TABLE I

ABSORPTION OF IODINE IN SOME "NON-ACTIVE" SOLVENTS

Solvent	Max., mμ	Ref.
Chloroform	520	2
Carbon tetrachloride	520	2
	517	3
	518	4
Carbon disulfide	520	2
	518	5

In the course of several investigations on the behavior of iodine in various solvents, the author noted two instances wherein iodine dissolved in solvents to give colors that were completely unexpected. This note is the result of these observations.

(A) Solvents Containing Nitrogen Atoms, Such as Pyridine, Quinoline, or Amines, Dissolve Iodine to form *brown* Solutions—These solvents are termed "active" solvents. Previous studies have revealed that in these cases the iodine reacts with the solvent.[6] When iodine was dissolved in completely fluorinated amines such as $(C_4F_9)_3N$, $(C_2F_5)_2N(C_3F_7)$ and $(C_2F_5)_3N$, the resulting solution was *violet*, showing an absorption maximum at 520 mμ. This band is consistent with other investigations for iodine in violet solutions (see Table I). Besides the maximum at 520 mμ, there is also observed a slight maximum at 380 mμ. The latter peak, however, is of much lower optical density and probably indicates some sort of interaction between the solvent and the iodine.

The surprising fact these fluorinated amines yield violet solutions becomes intelligible when one stops to consider the nature of these compounds. In these amines both steric and electronic effects must be considered. The three rather large alkyl groups surrounding the nitrogen atom and the presence of so numerous a group of highly electronegative fluorine atoms tremendously decrease the availability of the free pair of electrons present on the nitrogen atom. Hence, the nitrogen is no longer able to bond with the iodine as, for example, in the case of pyridine where the addition compound $(C_5H_5N)_2 \cdot I_2$ has been isolated.[7]

(B) Iodine Dissolves in Phosphorus(III) Chloride to Give *violet* Solutions.—Phosphorus(III) chloride is a highly reactive but unsaturated molecule. It readily adds oxygen from the air in the cold to form $POCl_3$. If refluxed with sulfur in the presence of aluminum chloride, PCl_3 readily adds sulfur to form $PSCl_3$.[8] Chlorine adds easily to PCl_3 to give PCl_5. Bromine also adds to PCl_3 to form the low melting solid PCl_3Br_2.[9] However, it has not been possible to add iodine to PCl_3 to form the hypothetical PCl_3I_2. The failure to isolate an adduct of iodine with PCl_3 may be due to the instability of the yet unknown PCl_3I_2. Another reasonable explanation would be that the iodine molecule is simply too large to approach close enough to the phosphorus atom to form an addition compound and thus increase the covalency of phosphorus to five.

That iodine does not react with PCl_3 is evidenced not only by the *violet* color of the resulting solution and the absorption band at 520–500 mμ but also by the persistence of the violet color even after refluxing iodine and PCl_3 for two hours.

Experimental[10,11]

Materials.—The completely fluorinated amines were obtained through the courtesy of the Minnesota Mining and Mfg. Co. and are colorless, odorless liquids. They were used directly as received. Iodine was J. T. Baker C.P. grade which was stored in a desiccator over phosphoric anhydride and used without further purification. Phosphorus(III) chloride was Merck reagent material, boiling range 75–78°, which was taken from a freshly opened bottle.

Apparatus and Procedure.—The spectrophotometric measurements were made on the Beckman quartz spectrophotometer, model DU. A pair of 1 cm. matched silica cells were used, one of which contained the solvent as the blank. The iodine solution was prepared prior to measurement and stored in the dark except for the period of use. Slight heating was necessary to effect solution of iodine in the amines. All solutions were *ca.* 10^{-3} *M*.

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(2) H. Rigollot, *Compt. rend.*, **112**, 38 (1891).

(3) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(4) W. R. Brode, *ibid.*, **48**, 1877 (1926).

(5) J. Groh, *Z. anorg. allgem. Chem.*, **162**, 287 (1927).

(6) J. Kleinberg, E. Colton, J. Sattizahn and C. A. VanderWerf, THIS JOURNAL, **75**, 442 (1953).

(7) M. Chatelet, *Compt. rend.*, **196**, 142 (1933).

(8) F. Knotz, *Österr. Chem. Z.*, **50**, 128 (1949).

(9) F. Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 1949, Fifth ed., p. 765.

(10) The assistance of Mr. E. G. Vassian in obtaining the measurements in PCl_3 is hereby ackowledged.

