to differ sharply for sodium *p*-toluenesulfonate. On the basis of the electrostriction of the solvent, all three neutral salt effects ought to be nearly the same. Neither of these hypotheses is consistent with the observed effects.

The present failure to observe a mass-law effect does not rule out the presence of a metastable reaction intermediate in the solvolysis of *s*-butyl bromide since the effect is a sufficient but not a necessary phenomenon. Our results are consistent with analogous observations on the solvolysis of *t*-butyl bromide[6,8] and chloride[9] where the mechanism is S_N1. Our results are not consistent with reports of small rate depressions (4–12%) due to added halide salts in the solvolysis of isopropyl bromide,[10] ethyl *p*-toluenesulfonate[11] and benzyl chloride[12] in partly aqueous media. While these rate depressions suggest that there is a mass-law effect, it must be admitted that, within present knowledge, they can also be accommodated as neutral salt effects.

Experimental Part

Materials.—*s*-Butyl bromide and isopropyl bromide, from Eastman Kodak Co., were dried over potassium carbonate and fractionated through a 30-plate all-glass column before use. Middle fractions with the following properties were used: *s*-butyl bromide, b.p. 90.6° (759 mm.), $n^{21.8}_D$ 1.4353; isopropyl bromide, b.p. 58.9° (754 mm.).

Sodium bromide was Baker and Adamson C.P. material and was dried at 110° before use. Sodium perchlorate was prepared halide-free by careful neutralization of Mallinckrodt 60% perchloric acid with J. T. Baker C.P. sodium hydroxide sticks to the phenolphthalein end-point. Concentration of the solution gave crystalline material which was washed with a little alcohol and dried to constant weight over magnesium perchlorate *in vacuo*. The dry salt contained less than 0.6% water by Karl Fischer titration for water. Sodium *p*-toluenesulfonate was prepared by careful neutralization of toluenesulfonic acid monohydrate with C.P. sodium hydroxide. It was purified several times by dissolving in water and reprecipitating with ethanol. Physical properties of the vacuum-dried salt: d^{25} 1.46; $\bar{V}_s^\circ$ 122.3 (water, 25.44°); 126.4 (75.00 wt. % ethanol, 25.44°). The salt contained less than 0.1% water.

The solvents redistilled water, absolute ethanol (<0.005% water by Karl Fischer titration), and 75.00% (by weight) ethanol in ethanol–water were prepared as described previously.[2] J. T. Baker "special" acetic acid was analyzed for water by freezing point determination, and enough Eimer and Amend C.P. acetic anhydride was added to make the resultant solvent 0.1 *M* in acetic anhydride. Sodium acetate solutions in this solvent were prepared by adding the required weights of reagent grade, dry sodium carbonate.

Rate Measurements.—Rates were measured by the usual sealed ampoule technique using the procedures described previously.[2,13] The vapor space in the ampoules was kept at less than 5% of the total volume to minimize errors due to volatilization of the alkyl halides. Measurements of temperature and time and methods of preparation and titration of the reaction mixtures met customary standards for precision work.

The kinetics was first order in 75.00% ethanol. In absolute ethanol, first-order rate constants decreased somewhat with time due to reaction of the hydrogen bromide product with the solvent and were extrapolated to zero time by a method described previously.[2,14] In the acetolysis experiments, initial concentrations of the alkyl halide were 0.2 and 0.1 *M*, and of the sodium acetate were 0.02 and 0.01 *M*. Over these ranges of concentration the kinetics was first order and there was no evidence of a second-order term due to direct reaction of alkyl halide with acetate ion even though the sodium acetate concentration varied in a typical run from 0.02 to 0.001 *M*.

Measurements of *R* for Salts.[15]—Refractive indices were measured with a Bausch and Lomb immersion refractometer; densities were measured with a 50-ml. pycnometer. The *R* values are accurate to about ±2%.

---

(8) O. T. Benfey, Ph.D. Thesis, University College, London, 1946.

(9) C. G. Swain and S. D. Ross, This Journal, **68**, 658 (1946).

(10) E. D. Hughes, C. K. Ingold and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

(11) G. W. Beste and L. P. Hammett, This Journal, **62**, 2481 (1940).

(12) H. R. McCleary and L. P. Hammett, *ibid.*, **63**, 2254 (1941).

(13) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(14) E. Grunwald and S. Winstein, *ibid.*, **69**, 2051 (1947).

(15) N. Bauer and K. Fajans, "Physical Methods of Organic Chemistry," A. Weissberger, editor, Interscience Publishers, Inc., New York, N. Y. 1949, Chapter 20.

