2, 3 and 4 and the relationship between the various substituent constants and σ is being actively explored.

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SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Participation of the Carboxylate Group in the Displacement of Chlorine in *o*-(Chloromethylsulfonyl)-benzoic Acid[1]

BY F. G. BORDWELL AND GLENN D. COOPER

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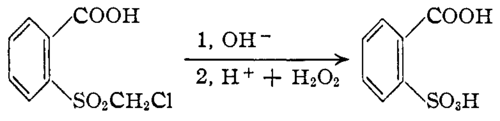
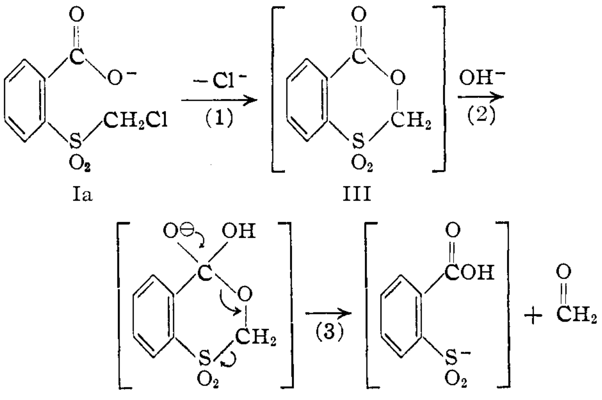
The fairly rapid release of chloride ion, at 100°, in neutral solution from *o*-(chloromethylsulfonyl)-benzoic acid, in contrast to the failure of release of any chloride ion from the *para* isomer under comparable conditions is interpreted as evidence for participation of the carboxylate ion in the reaction. Evidence from approximate rate data indicates that participation of the carboxylate ion may be increased by hydroxide ion.

The inertness of the halogen in chloromethyl phenyl sulfone to nucleophilic displacement[2] and the stereoselective sodium borohydride reduction of 2-(*p*-tolysulfonyl)-cyclohexanone[3] indicate that the phenylsulfonyl group is capable of exerting a large steric effect. In view of this, the observation[4] that the halogen could be released almost quantitatively from *o*-(chloromethylsulfonyl)-benzoic acid (I) by heating at 100° for 4 hr. in alkaline medium aroused our interest. *o*-Carboxybenzenesulfinic acid and formaldehyde are the initial products of this reaction, and *o*-sulfobenzoic acid (II) may be produced in high yield by mild oxidation of the reaction mixture.[4]



I II

The halogen in I is considerably more reactive than that in phenyl chloromethyl sulfone itself,[2] whereas models suggest that the *o*-carboxyl group should greatly increase the hindrance to attack by hydroxide ion, particularly since the group would bear a negative charge in neutral or alkaline solution. This suggested the probability of an intramolecular displacement,[5] with the carboxylate anion participating in the displacement in the manner shown in step 1. The rough kinetic measurements presented herein confirm this viewpoint.



Ia III IIIa IV

The participation by the carboxylate group in Ia was made evident by the fairly rapid release of chloride ion at 100° in *neutral solution*, whereas no reaction was observed for the *p*-isomer, *p*-$HOOCC_6H_4SO_2Cl$, under comparable conditions.

The pK_a's for the *o*- and *p*-chloromethylsulfonylbenzoic acids were found to be 2.38 and 3.44, respectively, at 25°.[6] The σ-constant for the *p*-$ClCH_2SO_2$ group is slightly greater than that for the *p*-CH_3SO_2 group[7] (+0.78 *vs.* +0.72), which is to be expected, since substitution of a Cl for H in CH_3SO_2 should lead to slightly more electron attraction.

Chloride ion is released from 0.16 *N* aqueous solutions of *o*-chloromethylsulfonylbenzoic acid at a rate about one-fourth that in neutral solution. This is the order of magnitude expected for intramolecular displacement by the carboxylate anion, since the acid is about 15% dissociated at this concentration.

In 2 *N* sodium hydroxide solution the release of chloride ion from Ia was about twice that observed in neutral solution. The increase in rate does not appear to be due to a salt effect, since an equivalent

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(1) This investigation was supported by the Office of Naval Research under Contract No. N7-onr-45007.