(11) The measurements of iodine in the fluorinated amines were performed by the author as part of his M.S. thesis, University of Kansas, 1952, under the direction of Dr. Jacob Kleinberg.

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The Oxidation of Oxalic Acid and Oxalate by Bromine and the Rôle of the Positive Bromine Ion

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Bromine in aqueous solution is known to oxidize oxalic acid and oxalates to carbon dioxide, itself being reduced to hydrobromic acid. No substitution occurs. The kinetics of this reaction have been investigated by several authors.[2–5] Josefowicz,[4] and later Griffith, McKeown and Winn[5] concluded the rate-determining step to take place between the acid oxalate ion and hypobromous acid. Liebhafsky and Makower[6] found for slightly acid solutions of hypobromous acid a rate constant agreeing well with this mechanism. More recently it has been pointed out by Hinshelwood[7] that the dependence of the rate of reaction on *p*H is equally compatible with the assumption that the rate-determining step takes place between the divalent oxalate ion and a bromine cation, and this reaction is shown to have a more plausible electronic mechanism than the reaction assumed previously. In the present paper the reaction has been reinvestigated under carefully controlled conditions at values of

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(1) To whom inquiries should be addressed.

(2) M. Roloff, *Z. physik. Chem.*, **13**, 346 (1894).

(3) A. Berthoud and H. Bellenot, *J. chim. phys.*, **21**, 308 (1924).

(4) E. Josefowicz, *Rocz. chem.*, **8**, 123 (1928).

(5) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932).

(6) H. A. Liebhafsky and B. Makower, *ibid.*, **29**, 597 (1933).

(7) C. N. Hinshelwood, *J. Chem. Soc.*, 694 (1947).

pH of 0.8 to 5, and the two mechanisms proposed in the literature are discussed.

Experimental

In order to avoid losses of bromine due to evaporation, the reaction mixtures were prepared in small glass-stoppered bottles (4–7 for each experiment). Only one sample was taken from each bottle at a suitable time after pipetting the necessary quantity of hypobromite solution into a known volume of a solution containing all the other components of the reaction mixture. The progress of the reaction was followed by iodometric titration, using 0.01 N thiosulfate.

The pH was kept constant by the use of buffer solutions (phosphate, chloroacetate or acetate), or, in the strongly acid range, by addition of perchloric acid. The pH was measured with a glass electrode and a Beckman Model G pH meter.

The hypobromous acid was prepared by mixing yellow mercuric oxide and bromine water, decanting and distilling *in vacuo*.

The experiments were carried out at 20 ± 0.1° (unless otherwise stated), in ordinary glass vessels, and in the absence of daylight and of direct electric light. Unless otherwise stated, the ionic strength was 0.15–0.24; changes within these limits had been found not to influence the reaction rate.

The initial bromine concentration was 4.8–6.3 mmoles l. $^{-1}$.

Results

The assumptions that hypobromous acid or the bromine cation are the reactive oxidizing agents *both* lead to the conclusion that the reaction rate must be equal to

$$\mathrm{d}x/\mathrm{d}t = k^*[\mathrm{Br_2}](b - x)/[\mathrm{Br^-}] \qquad (1)$$

where b is the initial concentration of the oxalate, x its decrease after a time t, and k^* a rate constant which depends only on pH.

Assuming the concentration of all other oxidizing species to be negligible in comparison with those of molecular bromine and the tribromide ion, we can get the following approximation

$$[\mathrm{Br_2}]/[\mathrm{Br^-}] = \frac{K_3(a - x)(K_3 + c + a + x)}{(c + 2x)[(K_3 + c + 2x)^2 - (a - x)(c + 2x)]} \qquad (2)$$

where a is the initial concentration of the oxidizing agent as obtained by titration, c the initial stoichiometric bromide concentration, and K_3 the dissociation constant of the tribromide ion.[8]

Inserting expression (2) into eq. 1 and integrating, we get

$$k^* = \frac{1}{t}\left[A\,\frac{1}{b - a}\ln\frac{a(b - x)}{b(a - x)} - B\ln\frac{b}{b - x} + C\ln\frac{K_3 + a + c + x}{K_3 + a + c} + 12x\right] \qquad (3)$$

where

$$A = (2a + c)(2a + c + K)$$

$$B = [2a(2a + 4b + 3K_3 + 4c) + 4b(3b + 4c + 2K_3) + c(7K_3 + 6c) + 2K_3^2]/(K_3 + a + b + c)$$

and

$$C = (3K_3 + 4a + 2c)(2K_3 + 2a + c)/(K_3 + a + b + c)$$

The experimental results can be summarized in the following statements: (a) The buffers used were found to exert no specific influence. (b) The reaction was confirmed to be of the first order with respect to total oxalate. (c) The effect of varying the initial bromide concentration is shown in Table I.[9] (d) The influence of pH is shown in Fig. 1, where log k^* is plotted *vs.* pH (circles) (initial bromide concentration: 41 mmole l. $^{-1}$). (e) In hypobromous acid solutions—in the presence of silver ion to prevent the formation of free bromine—the reaction is almost instantaneous at 0°.

