[Contribution from the Chemistry Department of the University of Portland]

POLAROGRAPHY OF SULFONIUM SALTS[1]

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Polarographic studies of sulfur linkages other than the disulfide group have been reported. Schwabe (1) studied the polarographic reduction of *p*-rhodaniline. Bonner and Kahn (2) investigated the polarography of several carbohydrate analogs of S-alkylthiuronium salts. The present report deals with the polarographic reduction of trimethylsulfonium and cresyldimethylsulfonium salts.

Early reports on the polarographic reduction of substituted ammonium and quaternary ammonium salts were made by Podrauzek (3) and Pech (4). The poorly defined waves found by Pech for quaternary ammonium salts suggested (5) the possibility that these reductions correspond merely to the decomposition voltage of water. Van Rysselberghe and McGee (6) showed that specific half-wave potentials can be found for different ammonium and quaternary ammonium ions. This later work (6) seems to indicate a "true" polarographic reduction for quaternary ammonium salts at the dropping mercury electrode.

A previous report (7) from this laboratory dealt with the mechanism of the polarographic reduction of iodonium salts. The present investigation of sulfonium salts extends the polarographic study of "onium" compounds.

Symmetrically substituted sulfonium salts are easily prepared by the usual bimolecular S_N2 "onium" reaction. If the sulfonium salt is not symmetrical, it will usually decompose partially into other more stable sulfonium salts that have smaller molecular weights and are symmetrically substituted. Disproportionation and recombination finally yields an equilibrium mixture if sufficient time is allowed. Ray and Levine (8) discuss the equilibrium problem in preparing "mixed" sulfonium salts. Alkyl and aralkyl halides or methosulfates formed in disproportionation reactions are capable of exchange type recombinations, thereby yielding "mixed" water-soluble sulfonium salts. By-products that are water-insoluble are often formed if aryl groups are involved in the reaction. In the present case, sulfate analyses indicate that the water-soluble layers correspond to two-thirds *o*- and *m*-cresyldimethylsulfonium methosulfates and one-third trimethylsulfonium methosulfate. No attempt has been made to separate these similarly soluble salts from their mixtures. Polarographic results on these naturally formed mixtures and on pure trimethylsulfonium salts confirm the conclusions indicated by sulfate analyses.

Typical composite recorded sulfonium salt polarograms are shown in Figure 1. Pertinent polarographic results are given in Tables I and II. Pure trimethyl-

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sulfonium methosulfate or iodide at 0.001 *M* in aqueous *p*H 8 solutions gave a single, well defined wave at −1.82 *v. vs* S.C.E. This value is in good agreement with that found for the second wave in the *o*- and *m*-cresyldimethylsulfonium salt solutions, and substantiates the presence of trimethylsulfonium salt as discussed above.

