[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Photolysis and Radiolysis of Liquid Alkyl Iodides[1]

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Several simple alkyl iodides have been irradiated as pure liquids with light of wave lengths 2537 and 3260 Å., and with 50 pkv. X-rays. Relative rates of iodine production have been measured and a correlation between these rates and molecular structure has been tested. Complex formation between iodine and alkyl iodide has been shown to influence the observed rate of iodine production at 3260 Å., but not at 2537 Å. Dilute solutions of alkyl iodides in hydrocarbons have also been photolyzed at 2537 A., and several evidences of distinction between the reactions in solution and the pure state have been obtained.

The quantum yields for the production of iodine in ultraviolet photolysis of liquid alkyl iodides have been measured previously in several instances[2-4] and a more detailed study of the mechanism of photolysis of ethyl iodide has been published[5] in which a hot radical mechanism was proposed. This mechanism accounts for the observed equality of alkane and alkene production[6] by a step which in generalized form may be represented as

$$\underline{RR'CHCH_2\cdot} + RR'CHCH_2I \longrightarrow RR'CHCH_3 + RR'\underset{\cdot}{C}CH_2I \quad (1)$$

$$RR'\underset{\cdot}{C}CH_2I \longrightarrow RR'C{=}CH_2 + I \quad (2)$$

where $\underline{RR'CHCH_2\cdot}$ is a hot radical.

Taking the best values of Φ_I from earlier studies (normalizing disagreements where possible and ignoring variations in wave length of actinic light) we discovered an interesting connection with molecular structure,[7] namely, that the quantum yield of iodine is an approximately linear function of the fraction, F_β, of hydrogen atoms in the β-position with respect to the C–I bond.

In view of the inadequacy of the past information for proper test of this relation we have undertaken to measure Φ_I for five simple alkyl iodides relative to that of ethyl iodide at two different wave lengths. For purposes of comparison we have also measured the rate of iodine production in photolysis of cyclohexane solutions of these iodides and in radiolysis of the pure iodides.

Experimental

Materials.—Ethyl iodide from the Matheson Chemical Co. was passed through a column containing 200-mesh silica gel, and then fractionated in a 4-ft. glass helix packed Todd fractionating column. The middle third, taken at a reflux ratio 20:1, 71.0 ± 0.2°, 749 mm., was stored in the dark over copper wire; $n^{15}D$ 1.5168.

Other alkyl iodides were washed with 0.1 *N* aqueous thiosulfate, water, dried over calcium chloride and fractionated in the Todd column at a reflux ratio of 20:1. Iodides boiling above 90° were distilled at reduced pressure. Middle cuts boiling at constant temperature were stored in the dark over copper or mercury.

Cyclohexane, commercial grade, was washed with fuming sulfuric acid, aqueous sodium carbonate, water and dried with calcium chloride prior to fractionation in the Todd column. The middle third, taken at a 10:1 reflux ratio, 80.0 ± 0.2°, 745 mm., was collected for use. Hexane was obtained from Skellysolve B by similar treatment and a fraction boiling over the range 65–68° was retained for use.

Radiation Sources.—Light of wave length 2537Å. was obtained from a Hanovia SC2537 low pressure mercury resonance lamp. The manufacturer states that 85% of the radiant energy is emitted in the mercury resonance line. Most of the remaining energy is emitted in visible wave lengths where the alkyl iodides have negligible absorption coefficients. Possible complication from the 1849 Å. line of mercury was eliminated by filters of cellophane or Corning 9–54 glass. The lamp was operated at a constant primary current of 1.7 amperes. A metal block rigidly attached to the lamp housing held the sample tubes in reproducible positions with respect to the lamp.

Light of wave length 3260 Å. was obtained from a cadmium resonance lamp of the type described by Steacie and Potvin.[8] Examination of the radiation of this lamp in a spectrophotometer indicated that the line at 3260 Å. was approximately ten times more intense than other lines at 3462 Å. and longer wave lengths. In view of the rapidly decreasing absorption coefficient of the alkyl iodides in this spectral region we have presumed that the actinic light is limited to the 3260 Å. line. Since the lamp envelope was Pyrex glass, shorter wave lengths could not interfere. A sample holder similar to that used with the mercury lamp was also attached to the cadmium lamp housing.

