and lithium aluminum hydride in THF was refluxed for 20 min before work-up to afford 0.83 g (28%) of phenylacetonitrile and 0.83 g (25%) of recovered phenylacetamide. As before, the remainder of the product consisted of tarry materials.

B. **With Benzamide.**—To a solution of 3.025 g (0.025 mole) of benzamide in 50 ml of anhydrous THF was added, during 8 min, a suspension of 0.361 g (0.0095 mole) of lithium aluminum hydride in 100 ml of THF. Although much foaming occurred, the reaction was only slightly exothermic. The gray suspension was refluxed for 4 hr during which time it lightened in color. Upon cooling to 0°, the reaction mixture was worked up as described in method A. Although the odor of benzonitrile could be detected, the amounts present were insufficient for isolation. Instead, 2.2 g (73%) of benzamide was recovered, mp, mmp 127–129°. A similar result was obtained in another experiment on four times the scale.

Registry No.—**1**, 103-81-1; **1′**, 14072-58-3; **1‴**, 14072-59-4; **1**-d_2, 14072-60-7; **2′**, 6393-50-6; **3**, 14072-62-9; **4**, 14072-63-0; **5**, 3508-98-3; **6**, 3508-99-4; **7**, 6304-33-2; **8**, 14072-67-4; **9**, 4695-13-0; **9″**, 14072-69-6; **9‴**, 14072-70-9; **10**, 86-29-3; **11″**, 14072-71-0; **12**, 602-88-0; *n*-butyllithium, 109-72-8; heptamide, 628-62-6; phenylacetonitrile, 140-29-4; phenylacetonitrile-α-d_1, 14072-73-2; heptanenitrile, 1885-40-1; dibenzamide, 614-28-8; phenylacetonitrile-α,α-d_2, 935-66-0.

The Reaction of Methanesulfinyl Chloride with Water[1a]

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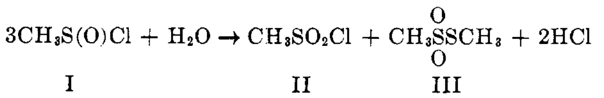
Methanesulfinyl chloride (I) reacts with a limited amount of water (mole ratio 3:1) or deuterium oxide yielding methanesulfonyl chloride (II) and methyl methanethiolsulfonate (III) as the only sulfur-containing products, according to the stoichiometry $3CH_3S(O)Cl + H_2O \rightarrow CH_3SO_2Cl + CH_3SO_2SCH_3 + 2HCl$. Evidence is presented that the reaction may occur by formation of methylsulfinyl methyl sulfone, $CH_3S(O)$-SO_2CH_3, which subsequently reacts with unhydrolyzed I. With greater quantites of water (up to I:H_2O = 0.33), although initially large amounts of methanesulfinic acid (IV) are formed, the final products are again II and III with lesser amounts of methanesulfonic acid (V). Although there is a rapid initial hydrolysis of I to form IV, as long as the mole ratio of water to sulfinyl chloride does not exceed 4:1, nmr spectroscopy reveals the presence of sulfinyl chloride in the reaction mixture. Its persistence is apparently due to reaction between hydrogen chloride and the sulfinic acid.

The ease with which methanesulfinyl chloride, CH_3-$S(O)Cl$(I), can be prepared by the controlled solvolysis of methylsulfur trichloride[2] or the chlorination of a mixture of methyl disulfide and acetic acid[3] has made this compound readily available.

We have always assumed that I reacts quantitatively with water to form methanesulfinic acid. Titration of its aqueous solutions with sodium hydroxide consumes 2 moles of base/mole of I. Our inability to obtain a satisfactory pmr spectrum of methanesulfinic acid from an equimolar mixture of the sulfinyl chloride and water, however, led to a systematic study of the reaction between I and different stoichiometric quantities of water.

In one case water and methanesulfinyl chloride were mixed in a molar ratio of 1:2.2. On distilling the reaction products, 12% of the initial sulfur was recovered as methanesulfonyl chloride (II), and 70% as methyl methanethiolsulfonate (III). These results suggested that the reaction shown in eq 1 might be taking place.



$$\underset{\mathrm{I}}{3CH_3S(O)Cl} + H_2O \rightarrow \underset{\mathrm{II}}{CH_3SO_2Cl} + \underset{\mathrm{III}}{CH_3\overset{O}{\underset{O}{S}}SCH_3} + 2HCl \quad (1)$$

The stoichiometry was later confirmed by adding I to water and determining the proton magnetic resonance (pmr) spectrum of the reaction mixture in carbon tetrachloride (CCl_4). Reverse addition of the reactants or the use of D_2O instead of H_2O had no effect upon the relative proportions of II and III.

Further experiments were carried out by mixing larger quantities of D_2O with I and periodically determining the pmr spectra of both the neat solutions and their carbon tetrachloride extracts. Results are given in Table I which contains data obtained by integrating spectra of neat solutions. Since the pmr spectra of the CCl_4 extracts could be run at spectrum amplitudes up to 40 times greater than those of the neat solutions, these were used to detect the presence of methanesulfinyl chloride traces. In all experiments a vigorous exothermic reaction was observed on mixing the reactants. With mixtures of up to 3 moles of D_2O to 1 mole of I, however, even though large quantities of methanesulfinic acid (IV) were initially formed, I was not completely destroyed. The final reaction products were principally II and III with smaller quantities of methanesulfonic acid (V).