CHEMISTRY DEPARTMENT
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

Polarographic Study of Various Diphenyl Disulfides

BY EUGENE L. COLICHMAN[1] AND DANIEL L. LOVE[2]

RECEIVED MAY 22, 1953

The biologically important cystine–cysteine system has been investigated by both potentiometric and polarographic methods. Kolthoff and Lingane[3] have summarized and discussed these investigations. It is seen that the disulfide linkage is usually reduced irreversibly to mercaptans at the dropping-mercury electrode. Additional polarographic results on disulfides have been reviewed by Wawzonek.[4] The present investigation concerns the polarography of various diphenyl disulfides.

Experimental

Previously reported[5,6] polarographic investigations from this Laboratory indicate the nature of the equipment and materials employed. Measurements were at 25.00 ± 0.05° and at a drop-time equal to 3.00 sec. The polarographic half-waves on dilute solutions reported in Table I did not require maxima suppressors.

The following buffer solutions were used: (a) *p*H 6.2, buffer in 95% ethanol was 0.06 *M* sodium phthalate; (b) *p*H 7.0, buffer in 50% ethanol was 0.05 *M* potassium dihydrogen phosphate and 0.006 *M* sodium hydroxide; (c) *p*H 7.0, buffer in 95% ethanol was 0.025 *M* potassium acetate and 0.041 *M* acetic acid; (d) *p*H 8.0, buffer in 95% ethanol was 0.10 *M* potassium acetate and 0.01 *M* acetic acid. Buffer values given are reproducible, however, since *p*H measurements were made with an ordinary Beckman, Model G, *p*H Meter, values given are not absolute. This is due to the uncertain liquid junction potential existing between the alcohol solutions and the reference glass electrode–aqueous solution used in making these *p*H measurements. The "*m*" value for the capillary was 2.00 mg. per second. $m^{2/3}t^{1/6} = 1.907$ mg.$^{2/3}$ sec.$^{-1/2}$ (open circuit) at $h = 64$ cm.

***o,o'*-Ditolyl Disulfide.**—This compound was prepared by the oxidation[7] of *o*-thiocresol (Eastman Kodak Co., White Label grade) with ferric chloride. The separated oily solid was purified by dissolving the by-product ferrous chloride in water. The disulfide was then recrystallized from ethanol. Yield was 43.7%. M.p. (reported)[8] was 38–39°; (found) 38°.

***m,m'*- and *p,p'*-Ditolyl Disulfides.**—Same procedure was used for preparing these compounds as employed with the

---

[1] North American Aviation, Inc., Atomic Energy Research Dept., Downey, California.

[2] Work described herein was from a thesis submitted by D. L. Love to the University of Portland in partial fulfillment of the requirements for the Degree of Master of Science.

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, Chap. XXX.

(4) S. Wawzonek, *Anal. Chem.*, **21**, 61 (1949).

(5) E. L. Colichman, This Journal, **74**, 722 (1952).

(6) E. L. Colichman and H. P. Maffei, *ibid.*, **74**, 2744 (1952).

(7) T. Zincke and W. Frehneberg, *Ber.*, **43**, 837 (1910).

(8) F. Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

o-isomer. Meta isomer: yield 44.5%, m.p. (reported)[9] −22°, (found) −21°; para isomer: yield 99.6%, m.p. (reported)[10] 47°, (found) 46°.

***o,o'*-Dimethoxydiphenyl Disulfide.**—0.24 mole of *o*-anisidine (Eastman Kodak Co., White Label grade) was dissolved in a solution of 150 g. of concd. hydrochloric acid and 450 g. of water. Enough sodium nitrite was added to give a positive starch–iodide test. While keeping the diazotized product cold (0°), 0.25 mole of 10% aqueous solution of sodium disulfide was added dropwise with constant shaking. The product formed was dissolved immediately while still cold in ethanol and then recrystallized from this solution. Unless this is done rapidly, the product will become tarry. The disulfide was freed from any ferrous chloride by the same procedure as described above. Finally it was recrystallized again from ethanol. Yield was 8.9%, m.p. (reported)[11] 119°, (found) 119°.

***m,m'*- and *p,p'*-Dimethoxydiphenyl Disulfides.**—Procedure for preparation was the same as with the ortho isomer. Meta isomer: yield 9.0%, m.p. (found) 109°. Combustion analyses for carbon, hydrogen and sulfur agreed well with theory. *m*-Anisidine needed in preparing this isomer was obtained from *m*-aminophenol (Eastman Kodak Co., Yellow Label grade) by the procedure of Reverdin and Luc.[12] Para isomer: yield 7.4%, m.p. (reported)[11,13] 120°, (found) 119°.

The diphenyl disulfide used polarographically was Eastman Kodak Co., White Label grade.