X-Irradiation of the alkyl iodides was accomplished with an AEG-50T X-ray tube manufactured by Machlett Laboratories. This tube was operated at 47.5 pkv. and 17 ma. and produces X-rays in the range 0.25 to 4.4 Å. with maximum intensity at 1.7 Å.

Procedure.—Samples of pure alkyl iodide or solution were introduced by vacuum distillation into the irradiation cells and sealed off. The cells consisted of cylindrical silica tubes approximately 1.4 × 10 cm. joined by a graded seal to Pyrex tubing of the same diameter. After irradiation of the liquid sample in the silica end, the tube was inverted for colorimetric iodine analysis in the Pyrex end. Apertures in the metal block cell holder confined the incident light to a narrow beam falling on a central portion of the cell and liquid sample.

In most ultraviolet photolyses two samples were irradiated simultaneously in fixed positions with respect to the lamp. One was ethyl iodide, which served as an actinometer to monitor the lamp output. Thus, relative quantum yields were computed directly from the iodine yield in a given exposure and an intensity factor for the two cell positions (0.85 for the mercury lamp and 1.09 for the cadmium lamp).

In a few experiments ethyl iodide was photolyzed at 2537 Å. simultaneously with a uranyl oxalate actinometer as described by Forbes and Heidt,[9] to obtain a value for the absolute quantum yield of iodine production from ethyl iodide.

For X-ray exposures both ends of the irradiation cell were made of Pyrex glass. The cell was clamped in a reproducible position with respect to the X-ray tube, and exposure

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[1] Taken from the Ph.D. thesis of E. L. Cochran. Work supported in part by the U. S. Atomic Energy Commission under Contract At(11-1)-38. Presented at the 124th A.C.S. Meeting, Chicago, Ill., Sept. 6-11, 1953.

[2] G. Emschwiller, *Ann. chim.*, **17**, 463 (1932).

[3] E. Olaerts and J. C. Jungers, *Disc. Faraday Soc.*, No. 2, 222 (1947).

[4] W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

[5] W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

[6] Reference 2, further confirmed by mass spectrometric analysis in this Laboratory to be reported subsequently.

[7] W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, AECU-1321, March 1, 1951.

[8] E. W. R. Steacie and R. Potvin, *Can. J. Research*, **16**, 337 (1938).

[9] G. S. Forbes and L. J. Heidt, THIS JOURNAL, **56**, 2363 (1934).

of the end of the cell to be used for analysis was prevented by an appropriate lead mask to prevent coloration of the glass. Single samples were exposed for 20 minutes, followed by colorimetric analysis for iodine.

In all irradiations, analysis for iodine was performed by measurement of optical density at 5000 or 6000 Å., depending on the magnitude of the iodine concentration. Calibration curves were determined for each alkyl iodide through use of solutions prepared by weighing resublimed iodine into known volume of alkyl iodide, followed by appropriate dilution. In addition, several samples of photolyzed alkyl iodide were analyzed by thiosulfate titration as well as colorimetrically, with satisfactory agreement.

Results

Complex Formation.—In the course of this work we became aware of the possibility of complex formation between alkyl iodides and iodine as shown by Keefer and Andrews.[10] In an effort to assess the influence of this phenomenon upon the rate of iodine production, we have made approximate measurements of the extinction coefficient of the ethyl iodide–iodine complex in hexane solution at 2537 and 3260 Å., using the value of the equilibrium constant determined by Keefer and Andrews. The measurement is rendered difficult by the large extinction coefficient of ethyl iodide, especially at 2537 Å., and we find the following approximate values: for ethyl iodide in hexane, 400 at 2537 Å. and unity at 3260 Å.; for ethyl iodide–iodine complex with excess ethyl iodide in hexane, 2.4×10^4 at 2537 Å. and 1.0×10^4 at 3260 Å. Calculations based on these values and the equilibrium constant indicate that absorption by the complex was negligible at 2537 Å. under our experimental conditions both in the pure alkyl iodide and in the hexane solutions used. However, at 3260 Å. it appears that the complex absorbs about 50% of the incident light at an iodine concentration of 3×10^{-4} M, which is taken to account for the decreased rate of iodine production as shown below. These calculations were verified in an experiment in which a sample of ethyl iodide was photolyzed to high iodine concentrations in comparison with a sample used intermittently. In the latter actinometric sample the iodine concentration was always below 2×10^{-4} M, while the iodine concentration in the former was allowed to reach 3×10^{-3} M. At 2537 Å. the yield ratio of the two samples was unity within experimental error, while at 3260 Å. in the more concentrated sample the rate of iodine production fell to half that of the actinometer.

