308 mμ as erroneously printed in the first paper of this series).

Analyses.—Aliquot portions of a stock solution of fluoroplatinic acid were titrated with 0.0219 *N* sodium hydroxide. The course of the reaction was followed with a Model G Beckman *p*H meter. The titation curve was typical of the reaction between a strong base and a strong acid.

Aliquot portions of the same stock solution were analyzed for platinum content by reduction of the acid with hydrazine. The results confirmed the existence of the dibasic fluoroplatinic acid.

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Some Solvent and Salt Effects in the Solvolysis of *s*-Butyl Bromide[1]

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The solvolysis of *s*-alkyl halides proceeds by a mechanism which cannot be classified as either S_N1 or S_N2.[2,3] On the one hand, there is stereochemical evidence of partial racemization in the solvolysis of 2-bromoöctane[4] and probably of *s*-butyl *p*-toluenesulfonate,[5] suggesting the existence of a metastable solvolysis intermediate. On the other hand, there is kinetic evidence for isopropyl bromide which indicates the nucleophilic participation of solvent in systems such as ethanol–water.[2]

We now wish to report some rate studies on the solvolysis of *s*-butyl bromide, a representative member of this interesting group of reagents. First-order rate constants have been measured in a number of solvents, including acetic acid, ethanol and ethanol–water mixtures, and are equal, within a few per cent., to the corresponding rate constants for isopropyl bromide. The results are shown in Table I. Without repeating the analysis of rate constants which was made previously for isopropyl bromide,[2] we may therefore conclude that there is nucleophilic participation of solvent in the solvolysis of *s*-butyl bromide in systems such as ethanol-water.

TABLE I

COMPARISON OF SOLVOLYSIS RATE CONSTANTS FOR ISOPROPYL AND *s*-BUTYL BROMIDE

Solvent	Temp., °C.	$10^6 k$ (sec.$^{-1}$) for Isopropyl bromide	$10^6 k$ (sec.$^{-1}$) for *s*-Butyl bromide
Abs. EtOH[a]	50.0	0.112	0.098
80 Vol. % EtOH[a]	50.0	1.18	1.06
60 Vol. % EtOH[b]	80.0	70.6	74.1
Glacial HOAc	100.0	0.89	0.96

[a] Data for isopropyl bromide in abs. and 80% EtOH were taken from ref. 2. [b] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948).

We also tried to obtain evidence for a metastable reaction intermediate by looking for a mass-law effect.[6] The pertinent data in 75.00 wt. % ethanol-water at 50° are shown in Table II. The Table lists the rate constants for solvolysis in the presence of varying concentrations of salt for sodium bromide, a common ion salt,[6] and for sodium perchlorate and sodium *p*-toluenesulfonate, two unreactive "neutral" salts. The rate constants are generally based on at least two rate runs, and their probable errors are about 1.6%. If, to a first approximation, the neutral salt effects are treated as colligative functions of the ionic strength, the rate constants at a given salt concentration should be equal for the two neutral salts, and possible decreases below this value due to sodium bromide should measure the magnitude of the mass-law effect. As is shown in the table, the rate constants at a given ionic strength are indeed approximately equal for the neutral salts, but are greater rather than less in the presence of sodium bromide. Thus there is no evidence for a mass-law effect.

TABLE II

EFFECT OF ADDED SALTS ON THE SOLVOLYSIS RATE OF *s*-BUTYL BROMIDE IN AQUEOUS ETHANOL, 75.00 WEIGHT % ETHANOL,[a] 50.00 ± 0.02°

Salt	*M*	$10^6 k$ (sec.$^{-1}$)[b]	Salt	*M*	$10^6 k$ (sec.$^{-1}$)[b]
None	..	1.06	$NaClO_4$	0.18	1.09
NaBr	0.20	1.20		.45	1.0
	.50	1.17		.80	1.09
	.77	1.19	NaOTs	.21	1.08
				.43	1.04

[a] 79.22 vol. %. [b] Probable errors in *k*: 0.45 *M* $NaClO_4$, 4%; all other values, 1.6%.

Within the limits of present knowledge, this conclusion cannot be reversed if the salt effects are treated as specific rather than colligative. In aqueous solution salt effects on non-electrolytes often parallel either the salt polarizability or the electrostriction of the solvent due to the electrolyte.[7] The relevant values of the apparent molar refractions, *R*, and of $(\bar{V}_s^\circ - V_s)$ are summarized in Table III. The values are apparently not very sensitive to change in solvent from water to 75.00% ethanol, as is illustrated for sodium *p*-toluenesulfonate. It is seen that, on the basis of the molar refractions, the neutral salt effects ought to be nearly equal for sodium bromide and sodium perchlorate but ought

TABLE III

Salt	Solvent	$(\bar{V}_s^\circ - V_s)^a$	*R*
NaBr	HOH	-10.5^b	12.78^d, 12.8^c
$NaClO_4$	HOH	-7.5^b	13.32^d
NaOTs	HOH	-10^c	43.4^c
	75.00% Ethanol	-7^c	43.2^c

[a] $\bar{V}_s^\circ$ = partial molar volume of salt in very dilute solution. V_s = molar volume of (metastable) pure liquid salt. [b] Taken from W. F. McDevit and F. A. Long, THIS JOURNAL, **74**, 1773 (1952). [c] Own measurements at 25.44°. For V_s use molar volume of crystalline solid salt. (See B. Lunden, *Z. physik. Chem.*, 192, 345 (1943).) [d] Taken from K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).

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(1) Supported in part by the Research Corporation and by the Office of Ordnance Research, U. S. Army.

(2) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

(4) E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

(5) J. Kenyon, H. Phillips and V. P. Pittman, *ibid.*, 1072 (1935).

(6) (a) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 979 (1940); (b) O. T. Benfey, E. D. Hughes and C. K. Ingold, *ibid.*, 2488 (1952).

(7) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

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.), $n^{21.8}\text{D}$ 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%.

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[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.

Polarographic Study of Various Diphenyl Disulfides

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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

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[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).