10^{-k_{I_2}[I_2]l})}{\mathrm{d}l}$$
$$= L_0 10^{-k_{I_2}[I_2]l} \ln 10\ k_{I_2}[I_2]$$

The reaction rate in such a layer is given by the equation

$$-\frac{\mathrm{d}[I_2]}{\mathrm{d}t} = \mathrm{k}^*_\lambda L_l^x\ [I_2]\frac{[C_2I_2]}{a_\lambda + b_\lambda\ [C_2I_2]}$$

The relation between k^*_λ and ϕ_λ for negligible changes in $[I_2]$, is obtained by evaluating

$$\int_0^d -\frac{\mathrm{d}[I_2]}{\mathrm{d}t}\ \mathrm{d}l$$

whereby we finally obtain

$$k^*_\lambda = \phi \left\{x\frac{k_{I_2}^{1-x}L_0{}^{1-x}}{[I_2]^x}\frac{1-T}{1-T_x}\frac{a_\lambda + b_\lambda\ [C_2I_2]}{[C_2I_2]}\right\}$$

in which each variable, x included, has the value appropriate to λ, and

$$T = 10^{-k_{I_2}[I_2]d}$$

the transmitted fraction of incident light energy at depth d in the layer.

In this equation

$$\phi = -\left[\frac{\mathrm{d}[I_2]}{\mathrm{d}t}\right]_{\text{over-all}}\frac{V}{A\,[L_0(1-T)]}$$

where V = volume of reaction mixture in cm.³ and A = cross section of the light beam in cm.². It thus appears that relative efficiencies are not expressible in terms of any concept more simple than the equation for k^*_λ.

Summary

The photoiodination rate of diiodoacetylene in hexane, with careful exclusion of oxygen, was studied quantitatively in red and in blue light. A chain reaction is found to occur. Tetraiodoethylene is shown to be formed quantitatively.

The equation

$$-\frac{\mathrm{d}[I_2]}{\mathrm{d}t} = k^\lambda L_0^{x_\lambda}[I_2]\frac{[C_2I_2]}{a_\lambda + b_\lambda\ [C_2I_2]}$$

generalizes the data obtained. k_λ, x_λ, a_λ and b_λ must be evaluated separately for each spectral interval considered.

The mechanism of the reaction appears to vary with the wave length of light employed. In blue light the exponent of L_0 is 0.4, in orange light between 0.6 and 0.7, and in red light 0.8. It appears that the expedients hitherto employed for treatment of photochemical data here lead to difficulties.

A specific rate constant was obtained by integration which is valid at any given wave length provided that proper values for four constants dependent upon wave length are supplied.

Tetraiodoethylene in hexane was photolyzed in ultraviolet light, λ = 254 mμ (oxygen removed). At first one molecule of free iodine appears for each molecule of tetraiodoethylene which disappears, and the quantum yield is 0.8. In the late stages of the photolysis an unidentified product was observed.

The photolysis of diiodoacetylene in hexane was studied qualitatively. Apparently it is complicated by formation of polymeric substances.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 8, 1939

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[23] Allmand, *J. Chem. Soc.*, 1557 (1929).