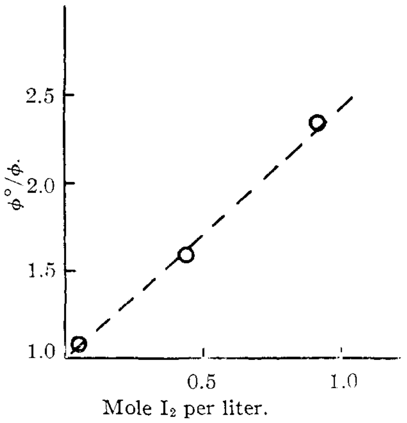

Fig. 1.—Effect of complex formation on photolysis of methyl iodide.

To obtain valid quantum yields for iodine formation at 3260 Å., we have expressed the observed quantum yield, Φ_{RI}, as an assumed function of the quantum yields for the alkyl iodide, Φ^0_{RI}, the complex, Φ^0_c, and the fractions of light absorbed by the two species in the solution, f_{RI} and f_c.

$$\Phi_{RI} = \Phi^0_{RI} f_{RI} + \Phi^0_c f_c \tag{3}$$

Since

$$\frac{[C]}{[RI]\,([I_2] - [C])} = K \tag{4}$$

when $[I_2] << [RI]$, it can be shown that

$$\frac{\Phi_{RI}}{\Phi^0_{RI}} = \frac{A + (\Phi^0_c/\Phi^0_{RI})[I_2]}{A + [I_2]} \tag{5}$$

where

$$A = \frac{\epsilon_{RI}}{\epsilon_c} \times \frac{(1 + K[RI])}{K} \tag{6}$$

and ϵ_{RI} and ϵ_c are the molar extinction coefficients of the two species. Experimentally it appears that $\Phi^0_c < \Phi^0_{RI}$, and tentatively we take $\Phi^0_c = 0$. Then

$$\frac{\Phi^0_{RI}}{\Phi_{RI}} = 1 + \frac{[I_2]}{A} \tag{7}$$

Although our data on iodine production at 2537 Å. do not extend to sufficiently high iodine concentration to test this expression, those of Schuler[11] on photolysis of methyl iodide with large added concentrations of iodine show satisfactory agreement with equation,[7] as indicated in Fig. 1. The slope of this line, $1/A = 1.53$, is consistent with $K = 0.22$,[10] $\epsilon_{MeI} = 400$ and $\epsilon_c = 1.5 \times 10^4$. The excellent linearity of the points confirms the assumption $\Phi_c = 0$.

Quantum Yields.—In correcting our data taken at 3260 Å. we have used a rearranged form of equation 7, making the substitution $\Delta[I_2]/\Delta t = \Phi I$, where t is time and I is absorbed light intensity.

$$(\Phi^0_{RI} I)^{-1} + [I_2](\Phi^0_{RI} IA)^{-1} = \Delta t(\Delta[I_2])^{-1} \tag{8}$$

Thus, if I is constant and the iodine concentration is measured periodically, a plot of $[I_2]$ *vs.* $\Delta t/\Delta[I_2]$ should give a straight line of slope $(\Phi^0_{RI} IA)^{-1}$ and intercept $(\Phi^0_{RI} I)^{-1}$. The intercept divided by the slope is A, and with this value Φ^0_{RI}/Φ_{RI} can be calculated at any iodine concentration by equation 7.