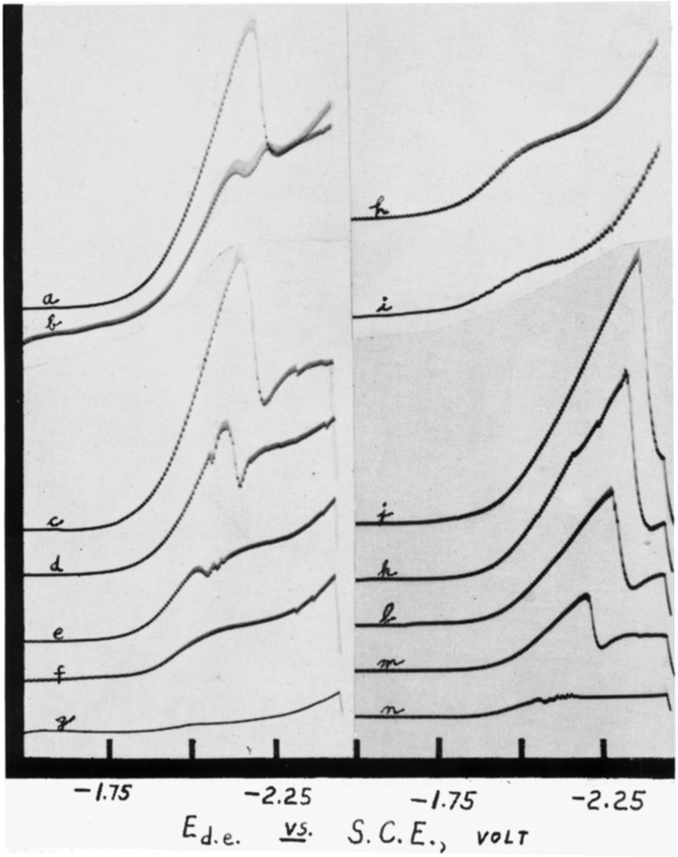

Fig. 1. Trimethylsulfonium Salts in 95% Ethyl Alcohol with Tetraethylammonium Bromide as Supporting Electrolyte at 0.04 *M* in (a–g), 0.02 *M* in (h) and (i), and 0.10 *M* in (j–n). (a–g) and (j–n) are iodide salt, (h) and (i) are methosulfate salt. (a) 0.002 *M* salt, (b) 0.002 *M* salt with 0.012% gelatin, (c) 0.002 *M* salt with 0.002 *M* tetradecyltrimethylammonium bromide (TTAB), (d) 0.0015 *M* salt with 0.0015 *M* TTAB, (e) 0.001 *M* salt with 0.001 *M* TTAB, (f) 0.0005 *M* salt with 0.0005 *M* TTAB, (g) supporting electrolyte alone, (h) 0.0005 *M* salt, (i) 0.00025 *M* salt, (j) 0.005 *M* salt, (k) 0.004 *M* salt; (l) 0.003 *M* salt, (m) 0.002 *M* salt, (n) 0.001 *M* salt. (a–g) f = 1/50, (h–i) f = 1/20, (j–n) f = 1/200.

Acid or neutral aqueous solutions of the cresyldimethylsulfonium salts yield catalytic hydrogen waves (9) that proceed simultaneously with the main reduction waves. In neutral solutions these catalytic waves are clearly separated from the true sulfonium reduction waves. In acid solutions these hydrogen waves merge with the main reduction waves. The non-constant I_d/C values (Table II) both in acid solutions and at the higher sulfonium salt concentrations in neutral solutions are attributed to the catalytic hydrogen wave phenomenon.

In the presence of adequate[4] but not large excess quantities of gelatin, cresyl sulfonium salt maxima are nicely suppressed without an appreciable effect on the height of the wave. When tetradecyltrimethylammonium bromide was used as a suppressor at *p*H 5 to 7, the reduction wave was enhanced about 15- or 20-fold, characteristic of an exalted catalytic hydrogen wave. The specific influence of solvent, *p*H, and nature of suppressor are all important in determining the extent of the catalytic hydrogen wave phenomenon.

TABLE I

HALF WAVE POTENTIALS ($-E_{1/2}$ *vs.* S.C.E.) AND SLOPE ANALYSES[a] OF THE VARIOUS SULFONIUM SALT WAVES

SALT	AQUEOUS SOLUTIONS[b]						
	*p*H			0.1 *M* NaOH			
	5.0	7.0	8.0				
0.00066 *M* *o*-cresyldimethylsulfonium methosulfate and	1.50 (.110) & CHA	1.51 (.155) & CHA	1.44 (.137)	1.45 (.106)			
0.00033 *M* trimethylsulfonium methosulfate	no wave	no wave	1.82 (.113)	no wave			
0.00066 *M* *m*-cresyldimethylsulfonium methosulfate and	1.50 (.135) & CHA	1.53 (.144) & CHA	1.53 (.143)	1.50 (.134)			
0.00033 *M* trimethylsulfonium methosulfate	no wave	no wave	1.85 (0.100)	no wave			
					90.5% DIOXANE SOLUTIONS[c]		
					0.02 *M* TEAB	0.05 *M* TEAB	
0.00100 *M* *p*-cresyldimethylsulfonium methosulfate	1.50 (.139) & CHA	1.55 (.104) & CHA	1.56 (.124)	1.57 (.122)	2.48 (.310)	1.76 (.370)	
					95% ETHANOL SOLUTIONS		
					0.05 *M* LiCl	0.1 *M* NaOH	0.02 *M* TEAB
0.001 *M* trimethylsulfonium methosulfate or iodide	no wave	no wave	1.82 (.192)	no wave	2.00 (.141)	1.33 (.184)	1.94 (.165)