(2) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951).

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468 (1956).

(4) B. B. Lampert, Ph.D. Dissertation, Northwestern University, June, 1951.

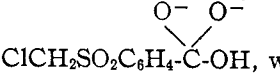
(5) Sterically hindered halides are known to undergo intramolecular displacements. For example, 1,1-dimethylcyclopropane is formed by the reaction of sodium and neopentyl chloride [F. C. Whitmore, A. H. Popkin, H. I. Berstein and J. P. Wilkins, *ibid.*, **63**, 124 (1941)], and the halogen is released readily from alkyl α-haloalkyl sulfones by an intramolecular mechanism [F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5187 (1951)].

(6) We wish to thank Dr. Pierre J. Boutan for making these determinations.

(7) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

quantity of sodium nitrate increased the rate but slightly. The effect of hydroxide ion on the rate is relatively minor, however, since an increase of roughly 10^7 in hydroxide ion (from neutral solution to 2 N NaOH) causes only a twofold increase in rate.

In 2 N sodium hydroxide solution p-(chloromethylsulfonyl)-benzoic acid also slowly released chloride ion at 100°. Approximate rate constants are: o-(chloromethylsulfonyl)-benzoic acid, neutral solution, $k_1 = 0.12$ hr.$^{-1}$; 2 N NaOH, $k_2 = 0.10$ mole^{-1} hr.$^{-1}$; p-(chloromethylsulfonyl)-benzoic acid, neutral solution, $k_1 = 0$; $k_2 = 0.018$ mole^{-1} hr.$^{-1}$.

The observation that the reaction with hydroxide ion proceeds almost six times faster with the o-isomer is surprising, since an examination of molecular models indicates that intermolecular displacement of chloride by hydroxide ion should be much more difficult sterically for the o- than for the p-isomer. The only reasonable interpretation appears to be that the hydroxide ion adds to some extent to the o-carboxylate anion giving a species,  $o\text{-ClCH}_2\text{SO}_2\text{C}_6\text{H}_4\text{-}\overset{\text{O}^-\ \text{O}^-}{\text{C}}\text{-OH}$, which gives rise to a very rapid intramolecular displacement of chlorine.

The possibility that sulfinate ion rather than chloride ion was being displaced in the initial reaction with hydroxide ion was eliminated by the failure of o- or p-methylsulfonylbenzoic acids to give sulfinates under these conditions.

No evidence is available concerning the manner in which III is converted to IV. It seems probable that the addition of hydroxide ion to the carbonyl group of III occurs, giving IIIa, which undergoes elimination in the manner indicated in the equations. Alternatively, attack of hydroxide ion and elimination of formaldehyde may be concerted so that III is converted directly to IV, or elimination of formaldehyde may be the slow step in which case o-(hydroxymethylsulfonyl)-benzoic acid would be formed as an intermediate. Formaldehyde was isolated in 75% yield as its dimethyldihydroresorcinol derivative. The sulfinate IV was not isolated, but its presence seems assured from the strong reducing properties of the reaction mixture and the isolation of good yields of o-sulfobenzoic acid (as its di-S-benzylthiuronium salt) after oxidation.[4]

Experimental[8]

o-Chloromethylsulfonylbenzoic Acid.—o-Chloromethylsulfonylbenzoic acid was prepared by the hydrolysis of 2-chloro-3-oxo-2,3-dihydrobenzothiophene 1-dioxide with sodium carbonate solution according to the procedure of Lampert.[4]

Anal. Calcd. for $C_8H_7O_4SCl$: neut. equiv., 234.65. Found: neut. equiv., 234.26.

