amine were removed under reduced pressure and the resulting viscous red oil was distilled. The fraction that boiled at 135–148° (1 μ), n^{25}D 1.5204, weighed 21 g. (85%).

Anal. Calcd. for $C_{15}H_{24}N_2O$: N_{AP}, 5.62. Found: N_{AP}, 5.64.

N-(2-Cyanoethyl)-N-(4-isopropylbenzyl)-dichloroacetamide.—The following is an example of the general procedure employed for the preparation of the haloacetamides (see Tables III and IV).

A mixture of 20.2 g. (0.1 mole) of N-(2-cyanoethyl)-4-isopropylbenzylamine, 125 ml. of a 1 *N* sodium hydroxide solution and 100 ml. of ethylene dichloride was cooled to 0° in an ice–salt bath. A solution of 14.7 g. (0.1 mole) of dichloroacetyl chloride in 50 ml. of ethylene dichloride was then slowly added with stirring (temperature <5°). After the addition was complete, stirring was continued while the mixture was allowed to warm to room temperature. The organic layer was separated, washed with 2 *N* hydrochloric acid and with water and filtered with charcoal. The solvent was removed under reduced pressure and the resulting solid, 26 g. (83%), was recrystallized once from isopropyl alcohol, m.p. 107.9–111.6°.

N-(2-Cyanoethyl)-N-(2-furfuryl)-dichloroacetamide. The procedure here was the same as above. The product was a brown non-distillable oil, that was dried at 60–70° (0.05 mm.) for 2 hours. The yield was 77%.

Anal. Calcd. for $C_{10}H_{10}Cl_2N_2O_2$: C, 45.99; H, 3.86; N, 10.73. Found: C, 45.44; H, 4.16; N, 10.58.

The haloacetamides of the 2-carbamylethylamines were prepared in the same manner as above. Two molar equivalents of base were employed when the starting material was the amine hydrochloride.

N-[2-(Ethylcarbamyl)-ethyl]-N-(4-isopropylbenzyl)-dichloroacetamide.—This compound was prepared from N-[2-(ethylcarbamyl)-ethyl]-4-isopropylbenzylamine. The product, a viscous red oil, was dried for one hour at 70° (0.3 mm.), (89%).

Anal. Calcd. for $C_{17}H_{24}Cl_2N_2O_2$: Cl, 19.73; N, 7.80. Found: Cl, 19.60; N, 7.65.

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[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Derivatives of Aromatic Sulfinic Acids. II. The Reaction of Thionyl Chloride with Sulfinic Esters[1,2]

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Esters of aromatic sulfinic acids react with thionyl chloride as do sulfurous esters to give the sulfinyl chloride and the alkyl chlorosulfinate. In the absence of added chloride ion, the reaction is slow. By the use of *l*-menthyl *l*-*p*-toluenesulfinate it has been shown that the reaction is first order in ester and first order in added chloride ion. Trace impurities of the thionyl chloride, probably mainly hydrogen chloride, also affect the rate.

The reactions of esters of sulfurous acid with acid chlorides and anhydrides illustrate the behavior of alkyl sulfites as mild alkoxylating agents.[3] Thionyl chloride, thionyl bromide,[3a] sulfuryl chloride,[3b,c] alkyl chlorosulfonates,[3b–d] phosphorus pentachloride,[3a] acyl halides and organic acid anhydrides[3b] have been used as alkoxide acceptors.

Esters of the aromatic sulfinic acids differ from the sulfites in having an aryl group attached to sulfur instead of one of the alkoxyl groups. It seemed of interest, in view of the fact that the covalence of sulfur is the same in these two classes of compounds, to determine whether or not the aromatic sulfinic esters would undergo a reaction comparable to that of the sulfurous esters.

Methyl benzenesulfinate and methyl *p*-toluenesulfinate, indeed, react smoothly at room temperature to yield the sulfinyl chloride and methyl chlorosulfinate in good yield.

$$ArSO_2CH_3 + SOCl_2 \longrightarrow ArSOCl + CH_3OSOCl$$

A trace of tetraethylammonium chloride added to the reactants[4] causes the reaction to become violent, and at the same time the methyl chlorosulfinate is decomposed to methyl chloride and sulfur dioxide.