CHA = catalytic hydrogen wave. TEAB = tetraethylammonium bromide. [a] Numbers in parentheses indicate slopes. [b] *p*H 5 contained 0.01% gelatin; *p*H 7 and 8 and 0.1 *M* aq. NaOH contained 0.006% gelatin. [c] Trimethylsulfonium salts showed no reduction waves in dioxane.

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[4] The pronounced influence of incorrect quantities of maxima suppressors has been demonstrated previously, see refs. 11, 12.

The slopes found (Table I) for the reduction waves of all the sulfonium salts in water, 95.5% ethanol (D = 26.4),[5] and 90.5% dioxane (D = 5.8)[6] are considerably above 0.059 and indicate irreversible reactions in all cases. Increasing *n* values indicate that these reductions become more irreversible in solvents of lower dielectric constant.

TABLE II

CONCENTRATION STUDIES ON VARIOUS SUBSTITUTED SULFONIUM SALTS

SALT	SUPPORTING ELECTROLYTE	CONC. OF SALT, *M*	CONC. OF GELATIN, %	$-E_{\frac{1}{2}}$ *vs.* S.C.E.	I_d/C, $\frac{\mu A}{mM}$
p-Cresyldimethyl	Aq. *p*H 5.0	0.0050	0.0160	1.50	15.0
		.0040	.0128	1.48	16.0
		.0030	.0096	1.47	17.0
		.0020	.0064	1.46	25.0
		.0010	.0032	1.45	49.3
	Aq. *p*H 7.0	.0050	.015	1.60	7.20
		.0040	.012	1.59	7.65
		.0030	.009	1.58	8.93
		.0020	.006	1.57	8.93
		.0010	.003	1.56	8.85
	Aq. *p*H 8.0	.0050	.020	1.60	5.50
		.0040	.016	1.59	5.42
		.0030	.012	1.58	5.50
		.0020	.008	1.57	5.42
		.0010	.004	1.55	5.43
	Aq. 0.1 *M* NaOH	.0050	.050	1.55	4.53
		.0040	.040	1.53	4.61
		.0030	.030	1.52	4.60
		.0020	.020	1.51	4.60
		.0010	.010	1.50	4.60
	90.5% dioxane, 0.05 *M* TEAB	.0025		2.57	3.60
		.0020		2.30	3.60
		.0015		2.03	3.52
		.0010		1.76	3.56
Trimethyl	95% alc., 0.04 *M* TEAB	.0020	.0020 *M*[a]	1.95	4.96
		.0015	.0015	1.95	4.95
		.0010	.0010	1.95	5.04
		.0005	.0005	1.95	4.96
	95% alc., 0.1 *M* TEAB	.0050		1.96	3.25
		.0040		1.96	3.30
		.0030		1.96	3.26
		.0020		1.96	3.12
		.0010		1.96	3.17

TEAB = tetraethylammonium bromide. [a] Tetradecyltrimethylammonium bromide is used as a suppressor here.

A greater stability toward reduction was noted for trimethylsulfonium ion as compared to cresyldimethylsulfonium ions in aqueous solutions. Trimethyl-

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[5] Dielectric constant data from Akerlof, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

[6] Dielectric constant data from Kraus and Fuoss, *J. Am. Chem. Soc.*, **55**, 21 (1933).

sulfonium ion could not be reduced before the water decomposition wave in neutral or acid aqueous solutions. The use of tetraethylammonium bromide as a supporting electrolyte in alcohol gives the best defined waves for the reduction of trimethylsulfonium salts. No reduction at all was found for trimethylsulfonium salts in 90.5% dioxane while *p*-cresyldimethylsulfonium methosulfate showed satisfactory polarographic waves (see Table II). These results further substantiate the greater stability toward reduction exhibited by the trimethylsulfonium ion.