p-Chloromethylsulfonylbenzoic Acid.—Chloromethyl p-tolyl sulfone was prepared in 90% yield by the oxidation of chloromethyl p-tolyl sulfide with 40% peracetic acid according to the directions previously given for chloromethyl phenyl sulfone.[2] Ten grams (0.049 mole) of chloromethyl p-tolyl sulfone was refluxed for 2 hr. with 50 ml. of water, 25 ml. of 95% sulfuric acid and 25 g. of sodium dichromate. The mixture was poured into 100 ml. of water and the precipitate collected on a filter and washed thoroughly with 5% sulfuric acid. The dark solid was warmed with 100 ml. of 5% sodium hydroxide and treated with activated charcoal. The solution was filtered and the filtrate was acidified with 6 N sulfuric acid, yielding 5.0 g. of light tan solid, m.p. 231–234° (cor.). After two recrystallizations from ethanol, there was obtained 4.5 g. (39%) of colorless needles, m.p. 237-239° (cor.).

Anal. Calcd. for $C_8H_7SO_2Cl$: C, 40.9; H, 3.0; neut. equiv., 234.65. Found: C, 41.2; H, 3.0; neut. equiv., 234.90.[6]

o-Methylsulfonylbenzoic Acid.—Ten grams of o-tolymethyl sulfide was refluxed for 4 hr. with 50 g. of potassium permanganate and 5 ml. of 10% sodium hydroxide in 400 ml. of water. The mixture was acidified with 96% sulfuric acid and decolorized with sodium bisulfite. The solution was extracted several times with ether and the ether solution evaporated to dryness. The yellow, partly solid residue was dissolved in 20 ml. of 10% sodium hydroxide. The solution was filtered and the filtrate acidified with 6 N hydrochloric acid. Extraction with ether yielded 5.5 g. of colorless needles, m.p. 130–134°. After three recrystallizations from toluene, there was obtained 3.9 g. (26%) of o-methylsulfonylbenzoic acid, m.p. 139–140°, lit.[9] m.p. 138–140°.

p-Methylsulfonylbenzoic Acid.—Twenty grams (0.145 mole) of methyl p-tolyl sulfide was refluxed for 2 hr. with 100 g. of potassium permanganate and 10 ml. of 10% sodium hydroxide in 800 ml. of water. The solution was cooled and decolorized with sodium bisulfite. The light tan precipitate was filtered off, dissolved in 200 ml. of 10% sodium hydroxide, treated with activated charcoal and filtered. Acidification of the filtrate with concd. hydrochloric acid yielded 18 g. of colorless needles, m.p. 271–273° (corr.). Recrystallization from glacial acetic acid yielded 16.6 g. (58%) of p-methylsulfonylbenzoic acid, m.p. 273–274° (corr.), lit. m.p. 240–241°[10], 267–268°.[11]

Decomposition of o-Chloromethylsulfonylbenzoic Acid in Acidic, Basic and Neutral Solutions. Neutral Solution.—o-Chloromethylsulfonylbenzoic acid (0.938 g., 0.004 mole), sodium bicarbonate (0.336 g., 0.004 mole) and precipitated calcium carbonate (1.5 g.) were weighed into a small beaker and stirred for a few minutes with 25 ml. of water (measured at 85° and cooled to room temperature). The pH was 6.5, measured with a Beckman model G pH meter. The mixture was transferred to a tube with a rubber stopper, secured with wire and immersed in boiling water. The tube was shaken frequently to suspend the calcium carbonate. From time to time the calcium carbonate was allowed to settle, and 5-ml. samples were withdrawn and titrated for chloride by the Mohr method.

Time, hr.	Reacted, %	k, hr.$^{-1}$
1.5	17.5	0.12
3.0	30.0	.12
6.0	47.9	.11

After 23 hr. the mixture was cooled and filtered. A 2-ml. aliquot was saturated with salt and treated with a few drops of solution of methone in alcohol. There was obtained 0.070 g. (75%) of the methone derivative of formaldehyde, m.p. 187–188°, lit.[12] m.p. 187°. The remainder of the solution was warmed with a few drops of 30% hydrogen peroxide, acidified with a few drops of concd. hydrochloric acid and treated with S-benzylthiuronium chloride, yielding 0.233 g. (28%) of the di-S-benzylthiuronium salt of o-sulfobenzoic acid, m.p. 205–206°, lit.[13] m.p. 205.5–206.5°. In other experiments, carried out on a preparative scale, the S-benzylthiuronium salt of o-sulfobenzoic acid was obtained in 84% yield.[4]

Basic Solution.—o-Chloromethylsulfonylbenzoic acid (0.938 g., 0.004 mole) was weighed into a Pyrex tube. Twenty-five milliliters (measured at 85°) of hot 2 N sodium hydroxide solution was added and the tube was immersed in boiling water. Samples were titrated for chloride as pre-

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[8] Microanalyses were by Miss Joyce Sorensen.