TABLE I

INFLUENCE OF INITIAL BROMIDE CONCENTRATION ON THE RATE CONSTANT

pH	b, mmole l. $^{-1}$	c, mmole l. $^{-1}$	k^*, sec. $^{-1}$ mole $^{-1}$ l.^{1}
1.97[a]	39.8	20.6	1.06×10^{-5}
		41.2	0.91×10^{-5}[a]
		82.4	0.86×10^{-5}
2.64–2.68	19.9	5.15	4.39×10^{-5}
		10.3	4.29×10^{-5}
		20.6	4.13×10^{-5}
		41.2	3.81×10^{-5}
		82.4	3.83×10^{-5}
4.54–4.56[b]	9.96	20.6	4.00×10^{-4}
		41.2	3.87×10^{-4}
		82.4	3.72×10^{-4}
		164.8	3.81×10^{-4}

[a] In the experiments at low pH, k^* calculated for the first two or three measurements is somewhat higher than the value for the remainder of the reaction; only the latter is given in the table. [b] Ionic strength 0.28.

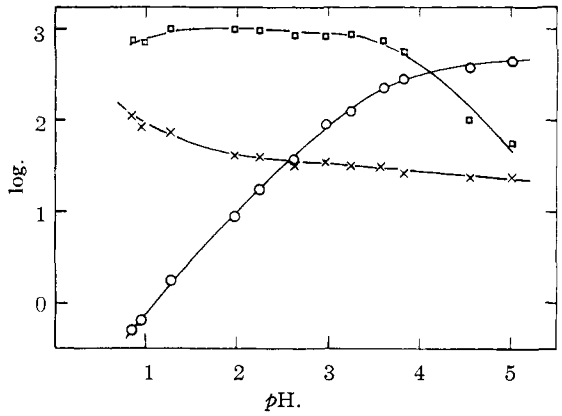

Fig. 1.—Dependence of rate constant on pH; log $k^* \times 10^6$ (circles), log $k^*F \times 10^{10}$ (crosses) and log $k^*a_\mathrm{H} \times 10^{10}$ (squares) *vs.* pH.

Discussion

An inspection of Table I shows the rate constant k^* to be almost constant for constant pH, over a fairly wide range of bromide concentration. Thus, *with respect to the dependence of the rate on bromide concentration, we corroborate on the whole the findings of previous authors,*[4–6] *and either hypobromous acid or the bromine cation may*

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[8] From the exact expression

$$1/[\mathrm{Br_2}] = \frac{[(c + x + a + K_3)^2 - 4(a - x)(c + 2x)]^{1/2} + c + 3x - a + K_3}{2K_3(a - x)}$$

one gets

$$1/[\mathrm{Br_2}] = \frac{(a - x)(c + 2x) + (c + 2x + K_3)(c + x + a + K_3)}{K_3(a - x)(c + x + a + K_3)}$$

(This expression is justified provided $4(a - x)(c + 2x)/(K_3 + c + a + x) << 1$, a condition which is easily seen to hold for all values of c.) Combining this expression with

$$[\mathrm{Br^-}]/[\mathrm{Br_2}] = 1 + (c + 3x - a)/[\mathrm{Br_2}]$$

we obtain (2). (The exact form of equation 1 can also be integrated; the result, however, is too cumbersome to be of any practical use.)

[9] The value of K_3 used for the evaluation of k^* is $5.8.10^{-2}$ (R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932); G. Jones and S. Bäckström, THIS JOURNAL, **56**, 1517 (1934)).