The values of $\Delta t/\Delta[I_2]$ obtained in a series of exposures of ethyl iodide at 3260 Å. are plotted according to equation 8 in Fig. 2. The line drawn gives a value of $A = 1.21 \times 10^{-3}$, in good agreement with values of $K = 0.37$[10], $\epsilon_{RI} = 1$, $\epsilon_c = 1 \times 10^4$. In comparing the quantum yield of higher alkyl iodide with that of ethyl iodide, this value of A was used in equation 7 to correct the observed quantum yield of the ethyl iodide actinometer. Then plotting

Φ^0_{EtI}/Φ_{RI} *vs.* $[I_2]$, according to

$$\frac{\Phi^0_{EtI}}{\Phi^0_{RI}} + \frac{\Phi^0_{EtI}[I_2]}{\Phi^0_{RI} A} = \frac{\Phi^0_{EtI}}{\Phi_{RI}} \tag{9}$$

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[10] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

[11] R. H. Schuler, *ibid.*, **75**, 3792 (1953). This work follows the quantum yields of gas methane and ethane production. These decrease in exact proportion with each other, and so also should the iodine yield.

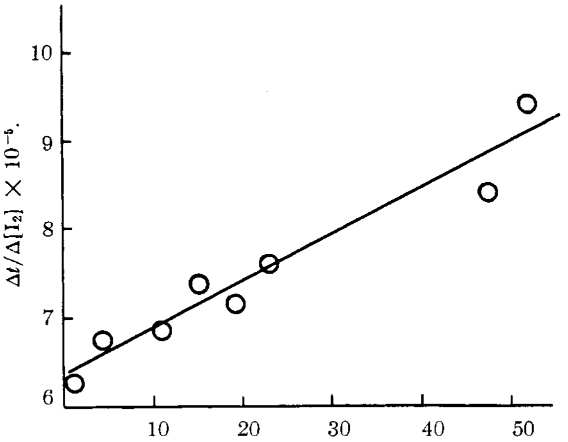

Fig. 2.—Photolysis of ethyl iodide at 3260 Å.

obtained from equation 7 multiplied by $\Phi^0_{\text{EtI}}/\Phi^0_{\text{RI}}$, we perform a straight-line extrapolation of the data to zero $[I_2]$, obtaining $\Phi^0_{\text{EtI}}/\Phi^0_{\text{RI}}$. The values thus obtained are given in Table I. The corrections are not large except in the case of isobutyl iodide, which apparently has an exceptionally large value of ϵ_c.

TABLE I

THE RELATIVE QUANTUM YIELDS FOR THE ALKYL IODIDES AT 3260 Å.

Cpd.	Aver. (I_2) $(10)^5$ in EtI	Aver. (I_2) $(10)^5$ in RI	$\frac{\Phi\text{EtI}}{\Phi\text{RI}}$	$\frac{\Phi_0\text{EtI}}{\Phi\text{EtI}}$	$\frac{\Phi_0\text{EtI}}{\Phi\text{RI}}$	$\frac{\Phi_0\text{EtI}}{\Phi_0\text{RI}}$
n-PrI	4.31	3.29	1.21	1.04	1.25	
	12.5	9.35	1.24	1.11	1.37	
	20.1	15.0	1.21	1.17	1.42	1.19
i-PrI	3.95	5.45	0.67	1.03	0.69	
	11.5	16.1	0.65	1.10	0.71	0.68
n-BuI	30.4	17.6	1.22	1.26	1.53	
	35.6	21.5	1.22	1.30	1.59	1.26
s-BuI	18.4	21.8	0.69	1.16	0.80	
	23.3	35.3	0.70	1.20	0.84	0.74
i-BuI	3.60	2.00	1.64	1.03	1.70	
	10.0	5.44	1.85	1.08	1.95	
	17.0	8.52	2.29	1.14	2.60	
	35.3	26.8	4.01	1.30	5.19	
	47.2	30.4	7.35	1.40	10.3	
	53.7	33.5	6.01	1.45	8.71	1.38

Since no correction for complex absorption is necessary at 2537 Å., the determination of relative quantum yields is a simple matter of comparing the relative rates of iodine production, which are linear with time and independent of $[I_2]$ in the range of interest. Replicate determinations of the ratios of quantum yields showed an average deviation of 0.01 and a maximum deviation of 0.04.

We have also redetermined the quantum yield of iodine production in ethyl iodide relative to the uranyl oxalate actinometer at 2537 Å. Taking the quantum yield of the latter to be 0.64 at this wave length,[9] we find the average quantum yield of ethyl iodide to be 0.26 in five experiments, with an average deviation of ±0.02. Two of these experiments were conducted with a screen of 15% transmission. Our value does not agree with the previous value reported at this wave length (0.41 at 2537 Å.[12]) and the reason for the discrepancy is not evident.