This reaction of the sulfinic esters may proceed in a manner similar to that of the alkyl sulfites.[4] Since the sulfur of these esters is asymmetric, optically active esters can be used in a kinetic study of the reaction. *l*-Menthyl *l*-*p*-toluenesulfinate[5] was used for kinetic measurements since the change in optical activity of the solution of reactants could be followed as the reaction took place at the asymmetric sulfur.

In nitrobenzene as a solvent at 25°, there was no detectable change in rotation of 0.08 *M* ester with 0.12 *M* thionyl chloride over a period of 1 hr. However, with tetraethylammonium chloride added to the two reactants to the extent of 0.0009–0.02 *M*, the rate-of-change in rotation became easily measurable. Typical results are those of Fig. 1 which illustrate the strict linearity for a period of over two half-lives of a first-order plot of the rotation. These also demonstrate the marked dependence of the rate on added chloride ion; this dependence on chloride ion concentration of the pseudo-first-order rate constant for the first twelve runs of Table I is presented graphically in Fig. 2. The water content, as determined by Karl Fischer titrations, of the tetraethylammonium chloride solution in nitrobenzene and of the nitrobenzene used as a solvent for the kinetic runs was not demonstrably different from zero (<0.001 *M*).[6] Yet to exclude the possibility that a species other than the quaternary chloride was the active catalyst, the additional reagents in amounts listed in

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(1) Acknowledgment is made of partial support of this work by the Office of Naval Research, Project NR055-313, Contract Nonr-591(03).

(2) Paper I in this series, H. F. Herbrandson, R. T. Dickerson, Jr., and J. Winstein, THIS JOURNAL, **76**, 4046 (1954).

(3) (a) P. Carré and D. Libermann, *Bull. soc. chim. France*, **53**, 1050 (1933); (b) R. Levaillant, *Ann. chim.*, **6**, 461 (1936); (c) C. M. Suter and H. L. Gerhart, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 111; (d) C. Barkenbus and J. J. Owen, THIS JOURNAL, **56**, 1204 (1934).

(4) P. D. Bartlett and H. F. Herbrandson, *ibid.*, **74**, 5971 (1952).

(5) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925). The diastereoisomer of this compound, *l*-menthyl *d*-*p*-toluenesulfinate, which differs only in the configuration of the sulfur, never has been obtained optically pure.

(6) This determination was kindly made by Dr. Andrew A. Laurene.

Table I were tested. Hydrogen chloride, methanol and water added separately to the reactants in nitrobenzene caused no reaction to take place.

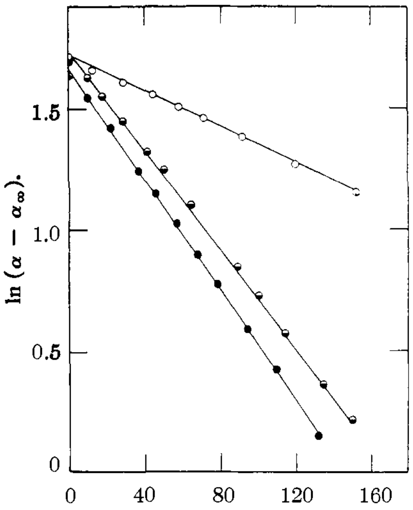

Fig. 1.—*l*-Menthyl *l*-*p*-toluenesulfinate and thionyl chloride in nitrobenzene with different amounts of tetraethylammonium chloride (in mole/l.) at 24.88 ± 0.05°: ○, 0.00093; ◒, 0.00309 (thionyl chloride, 0.0616 mole/l.); ●, 0.00309 (thionyl chloride, 0.123 mole/l.).

Figure 1 illustrates the first-order dependence of the rate on the ester concentration. This dependence holds over a twofold variation in the initial concentration of ester (Table I).