be the oxidizing agent (This conclusion is confirmed by the high rate of the reaction in hypobromous acid solution). In the former case, the meaning of k^* becomes

$$k^* = \frac{1}{F} \times \frac{K_{\mathrm{h}}K_3}{a_{\mathrm{H}}\gamma_{\mathrm{Br^-}}} [k_{(\mathrm{HBrO} + \mathrm{H_2C_2O_4})}\, a_{\mathrm{H}}{}^2\gamma_{\mathrm{HC_2O_4^-}} + k_{(\mathrm{HBrO} + \mathrm{HC_2O_4^-})}\, K_1a_{\mathrm{H}} + k_{(\mathrm{HBrO} + \mathrm{C_2O_4^=})}\, K_1K_2\gamma_{\mathrm{HC_2O_4^-}}/\gamma_{\mathrm{C_2O_4^=}}] \quad (5)$$

where K_{h} is the hydrolysis constant of bromine, a_{H} the hydrogen ion activity, K_1 and K_2 are the first and second dissociation constants of oxalic acid, respectively, the γ's activity coefficients, and

$$F = F(a_{\mathrm{H}}) = a_{\mathrm{H}}{}^2\gamma_{\mathrm{HC_2O_4^-}} + K_1a_{\mathrm{H}} + K_1K_2\gamma_{\mathrm{HC_2O_4^-}}/\gamma_{\mathrm{C_2O_4^=}}$$

Now, if all the three oxalate species were oxidized at approximately equal rates, k^*a_{H} would be independent of *p*H. In Fig. 1, the logarithm of this quantity is plotted *vs.* *p*H (squares), and is seen to decrease sharply at $p\mathrm{H} > 3.2$. On the other hand if, as assumed by previous authors,[4,5] only $k_{(\mathrm{HBrO} + \mathrm{HC_2O_4^-})}$ has an appreciable value, k^*F must be independent of *p*H. Figure 1 shows the logarithm of this quantity (crosses)[10] to be fairly constant, except at very low values of *p*H where it is higher than expected. This leads to the assumption that *not only the acid anion but also oxalic acid* (but *not* the divalent anion) *is oxidized by hypobromous acid at an appreciable rate.* A plot of k^*F *vs.* a_{H} for the *p*H range <3 gave a fairly straight line. Its intercept is $k_{(\mathrm{HBrO} + \mathrm{HC_2O_4^-})}K_{\mathrm{h}}K_3K_1/\gamma_{\mathrm{Br^-}}$ and its slope is $k_{(\mathrm{HBrO} + \mathrm{H_2C_2O_4})}K_{\mathrm{h}}K_3$,[11] whence we calculated $k_{(\mathrm{HBrO} + \mathrm{H_2C_2O_4})} = 222$ mole^{-1} l.^{1} sec.$^{-1}$ and $k_{(\mathrm{HBrO} + \mathrm{HC_2O_4^-})} = 282$ mole^{-1} l.^{1} sec.$^{-1}$.[12] Griffith, McKeown and Winn,[5] and Liebhafsky and Makower,[6] found 320 and 350 mole^{-1} l.^{1} sec.$^{-1}$, respectively, for the value of the rate constant at 20° (calculated from the data given for 21.5 and 0°, respectively), in good agreement with the above.

Let us now consider the second alternative, *i.e.*, that the bromine cation (or $\mathrm{H_2BrO^+}$) is the oxidizing agent. The rate-determining step would then consist in the oxidation of the mono- and the divalent oxalate anions; $k_{(\mathrm{Br^-} + \mathrm{HC_2O_4^-})}K_{\mathrm{Br_2}}K_1$ would take the place of $k_{(\mathrm{HBrO} + \mathrm{H_2C_2O_4})}K_{\mathrm{h}}$ of eq. 5, and $k_{(\mathrm{Br^+} + \mathrm{C_2O_4^=})}K_{\mathrm{Br_2}}K_2$ that of $k_{(\mathrm{HBrO} + \mathrm{HC_2O_4^-})}K_{\mathrm{h}}$, where $K_{\mathrm{Br_2}}$ is the ionization constant of bromine. This would lead to

$$k_{(\mathrm{Br^+} + \mathrm{HC_2O_4^-})} = 2.7 \times 10^{-5}/K_{\mathrm{Br_2}} \text{ mole}^{-1}\text{ l.}^1\text{ sec.}^{-1}$$

and

$$k_{(\mathrm{Br^+} + \mathrm{C_2O_4^=})} = 3 \times 10^{-2}/K_{\mathrm{Br_2}} \text{ mole}^{-1}\text{ l.}^1\text{ sec.}^{-1}$$