Relative quantum yields of the alkyl iodides at two volume per cent. in cyclohexane solution were determined only at 2537 Å., where no correction for complex formation is necessary and the iodine yield is linear with time of exposure. The measurements were made in comparison with an actinometer of pure ethyl iodide and the results are indicated in Fig. 3. Each value given is the average of at least two determinations.

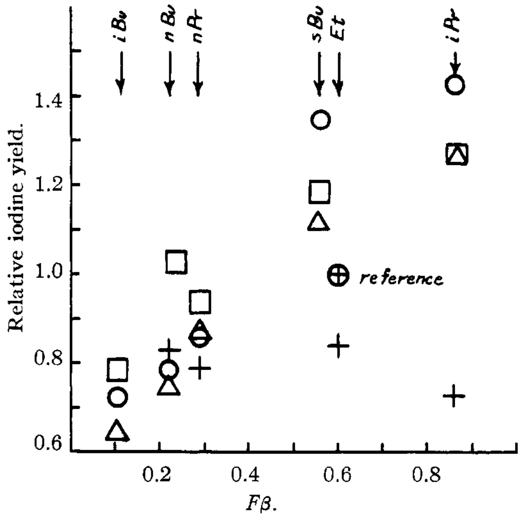

Fig. 3.—Relative iodine yields in photolysis and radiolysis of alkyl iodides: ○, pure liquids, 3260 Å.; □, pure liquids, 2537 Å.; △, pure liquids, radiolysis; +, solutions, 2537 Å.

Relative radiation yields for pure alkyl iodides were determined by timed exposures to X-radiation. Tests showed that the iodine production was strictly linear with time. Comparisons are based on equal exposures of one sample at a time and we have assumed that energy absorption is independent of the nature of the sample. This is justified in spite of the density variations of the samples, since X-rays of wave length used have a half-thickness less than one millimeter in the alkyl iodides. The relative yields observed are indicated in Fig. 3. Each value is the average of at least two determinations.

Products of Solution Photolysis.—We have briefly examined by mass spectroscopy the gaseous products of the photolysis of ethyl iodide in dilute solution. To facilitate complete collection of the gases, the solvent used was a high grade paraffin oil, which had a negligible vapor pressure at 100° and no detectable infrared absorption due to double bonds. After photolysis of a solution, the volatile products were withdrawn at 100°, followed by a further separation at Dry Ice temperature to remove ethyl iodide and iodine. We found: H_2, 11.8 μmoles; C_2H_4, 26.7 μmoles; C_2H_6, 10.9 μmoles; I_2, 18.5 μmoles.

In another experiment partially deuterated hexane was the solvent. This was prepared by low temperature catalytic deuteration of butylacetylene and mass analysis of the hexane indicated

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[12] B. M. Norton, THIS JOURNAL, 56, 2294 (1934).

chiefly hexane-d_5 with small amounts of more highly deuterated hexanes. With this solvent, quantitative separation and estimation of photolysis products was not possible, but examination of the gases and vapors collected indicated clearly that about 20% of the hydrogen was HD and that somewhat less than 10% of the ethane contained deuterium. Further examination of this reaction is in progress.

Discussion

In Fig. 3, the relative iodine yields measured under the four conditions are plotted *vs.* F_β, the fraction of hydrogen atoms beta to the C–I bond. The correlation obtained with the new data is not as clear as when the older quantum yields were used.[7] However, certain qualitative regularities appear. In photolysis of the pure liquids at 3260 Å. the primary iodides (*i*-Bu, *n*-Bu, *n*-Pr, Et) follow a linear progression and it may be that the secondary iodides (*s*-Bu, *i*-Pr) would follow a similar, though distinct, progression. In photolysis of the pure liquids at 2537 Å. and in radiolysis, only an irregular trend of increase in yield with F_β can be seen. Photolysis of alkyl iodides in hexane solution at 2537 Å. appears to be quite distinct from the three former processes in that variation of yield is practically absent.