TABLE I

l-MENTHYL *l*-*p*-TOLUENESULFINATE WITH THIONYL CHLORIDE IN NITROBENZENE AT 24.88 ± 0.05°

Initial ester, mole/l.	Initial thionyl chloride, mole/l.	Tetraethylammonium chloride and/or other reagent, mole/l.	$k \times 10^4$, sec.$^{-1}$
0.0554	0.0616	0.00093	0.62
.0551	.0616	.00213	1.18
.0626	.0616	.00309	1.68
.0590	.123	.00309	1.92
.0516	.0616	.00425	2.30
.0604	.0616	.00463	2.06
.0779	.0616	.00463	2.12
.0520	.0616	.00850	3.55
.0409	.0616	.0106	3.80
.0635	.0616	.0160	4.28
.0548	.0492	.0213	3.82
.0423	.0492	.0213	4.24
.0774	.123	0	0
.0542	0	.00617	0
.0845	0	.0213	0
.0663	0	.00525 (HCl)	0
.0594	.0616	.00525 (HCl)	0
.0510	.0616	.00378 (CH_3OH)	0
.0408	.0616	.00335 (H_2O)	0
.0732	.0860[a]	.0232	7.30
.0703	.0860[a]	.0232 + 0.1 M SO_2	7.63

[a] The thionyl chloride used for these runs was different from that used in obtaining the other results reported above but was purified in the same way.

The effect of thionyl chloride on the reaction was difficult to assess. Using thionyl chloride in nitrobenzene from a single stock bottle, a twofold increase in thionyl chloride concentration increased the rate 15%. With a single source of thionyl chloride it thus was possible to achieve the results recorded in Table I and illustrated in Fig. 2. Even extreme care in the purification of the thionyl chloride and in its handling gave rise to variable results from different batches. This led to the discontinuance of further kinetic study of the reaction of sulfinic esters with thionyl chloride. A more satisfactory alkoxide acceptor for kinetic measurements was obtained by the use of anhydrous hydrogen chloride.[2]

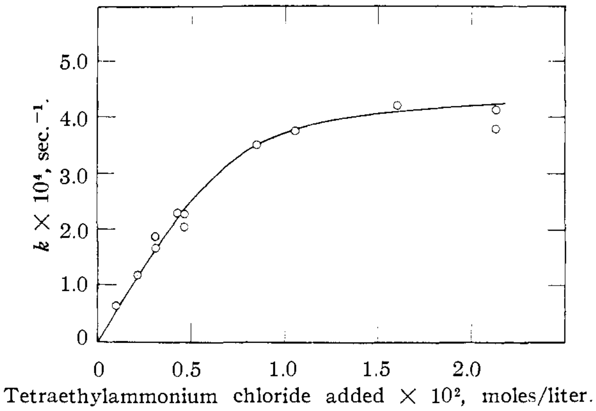

Fig. 2.—Dependence on tetraethylammonium chloride of the pseudo-first-order rate constant for reaction between *l*-menthyl *l*-*p*-toluenesulfinate and thionyl chloride.

Phillips[5] found that *l*-menthyl *l*-*p*-toluenesulfinate and other optically active sulfinic esters underwent mutarotation very slowly. It was later shown[7] that this was the result of catalysis by *p*-toluenesulfinic acid or by both the acid and alcohol. The quantities necessary to effect this were, however, much greater than could have been present as contaminants in this study: with approximately 5% acid and 18% alcohol added the half-life was about 10 hr. From the results reported here, the addition of 9.3×10^{-4} M tetraethylammonium chloride to the ester and thionyl chloride, which alone are completely unreactive, gives a half-life of about 3 hr. It seems likely[2] that a trace amount of hydrogen chloride as a contaminant of the thionyl chloride may account for the variability of the results with different sources of thionyl chloride.