It easily can be seen that the two alternative assumptions lead to activated complexes having the same net charge and the same composition (with the possible difference of one molecule of water). It is this fact which makes the two mechanisms kinetically indistinguishable; factors such as bromide concentration, *p*H or ionic strength will influence the reaction rate in exactly the same way on either assumption.[13] We can, however, draw some conclusions from the value of the rate constants which the latter assumption would lead to. Now, the value of $K_{\mathrm{Br_2}}$ is not known. Various attempts to estimate its upper limit,[14,15] though based on doubtful assumptions, give results compatible with the value which Bell and Gelles[16] obtained from thermochemical data and a consideration of certain analogous reactions; they found $[\mathrm{H_2BrO^+}]\,[\mathrm{Br^-}]/[\mathrm{Br_2}] \approx 10^{-20}$, considered correct to within a few powers of ten. The value of $[\mathrm{Br^+}]\,[\mathrm{Br^-}]/[\mathrm{Br_2}]$ was found to be still much lower. Although the assumption of $\mathrm{H_2BrO^+}$ existing in solution seems to offer the most plausible explanation of certain reactions,[17,18] no *direct* experimental evidence for its existence is available. Accepting the experimental results of Körösy and Székely[19] we can conclude that $K_{\mathrm{Br_2}} < 3 \cdot 10^{-19}$ which again is compatible with Bell and Gelles' value. Using the latter, we obtain $k_{(\mathrm{Br^+} + \mathrm{C_2O_4^=})} \approx 10^{18}$ mole^{-1} l.^{1} sec.$^{-1}$. The fastest ionic reactions measured have a far lower rate constant, *e.g.*, 1.5×10^{11} for the reaction between $\mathrm{OH^-}$ and $\mathrm{H^+}$ and 10^{11} for that between $\mathrm{H^+}$ and $\mathrm{SO_4^=}$.[20] Values appreciably higher than these have been shown to be incompatible with theoretical considerations.[21-24] We can thus conclude that, because of its extremely low concentration, *positive bromine cannot be the main reacting species in the oxidation of oxalate,* a possibility suspected by Hinshelwood[7] himself.[25] An *intermediate* compound containing positive bromine has recently been suggested by Morgan[26] in an attempt to reconcile the two assumptions. This suggestion, concerning the details of the reaction path, does not affect our above conclusion on the *kinetics* of the reaction.

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(10) The values of the dissociation constants used for the calculation of F are $K_1 = 3.5 \times 10^{-2}$ (extrapolated to 20° from the values given by H. N. Parton and A. J. C. Nicholson, *Trans. Faraday Soc.*, **35**, 546 (1939)) and $K_2 = 5.4 \times 10^{-5}$ (H. S. Harned and L. D. Fallon, THIS JOURNAL, **61,** 3111 (1939)). The activity coefficients were calculated from an expression suggested by the work of Harned and Fallon, namely, $\log \gamma = -z^2A\sqrt{\mu}/(1 + \sqrt{2\mu})$. The change of K_3 with ionic strength was neglected.

(11) Assuming $\gamma_{\mathrm{HC_2O_4^-}} = \gamma_{\mathrm{Br^-}}$.

(12) Using $K_{\mathrm{h}} = 4.2 \times 10^{-9}$ (calculated from the formula given by H. A. Liebhafsky, THIS JOURNAL, **61**, 3513 (1939)).

(13) Theoretically, the two activated complexes might have different dipole moments, so that their equilibrium concentrations would be affected differently by changes in ionic strength. It can be shown, however, that such an effect would be extremely small (*cf.* J. G. Kirkwood, *Chem. Revs.*, **24**, 233 (1939)).

(14) P. D. Bartlett and D. S. Tarbell, THIS JOURNAL, **58,** 466 (1936).

(15) N. V. Sidgwick, "Chemical Elements and their Compounds," Oxford University Press, 1950, Part II, p. 1241.

(16) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

(17) D. H. Derbyshire and W. A. Waters, *ibid.*, 564 (1950).

(18) S. J. Branch and B. Jones, *ibid.*, 2317 (1954).

(19) F. Körösy and G. Székely, *Nature*, **168**, 77 (1951).

(20) M. Eigen, *Z. physik. Chem.*, *N.F.*, **1**, 176 (1954).

(21) J. Q. Umberger and V. K. La Mer, THIS JOURNAL, **67**, 1099 (1945).

(22) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(23) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1933).

(24) M. Eigen, *Discs. Faraday Soc.*, **17**, 194 (1954).

(25) It should be noted that the rate of recombination of positive and negative bromine ions must be considerably higher than the rate of the reaction between the positive bromine ion and the oxalate anion, since otherwise the latter reaction could not show second order kinetics. On this basis it can be shown easily that the reaction scheme involving positive bromine requires a rate constant still higher than 10^{18}.

(26) K. J. Morgan, *Quart. Rev.*, **8**, 123 (1954).