The existence of the observed qualitative connection between structure and quantum yield is in keeping with the generalized mechanism given in the introduction, although it cannot be regarded as a proof in any sense. Indeed, the proposed mechanism, which rests more on the fact of equality of alkane and alkene than on the present data, raises the additional problem of the apparent inability of the hot alkyl radical to react with hydrogens in positions other than beta. This would produce diiodide and destroy the alkane–alkene equality. Since the facts are to the contrary, one can only presume that reaction at the β-position is favored energetically by concerted loss of the iodine atom and formation of the double bond, that is, simultaneous accomplishment of reactions 1 and 2.

The observed similarity of variation of radiation yield and quantum yield indicates that the product-forming processes must be similar, in spite of the obvious differences in the primary processes. It has been shown in these laboratories[13] that the principal radical produced in radiolysis of the simple alkyl iodides is that formed by breaking the C–I bond, rather than C–C or C–H bonds. Therefore the principal reactive species is the same as in photolysis and we may easily imagine that this radical is an energetic one when formed in the highly exothermic ion neutralization process.

Previously proposed mechanisms of photolysis of alkyl iodides in solution treated the solvent as formally inert, and centered attention upon reactions of the alkyl iodide or radicals formed from it.[14] This view seems no longer even formally satisfactory. The presence of hydrogen in the products of solution photolysis, the observation of HD production in a deuterated solvent, evidence for the formation of cyclohexene and cyclohexyl iodide,[5] and the behavior of the quantum yields all point clearly to a mechanism in which the solvent contributes to the products.

[13] L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

[14] W. West and J. Fitelson, THIS JOURNAL, **62**, 3021 (1940).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM WILLIAM H. NICHOLS CHEMISTRY LABORATORIES, NEW YORK UNIVERSITY]

The Photochemical Oxidation of *n*-Heptaldehyde[1]

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The photoöxidation of liquid *n*-heptaldehyde under conditions that ensure continuous saturation of the liquid by oxygen proceeds at a rate proportional to the pressure of oxygen (if this pressure be in excess of 400 mm.), at a rate proportional to the aldehyde concentration and at a rate proportional to the square root of the absorbed light intensity. When the oxygen pressure is between 200 and 400 mm., the oxidation rate is nearly independent of oxygen pressure. Below 200 mm. the reaction appears once again to be approximately of first order with respect to oxygen. The reaction is inhibited by the products of illumination formed either in the presence or in the absence of oxygen and is slightly inhibited by water. Acid and peracid are the main products but a little carbon dioxide is formed as well. The ten-degree temperature coefficient at constant pressure is 1.25.

The photochemical oxidation of aldehydes in the liquid phase has been studied by a number of investigators.[2] The oxidation appears to proceed chainwise with rather large quantum yields although in some instances the photal rates only slightly exceed thermal rates. The reactions are variously observed to proceed at rates proportional to the light intensity either to the one-half power or to the first power and to proceed at rates proportional to P^n where P is the oxygen pressure and n is a number between 0 and 1.

We have undertaken a study of *n*-heptaldehyde oxidation in the liquid state where the reaction is induced by ultraviolet radiation. We have examined the process as a function of (a) agitation, (b) oxygen pressure, (c) temperature, (d) rate of light absorption and (e) concentration of an inert

[1] This paper reports work done under contract with the Chemical Corps, Washington 25, D. C

[2] H. L. J. Bäckström, THIS JOURNAL, **49**, 1460 (1927); *Medd. K. Vetenskapsakad. Nobel Inst.*, **6**, No. 15 and 16 (1927); *Z. physik. Chem.*, **B25**, 99 (1934); H. L. J. Bäckström and H. A. Beatty, *J. Phys. Chem.*, **35**, 2530 (1931); C. E. H. Bawn and J. B. Williamson, *Trans. Faraday Soc.*, **47**, 721, 735 (1951); E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930); R. Cantieni, *Z. wiss. Phot.*, **36**, 119 (1937); H. R. Cooper and H. W. Melville, *J. Chem. Soc.*, 1984 (1951); W. P. Jorissen and P. A. A. van der Beek, *Rec. trav. chim.*, **45**, 245 (1926); *ibid.*, **49**, 138 (1930); E. Raymond, *J. chim. phys.*, **38**, 316, 421, 480 (1941).