Experimental[8]

Methyl Benzenesulfinate.—Benzenesulfinyl chloride[9] (22.5 g., 0.14 mole) was added to a solution of 11.1 g. (0.14 mole) of dry pyridine and 5 g. (0.156 mole) of dry methanol in 60 cc. of dry ether. The reaction mixture was maintained at −10° until the color of the benzenesulfinyl chloride had completely disappeared and precipitation of the pyridine hydrochloride was complete. Water was then added to dissolve the pyridinium salt and the ethereal layer was washed with water. After drying of the ether solution with calcium sulfate and removal of the ether, the residue was distilled to obtain 14.0 g. (0.090 mole, 64%) of methyl benzenesulfinate of b.p. 67–68° (0.04 mm.). The ester was redistilled

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[7] K. Ziegler and A. Wenz, *Ann.*, **511**, 109 (1934).

[8] Except where noted, melting points and boiling points are uncorrected. Analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

[9] J. v. Braun and W. Kaiser, *Ber.*, **56B**, 549 (1923).

and a middle fraction, b.p. 63° (0.03 mm.) and n^{20}_{D} 1.5400, was taken for analysis.

Anal. Calcd. for $C_7H_8SO_2$: C, 53.82; H, 5.16; S, 20.52. Found: C, 53.44; H, 5.30; S, 20.57.

Methyl *p*-Toluenesulfinate.—This compound was prepared in the same manner as the methyl benzenesulfinate in a 91% yield. It had a b.p. of 68° at 0.001 mm. (lit.[10] b.p. 135° at 14 mm.) and n^{20}_{D} 1.5380.

Reaction of the Sulfinic Esters with Thionyl Chloride. (A) Methyl *p*-Toluenesulfinate with Thionyl Chloride.—In a 125-cc. claisen flask were placed 20.1 g. (0.118 mole) of pure, colorless methyl *p*-toluenesulfinate and 14.0 g. (0.118 mole) of pure colorless thionyl chloride. All the flask openings were closed, and the flask was placed in the dark. There was no immediate color change, but within 15 minutes a light yellow color began to develop. After standing a few days, the product was distilled. The colorless first fraction, 3.5 g. (0.031 mole, 30%), which distilled below 30° at 65 mm. and was collected in a receiver cooled with Dry Ice, was methyl chlorosulfinate that on redistillation had a b.p. of 104–106°, n^{20}_{D} 1.4629.[11] *p*-Toluenesulfinyl chloride, a lemon-yellow oil, distilled as the second fraction, 18.7 g., 0.107 mole, 90.6% at 79° (0.012 mm.), n^{20}_{D} 1.6007 (lit.[9] b.p. 115–120° at 4 mm.).

p-Toluenesulfinamide, prepared from the acid chloride in dry ether and a dry ethereal solution of ammonia, was recrystallized from aqueous ethanol, m.p. 120–120.5° (lit.[9] m.p. 120°).

(B) Methyl Benzenesulfinate with Thionyl Chloride.—The reaction was carried out in a manner similar to that used for the reaction of methyl *p*-toluenesulfinate. No attempt was made to collect the methyl chlorosulfinate. The benzenesulfinyl chloride, b.p. 65° (0.012 mm.), was obtained as a yellow oil in 84% yield. Both sulfinyl chlorides were hydrolyzed almost instantaneously to the solid acids by moist air.

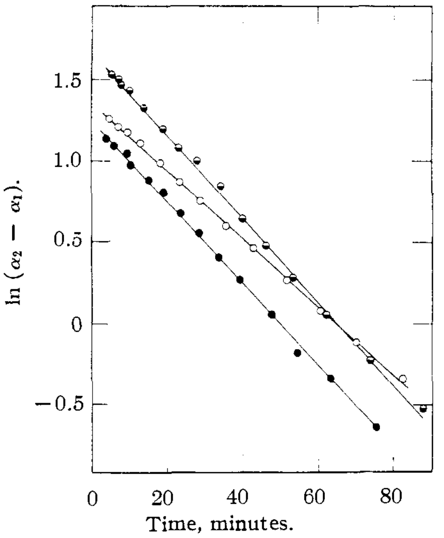

Fig. 3.—*l*-Menthyl *l*-*p*-toluenesulfinate and thionyl chloride in nitrobenzene with different amounts of tetraethylammonium chloride (in mole/l.) at 24.88 ± 0.05°: ○, 0.00850; ◒, 0.0160; ●, 0.0213.