The diffusion current of trimethylsulfonium iodide in alcohol solutions containing tetraethylammonium bromide as a supporting electrolyte was found to be proportional to the concentration of reducible material at least over the range tested, 0.0005—0.0050 *M*. A similar constancy of I_d/C (see Table II) was found for *p*-cresyldimethylsulfonium methosulfate in alkaline aqueous solutions, buffered or unbuffered.

Wave heights obtained for the reduction of either trimethylsulfonium iodide or methosulfate in alcohol are approximately twice those obtained for the first reduction waves of diphenyliodonium iodide under similar conditions using the same capillary. Previously (7) it was shown that the first reduction wave of diphenyliodonium iodide involves *one* electron. Based[7] on the assumption that the two comparable "onium" ions have similar diffusion coefficients, the polarographic reduction in the case of sulfonium salts is seen to involve *two* electrons.

EXPERIMENTAL

o-Cresyldimethylsulfonium methosulfate. o-Thiocresol (Eastman Kodak Co. White Label) (50 g., 0.403 mole) was dissolved in 100 g. of a 50% ethanol solution. Then (51 g., 0.405 mole) of methyl sulfate (Eastman Kodak Co. Yellow Label) was added in 5-ml. portions. The solution was made basic with c.p. sodium carbonate (J. T. Baker's Co.) after each 5-ml. portion of methyl sulfate was added. The solution was refluxed for about ten minutes following each addition. After refluxing for a total of three hours, the *o*-cresylmethyl sulfide was extracted with c.p. ether (J. T. Baker's Co.) and then vacuum-distilled. The boiling point of the sulfide was 80–90° at 10 mm. The yield was 42 g. (0.303 mole, 75%). The sulfide (10 g., 0.0725 mole) was sealed in a tube at 40° with 9.13 g. of methyl sulfate (0.0725 mole). The solution slowly separated into two layers, and at the end of two months these layers apparently had come to equilibrium. The upper layer (4.1 g.) was insoluble in water. The lower layer (12.8 g.) was soluble in water. By sulfate analysis (discussed below), it was inferred that the lower layer contained two-thirds of the desired sulfonium salt (44.6% yield).

m-Cresyldimethylsulfonium methosulfate. This salt was prepared by the same method as was employed with the *ortho* isomer. Using an equivalent amount of materials, 44 g. (79% yield) of *m*-cresylmethyl sulfide were obtained, b.p. 120–30° at 10 mm. The upper layer (3.1 g.) was insoluble in water. The lower layer (16.0 g.) was soluble in water. Sulfate analysis again was used to show that this lower layer contained two-thirds of the desired sulfonium salt (55.5% yield).

p-Cresyldimethylsulfonium methosulfate. Eastman Kodak Co. White Label *p*-cresylmethyl sulfide (10 g., 0.0725 mole) was sealed in a tube with 9.13 g. of methyl sulfate (0.0725 mole) for 14 hours at 40°. A white crystalline product was formed that was soluble in water. No

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[7] Muller in Weissberger's, *Physical Methods of Organic Chemistry*, 2nd Ed., Interscience Publishers, Inc., New York, 1949, Vol. I, part II, Chap. 28, p. 1807, suggests this general method of deducing unknown *n* values.

water-insoluble fraction was obtained here; the yield was 19.1 g. By sulfate analysis, it was shown that the product was the desired sulfonium salt in substantially 100% yield.

Trimethylsulfonium iodide. Eastman Kodak Co. White Label dimethyl sulfide (10 g., 0.161 mole) was heated to 40° in a sealed tube for one week with 24.6 g. of Eastman Kodak Co. White Label methyl iodide (0.173 mole). The white crystalline product formed was filtered, washed with ethanol, and recrystallized from ethanol. M.p. reported (10) 203–207°, found 202–204°. The yield was 24 g. (73.0%).