[9] F. Arndt, A. Kirsch and P. Nachtwey, *Ber.*, **59**, 1074 (1926).

[10] Ng. Ph. Buu-Hoi and J. Lecocq, *Bull. soc. chim.*, 145 (1946).

[11] A. T. Fuller, I. M. Tonkin and J. Walker, *J. Chem. Soc.*, 633 (1945).

[12] W. Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

[13] S. Veibel and H. Lillelund, *Bull. soc. chim.*, [5] **5**, 1153 (1938); E. E. Campaign and C. M. Suter, THIS JOURNAL, **64**, 3040 (1942).

viously described. The value of k_2 was calculated from the equation, $k = k_1 + k_2(\mathrm{OH})$, using the k_1 value obtained in neutral solution.

Time, hr.	Reacted, %	$k = k_1 + k_2(\mathrm{OH}^-)$	k_2, (l. mole^{-1} hr.$^{-1}$)
0.5	15.2	0.32	0.11
1.5	37.0	.31	.11
3.0	55.5	.28	.09

Acid Solution.—*o*-Chloromethylsulfonylbenzoic acid (0.469 g., 0.002 mole) was dissolved in 12.5 ml. of water in a tube, and the tube was immersed in boiling water. Samples were titrated for chloride as previously described.

Time, hr.	Reacted, %	k, hr.$^{-1}$
3.0	8.3	0.029
4.5	11.6	.028

Decomposition of *p*-Chloromethylsulfonylbenzoic Acid in Neutral and Basic Solutions. Neutral Solutions.—*p*-Chloromethylsulfonylbenzoic acid was neutralized with sodium bicarbonate as described above for *o*-chloromethylsulfonylbenzoic acid. After 20 hr. at 100° no detectable amount of chloride had been released.

Basic Solution.—*p*-Chloromethylsulfonylbenzoic acid was heated in 2 *N* sodium hydroxide solution as described above for *o*-chloromethylsulfonylbenzoic acid.

Time, hr.	Reacted, %	k, l. mole^{-1} hr.$^{-1}$
1.1	3.3	0.016
6.3	19.0	.018
18.6	48.4	.019

The solution readily decolorized a 2% potassium permanganate solution. On warming with 30% hydrogen peroxide and treatment with S-benzylthiuronium chloride, a small amount (7%) of the S-benzylthiuronium salt of *p*-sulfobenzoic acid, m.p. 213–214°, was obtained; lit.[9] m.p. 212.6–214.4°. The melting point of a mixture with an authentic sample was undepressed.

Attempted Reaction of *p*-Methylsulfonylbenzoic Acid with Sodium Hydroxide Solution.—Two grams of *p*-methylsulfonylbenzoic acid was heated under reflux in a stream of nitrogen with 25 ml. of 2 *N* sodium hydroxide solution for 48 hr. The solution did not decolorize 2% potassium permanganate. Acidification and recrystallization of the precipitate from glacial acetic acid yielded 1.8 g. (90%) of the starting material.

Attempted Reaction of *o*-Methylsulfonylbenzoic Acid with Sodium Hydroxide Solution.—Two grams of *o*-methylsulfonylbenzoic acid was heated under reflux in a stream of nitrogen with 25 ml. of 2 *N* sodium hydroxide for 4 hr. The solution did not decolorize 2% potassium permanganate. Acidification, extraction with benzene and recrystallization from benzene–petroleum ether yielded 1.3 g. (65%) of starting material.