Benzenesulfinamide, prepared from the benzenesulfinyl chloride and recrystallized from aqueous ethanol, had a m.p. 122° (lit.[9] m.p. 121°). The benzenesulfinopiperidide prepared from the acid chloride and recrystallized from petroleum ether, had a m.p. 82–83° (lit.[9] m.p. 83°).

Kinetic Measurements. Reagents.—Nitrobenzene was a commercial grade, steam distilled from dilute sulfuric acid, dried with calcium chloride and treated with phosphorus pentoxide until the product, washed with alkali and water, no longer gave a violet color.[12] After drying, the nitrobenzene was subjected to two fractional freezings and distilled *in vacuo* into bottles in which the solutions were prepared. The stock nitrobenzene, used for dilutions, was finally dried by removal of 20–25 ml. *in vacuo*.

Thionyl chloride was purified by refluxing with sulfur and by two fractional distillations.[13] The water-white thionyl chloride was transferred by pipet into a stock bottle of nitrobenzene, and 10–15 ml. of nitrobenzene was removed *in vacuo* to assure removal of hydrogen chloride and sulfur dioxide. The thionyl chloride content was determined by Volhard titration of the chloride.

l-Menthyl *l*-*p*-toluenesulfinate was prepared according to the method of Phillips[5] and recrystallized five times from aqueous acetone (3:17) to a constant rotation: $[\alpha]^{25}_{\text{D}}$ −199.19° (*c* 2, acetone); $[\alpha]^{25}_{\text{D}}$ −205.84° (*c* 2.5, nitrobenzene) m.p. 106–107° (cor.) (lit.[4] 108–109°). This was stored in the dark in a vacuum desiccator over phosphorus pentoxide. A fresh solution of *l*-menthyl *l*-*p*-toluenesulfinate was made up by weight for each kinetic run.

Tetraethylammonium chloride was prepared by treating tetraethylammonium bromide (Eastman Kodak Co. White Label) in distilled water with a slight excess of freshly prepared silver oxide. The reactants were triturated twice, after which the filtrate gave a negative test for bromide ion. Careful acidification to congo red with 20% hydrochloric acid and concentration *in vacuo* yielded the tetraethylammonium chloride which was recrystallized twice from acetone–ethanol. Further recrystallization caused no change in its kinetic behavior. The tetraethylammonium chloride was made up as a stock solution in the purified nitrobenzene and dryness was then assured by removing about 10% of the nitrobenzene *in vacuo*. The tetraethylammonium chloride content was determined by Volhard titration of the chloride.

Method.—For each kinetic determination the reagents in nitrobenzene were added to a weighed quantity of *l*-menthyl *l*-*p*-toluenesulfinate and the solution diluted to the appropriate volume. Rotations were measured in fully enclosed, jacketed, 2-dm. tubes which were thermostated at 24.88 ± 0.05°.

Satisfactory plots of the rotations as a simple first-order reaction were obtained, Fig. 1, so most rate constants were obtained by plotting the data according to Guggenheim[14] from the expression $\ln(\alpha_2 - \alpha_1) = kt + C$ with the intervals between the readings α_1 and α_2 of 100–120 min. as in Fig. 3.

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[10] F. Arndt and H. Scholz, *Ann.*, **510**, 62 (1934).

[11] A. Stähler and E. Schirm, *Ber.*, **44**, 319 (1911), report for methyl chlorosulfinate a b.p. of 102° with some decomposition; B. Trunel, *Compt. rend.*, **200**, 555 (1935), reports n^{20}_{D} 1.4648 for the compound.

[12] A. Weissberger and E. Proskauer, "The Purification of Organic Solvents," Oxford University Press, Oxford, 1935, p. 163.

[13] D. L. Cottle, THIS JOURNAL, **68**, 1389 (1946).

[14] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).