Trimethylsulfonium methosulfate. Dimethyl sulfide (5 g., 0.081 mole) was heated to 40° in a sealed tube for one week with 10.2 g. of methyl sulfate (0.081 mole). The white crystalline product formed was filtered, washed with ethanol, recrystallized from c.p. ethyl acetate (J. T. Baker's Co.), and dried over 85% phosphoric acid. The yield was 14 g. (92.0%). On metathesizing a small portion of the methosulfate with an excess of potassium iodide, the precipitated iodide obtained had the same melting point as the previously reported trimethylsulfonium iodide.

Sulfate analyses. The procedure for determining the percentage sulfate was as follows: about 0.5 g. of the sulfonium salt to be analyzed was refluxed with enough sodium hydroxide to make the solution strongly alkaline. This alkaline solution was made acid with hydrochloric acid and boiled to expel carbon dioxide. The solution was then neutralized to the phenolphthalein end-point with 0.1 *N* sodium hydroxide solution. Enough ethanol was added to dissolve any precipitate that formed. More than an equivalent amount of 0.1 *N* barium chloride solution was added to precipitate the sulfate present as barium sulfate. The amount of barium sulfate precipitated was determined by the usual gravimetric procedures.

The theoretical sulfate percentage for any of the pure cresyldimethylsulfonium methosulfates is 36.4. If the cresyl methosulfates disproportionated into two-thirds cresyldimethylsulfonium methosulfate and one-third trimethylsulfonium methosulfate, then the average sulfate percentage would be 40.2. The sulfate percentages found for the "mixed" *o*- and *m*-cresyldimethylsulfonium methosulfates were: 40.6 and 40.3. The *p*-cresyldimethylsulfonium methosulfate percentage found was 36.6. The reason why "mixed" salts are obtained in the preparation of unsymmetrically substituted sulfonium salts was discussed above.

Buffer solutions. Aqueous *p*H 5.0 buffer was a solution of 0.05 *M* sodium dihydrogen phosphate and 0.0239 *M* sodium hydroxide. The aqueous *p*H 7.0 buffer was a solution of 0.05 *M* sodium dihydrogen phosphate and 0.030 *M* sodium hydroxide. Aqueous *p*H 8.0 buffer was 0.05 *M* sodium dihydrogen phosphate and 0.047 *M* sodium hydroxide.

The 95% ethanol *p*H 6.2 buffer solution was 0.06 *M* sodium dihydrogen phosphate. Buffer *p*H 7.0 in 95% ethanol was 0.025 *M* potassium acetate and 0.041 *M* acetic acid.

Chemicals. C.p. or Reagent Grade chemicals were used in preparing all solutions. The tetraethylammonium bromide was prepared from triethylamine and ethyl bromide (Eastman Kodak Co. White Label chemicals) and recrystallized several times from ethanol. The tetradecyltrimethylammonium bromide was described previously (11).

Polarographic apparatus. The Sargent-Heyrovský Polarograph, Model XII, accessories, oxygen removal technique and H-Cell used in this investigation at 25.00 ± 0.05° were described previously (7, 12). As before (7), a 3.00 sec. drop time was employed. Capillary characteristics were: "m" equal to 2.00 mg. per second in aqueous and alcoholic solutions and $m^{2/3}t^{1/6}$ equal to 1.907 mg.$^{2/3}$ sec.$^{-1/2}$ (open circuit), h = 64 cm.

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SUMMARY

Polarographic reduction waves are noted and reported for sulfonium salts. Catalytic hydrogen waves are observed to form in addition to the main reduction

waves. Slope analyses data indicate that the reduction is irreversible in all of the several solvent systems studied.

Trimethylsulfonium salts are seen to be more stable toward reduction than the unsymmetrically substituted cresyldimethylsulfonium salts. Diffusion current is seen to be proportional to concentration, but the upper limit of concentration proportionality is determined by the catalytic hydrogen wave phenomenon in some cases. The influence of solvent, supporting electrolyte, and acidity have been studied in relation to the reduction of both types of sulfonium salts.

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