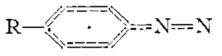
These predictions have been experimentally borne out recently by Hey and co-workers[28] and others. These workers have studied the homolytic reactivity of various benzene derivatives to attack by phenyl radicals and have found that, in fact, as predicted the reactivity postulated by Wheland and others is valid.[29] This work on the relative energies of the intermediates in homolytic aromatic substitutions is consistent with the half-wave values of the postulated intermediates, XI, obtained in the polarography of diazonium salts.



XI

A much more complete description of the reductions postulated in equation (a)[30] must await further intensive efforts to determine the reversibility or to eliminate the possibility of rate-controlled limiting currents[31] in the first polarographic waves. A study of the slope $i(i_d - i)$ is at present inconclusive.[32] Perhaps a more definitive test would be made by the method of oscillographic polarography. At this point we can only emphasize the necessarily qualitative nature of our arguments. Quantitative correlations between substituent effects and some polarographic property cannot be too enthusiastically pursued, especially in cases where the mechanism of the electrode process is not definitely known.

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[28] D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953); D. H. Hey, R. R. Augood and G. H. Williams, *J. Chem. Soc.*, 2094 (1952), 3412 (1953); R. L. Dannley and M. Sternfeld, THIS JOURNAL, **76**, 4543 (1954) and earlier papers.

[29] The relevance of these experiments may be in doubt in view of recent discoveries regarding radical complexes in solution. See C. E. Boozer and G. S. Hammond, THIS JOURNAL, **76**, 3861 (1954).

[30] We have not completely eliminated the possibility of equation (b) being the process for the first wave. The rationale for the stabilization of the various radicals may apply equally well to the substituted phenyl radicals. See S. G. Cohen and C. H. Wang, THIS JOURNAL, **75**, 5594 (1953).

[31] P. Delahay, *ibid.*, **73**, 4944 (1951).

[32] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York, N. Y., 1952.

NOTES

The Vapor Pressure of Polonium

BY LEROY S. BROOKS[1]

RECEIVED FEBRUARY 11, 1955

The vapor pressures of polonium between 0.3 and 90 mm. with corresponding temperatures of 438° and 745° have been measured by the method[2] employed to measure the vapor pressure of two other sixth-group elements, selenium and tellurium.

Experimental

Sample Preparation.—Polonium was vacuum-distilled seven times, reduced in a dry hydrogen atmosphere, and distilled into a quartz sample tube. The sample tube was attached to the vapor pressure apparatus which was outgassed for 48 hours at 780° while it was being evacuated to a pressure of 10^{-6} mm. The sample tube was opened to the vacuum system, the accumulated helium from the alpha decay was pumped off, and the polonium was volatilized into the sample bulb of the vapor pressure apparatus.

Pressure Measurement.—The temperature of the sickle gage was maintained at 770° during all of the measurements. During each set of measurements, the null position of the gage, which had a sensitivity of 0.03 mm. pressure per scale division deflection of the gage pointer, changed an amount equivalent to about 1 mm. The null position for each vapor pressure measurement was recorded as though the gage had drifted uniformly with time.

Temperature Measurement.—At the time of each pressure measurement, temperature measurements of the sample bulb containing the polonium and a copper block around the sample bulb revealed a temperature difference due to the energy from the decay of the polonium. This difference was about 6° at 400°, 4° at 580° and 2° at 740°. This difference decreased as the temperature increased because some of the polonium volatilized from the sample bulb to the gage.

Results

The least-squares representation of nine measurements of vapor pressures between 438 and 745° is

$$\log p = \frac{-5377.8 \pm 6.7}{T} + 7.2345 \pm 0.0068$$

when p is the pressure in mm., T is the absolute temperature, and the probable errors are as stated. These measurements were taken the first two days. Due to the decay products of the polonium or an impurity, measurements on the fourth, fifth, sixth and eighth days gave a lower vapor pressure curve each day.

From the above equation, the calculated boiling point is 962.04 ± 1.93°C. and the latent heat of vaporization is 24.597 ± 0.031 kcal./mole.

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[1] Ford Motor Company, Ford Scientific Laboratory, Dearborn, Michigan.

[2] L. S. Brooks, THIS JOURNAL, **74**, 227 (1952).

[3] Mound Laboratory is operated by Monsanto Chemical Company for the United States Atomic Energy Commission under Contract Number AT-33-1-GEN-53.

Iodine Solutions of Unexpected Color

BY ERVIN COLTON

RECEIVED JANUARY 26, 1955

It is well known that iodine in "non-active" solvents yields *violet* solutions[1] with an absorption maximum in the proximity of 520 mμ. In these solvents the iodine dissolves without reaction. Table I lists the absorption for iodine in three "non-active" solvents.

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[1] J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

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

BY Y. KNOLLER AND B. PERLMUTTER-HAYMAN[1]

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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).