Results and Discussion

In acidic and basic buffered and unbuffered alcoholic solutions all the diphenyl disulfides investigated (see Table I) were found to be irreversibly reduced at the dropping-mercury electrode as evidenced by the linear slope analysis plots obtained with slope values in the range 0.13 to 0.28. Similar slope analysis considerations showed that the methoxy substituted diphenyl disulfides are reduced reversibly in 50% alcohol *p*H 7 phosphate buffer solutions. Slope values equal to 0.027 to 0.031 were obtained for the various methoxy isomers indicating that 2 electrons are involved in the reduction as to be expected on the basis of: $RSSR + 2H^+ + 2e^- = 2RSH$. The unsubstituted and methyl substituted diphenyl disulfides are irreversibly reduced in 50% alcohol *p*H 7 phosphate buffer solutions. Slope values for the linear plots of $E_{d.e.}$ *vs.* $\log I/(I_d - I)$ in these cases were 0.09 to 0.11.

TABLE I

HALF-WAVE POTENTIALS (VOLT *vs.* S.C.E.) OF THE DIPHENYL DISULFIDES IN ALCOHOL

	*p*H				
	6.2	7.0[a]	7.0[b]	8.0	0.1 M NaOH
Unsubst.					
0.0003 M	−0.52		−0.46		
.001		−0.53		−0.60	−0.62
o,o'-Dimethyl-					
0.0003 M	− .55		− .44		
.001		− .52		− .57	− .63
m,m'-Dimethyl-					
0.0003 M	− .56		− .47		
.001		− .55		− .61	− .64
p,p'-Dimethyl-					
0.0003 M	− .56		− .47		
.001		− .56		− .62	− .66
					0.02 M NaOH
o,o'-Dimethoxy-					
0.0003 M	− .97	− .88[c]	− .58		
.001		−1.02		− .85	−0.75
m,m'-Dimethoxy-					
0.0003 M	− .97	−0.86[c]	− .58		
.001		−1.02		− .85	− .82
p,p'-Dimethoxy-					
0.0003 M	− .94	−0.88[c]	− .59		
.001		−1.04		− .91	− .80

[a] *p*H 7.0, acetate buffer in 95% ethanol. [b] *p*H 7.0, phosphate buffer in 50% ethanol. [c] $E_{d.e.}$ *vs.* mercury pool, volt.

The marked influence of the methoxy group is demonstrated further by the fact that only these substituted disulfides yielded catalytic hydrogen waves (excessive I_d/C values) in 95% alcohol in all except the sodium hydroxide solutions. Diffusion currents of the unsubstituted and methyl substituted diphenyl disulfides were found to be proportional to the concentrations of reducible materials, at least over the 0.0003 to 0.0050 M range in all the alcoholic solutions investigated here. For example, the average I_d/C values in μa./mM for diphenyl disulfide were: 5.05 in 95% alcohol, *p*H 7 acetate buffer; 3.20 in 50% alcohol, *p*H 7 phosphate buffer; 5.46 in 95% alcohol, *p*H 8 acetate buffer; and 5.00 in 0.10 M sodium hydroxide in 95% alcohol.

It is seen that solvent, buffer components, *p*H and nature of the substituent group can all influence the polarographic results obtained on the various diphenyl disulfides.

Acknowledgment.—We wish to express our appreciation to the Research Corporation for supporting this investigation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PORTLAND
PORTLAND 3, OREGON

---

[9] H. Hubner, *J. Chem. Soc.*, **27**, 60 (1874).

[10] W. M. Ziegler and R. Connor, THIS JOURNAL, **62**, 2596 (1940).

[11] L. Gattermann, *Ber.*, **32**, 1136 (1899).

[12] F. Reverdin and A. Luc, *ibid.*, **47**, 1537 (1914).

[13] F. Fichter and W. Tamm, *ibid.*, **43**, 3032 (1910).

Synthesis of Fluorocarbon Iodides Without the Use of Liquid Solvents or Diluents

BY G. H. CRAWFORD AND J. H. SIMONS

RECEIVED JUNE 16, 1953

A method of preparing fluorocarbon iodides which consisted of the decarboxylation of the silver salt of a fluorocarbon carboxylic acid (S) in the presence of iodine was developed by Simons and Brice.[1] The reaction mixture was kept in suspension in a fluorocarbon diluent by means of mechanical stirring. The process was carried out under strictly anhydrous conditions.

Others[2-4] prepared the iodides by heating intimate mixtures of (S) and iodine.

The method herein reported consists of bringing the iodine vapors in contact with (S) under controlled conditions of temperature and pressure without a solid or liquid diluent being present. A sharp reaction zone progresses through the material until (S) is consumed. The fluorocarbon iodide passes from the reactor and is collected as in the original method. Power stirring, and pre-purification and drying of the iodine, as well as the limitations imposed by the diluent, are eliminated. Maintenance of anhydrous conditions, recovery of silver

---

[1] J. H. Simons and T. J. Brice, U. S. Patent 2,554,219, May 21, 1951.

[2] A. L. Henne and W. G. Finnegan, THIS JOURNAL, **72**, 3806 (1950).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

[4] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).