Acidity Constant Measurements.[6]—The acidity constants were determined with a Beckman model G *p*H meter according to the method described previously.[14]

Pertinent data are summarized in Table I.

TABLE I

C	C = concn., mole/liter C_b	C_a	*p*H (av.)	pK_a	pK_a (av.)
		o-Chloromethylsulfonylbenzoic acid			
0.01435	0.00368	0.01067	2.46	2.46	
.01769	.00735	.00974	2.51	2.33	
.01691	.01011	.00680	2.74	2.36	
.01590	.00368	.01192	2.38	2.36	2.38
		p-Chloromethylsulfonylbenzoic acid			
0.003232	0.000735	0.002497	3.27	3.46	
.004112	.001618	.002495	3.40	3.42	
.004276	.002572	.001704	3.70	3.44	3.44

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[14] See F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 854 (1956), and previous papers cited therein.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Free-Radical, Chain Reactions of Diazomethane with Polybromo- and Polyiodomethanes

BY W. H. URRY, J. R. EISZNER AND J. W. WILT

RECEIVED JULY 9, 1956

A high quantum yield (298 at 0–2°) confirms previous suggestions that the photochemical reaction of diazomethane with carbon tetrachloride to give pentaerythrityl chloride and nitrogen is a free-radical, chain reaction. The more rapid chain reactions of diazomethane with polybromo- or polyiodomethanes give halide products of a different type—dibromo- or diiodomethane and vinyl or vinylidene bromides or iodides. β-Elimination of a bromine or iodine atom from an intermediate free radical is postulated.

The reactions of diazomethane with polybromo- or polyiodomethanes give the respective dihalomethanes and vinyl or vinylidene halides as well as nitrogen and higher boiling telomeric products of secondary reactions of the polyhalomethanes with the haloethylenes. In our initial studies, the following reactions were observed when gaseous diazomethane was passed into irradiated solutions of the polyhalomethane (yields based upon diazomethane in parentheses; theoretical yield of each halide is 50%)

$$\mathrm{CBr_4 + 2CH_2N_2 \longrightarrow CH_2Br_2(25\%) + CH_2{=}CBr_2(25\%) + 2N_2} \quad (1)$$

$$\mathrm{CHI_3 + 2CH_2N_2 \longrightarrow CH_2I_2(45\%) + CH_2{=}CHI(27\%) + 2N_2} \quad (2)$$

$$\mathrm{CHBr_3 + 2CH_2N_2 \longrightarrow CH_2Br_2(15\%) + CH_2{=}CHBr\text{-}telomer + 2N_2} \quad (3)$$

Later experiments (with $\mathrm{CBr_2Cl_2}$) showed, however, that these reactions occur when diazomethane is added to these halides in ordinary room light (at 0–35°) with no additional irradiation.

These reactions differ in two significant ways from the previously studied reactions[1] of diazomethane with polyhalomethanes ($\mathrm{CCl_4}$, $\mathrm{BrCCl_3}$ and $\mathrm{CHCl_3}$) and α-haloesters ($\mathrm{Cl_3CCOOCH_3}$ and $\mathrm{BrCH_2COOCH_3}$): (1) they are much faster (reaction occurred with mixing), and (2) the products of the latter reactions are neopentyl derivatives[2]

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[1] W. H. Urry and J. R. Eiszner, THIS JOURNAL, **73**, 2977 (1951); **74**, 5822 (1952).

[2] Recent work has shown that products formed by reactions of free radical intermediates with the polyhalomethanes are also formed. For example, when diazomethane was passed into bromotrichloromethane at 0° over a period of 90 minutes, the products 1-bromo-1,1,2-trichloroethane (0.8%), 2-bromo-1,2,3-trichloropropane (17%), 2-bromo-2-chloromethyl-1,3-dichloropropane (16%), and 2-bromomethyl-2-chloromethyl-1,3-dichloropropane (15%, yields based upon diazomethane) were obtained. Such products are formed in largest amounts with the most reactive polyhalomethanes and when the concentration of diazomethane in the reaction mixture is kept low; W. H. Urry and N. Bilow, unpublished work.