With 4 moles of D_2O/mole of I only a faint trace of I could be detected in the reaction mixture. The methanesulfinic acid formed under these conditions remained virtually unchanged after 120 hr.

The unexpected persistence of I in the presence of excess water is believed to be due to an equilibrium reaction (eq 2). The reverse reaction was demonstrated by passing gaseous hydrogen chloride into a solution of IV obtained by saponification of its methyl ester. Extraction of the resulting solution with carbon tetrachloride and pmr analysis clearly demonstrated the presence of I.

$$\underset{\mathrm{I}}{CH_3S(O)Cl} + H_2O \rightleftharpoons \underset{\mathrm{IV}}{CH_3SO_2H} + HCl \qquad (2)$$

The formation of II and III may be explained in two ways, both involving an initial rapid attainment of the equilibrium shown in eq 2. In the first, one may pos-

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[1] (a) Taken in part from a thesis presented by R. V. Norton in partial fulfillment of the requirements of the Ph.D. degree, June 1967. (b) To whom inquiries should be directed.

[2] I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

[3] I. B. Douglass, B. S. Farah, and E. G. Thomas, *ibid.*, **26**, 1996 (1961); *Org. Syn.*, **40**, 62 (1960).

TABLE I

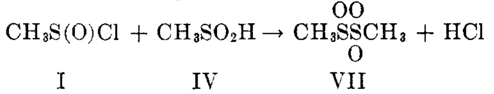
THE REACTION OF METHANESULFINYL CHLORIDE WITH DEUTERIUM OXIDE[a]

Mole ratio of reactants $CH_3S(O)Cl/D_2O$	Elapsed time, hr	Reaction mixtures, mole %				
		$CH_3S(O)Cl$	CH_3SO_2H	CH_3SO_2Cl	$CH_3SO_2SCH_3$	CH_3SO_3H
1	0.25	38	60	0.5	1	. . .
1	3	33	55.5	5	6	. . .
1	18	28	37	15	17	3
1	29	16	35	20.5	24.5	4
1	43	14	32	23	27	4
1	68	6	27	28	35	4
0.5	0.25	10	88	0.5	1	. . .
0.5	5	12	78	3.5	6.5	. . .
0.5	19	9	59.5	11	13.5	7
0.5	45	7	50	16	22	5
0.5	144	b	32.5	23	36	8
0.33	0.5	b	100	. . .	. . .	. . .
0.33	3	b	97	1	2	. . .
0.33	18	b	88	3.5	5	3.5
0.33	44	b	80	7	9	4
0.33	144	b	61	11	20	7
0.25	0.5	b	100	. . .	. . .	. . .
0.25	120	. . .	96	. . .	2	2

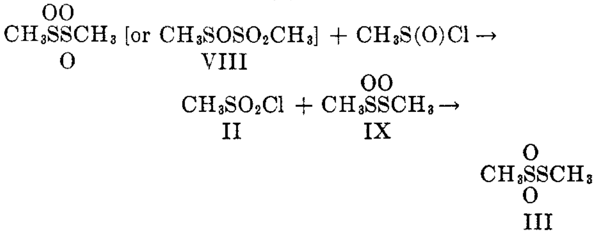
[a] Composition of the reaction mixtures at various time intervals. [b] Detectable only in CCl_4 extracts of the reaction mixture.

tulate a subsequent disproportionation of I into methanesulfenyl chloride, CH_3SCl (VI), and II as has previously been shown to occur.[4] The sulfenyl chloride VI thus formed would immediately combine with sulfinic acid IV by a well-known reaction to form III.[5] This explanation would seem to require a rapid disproportionation of I whereas, at least under anhydrous conditions, the disproportionation is slow, being only 26% complete in 23 days at 25°.

A second, more plausible explanation for the formation of II and III involves a mechanism analogous to that postulated by Kice for the disproportionation of arenesulfinic acids.[6] According to this mechanism, after the initial hydrolytic equilibration of I, a second (and probably rate determining) step is the reaction of unchanged I with the sulfinic acid IV to form methylsulfinyl methyl sulfone (VII) as shown in eq 3. Compound VII, possible after rearranging to $CH_3SOSO_2CH_3$ (VIII) (continuing the analogy to Kice's mechanism), then reacts with I to form products II and dimethyl disulfoxide (IX) which rapidly disproportionates to III (eq 4).

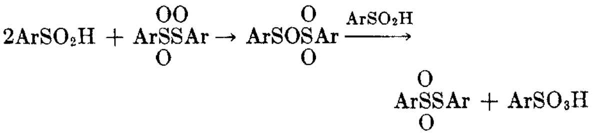

(3)

$$\underset{\text{I}}{CH_3S(O)Cl} + \underset{\text{IV}}{CH_3SO_2H} \rightarrow \underset{\text{VII}}{CH_3\underset{O}{\overset{O}{S}}\overset{O}{S}CH_3} + HCl \qquad (3)$$


(4)

$$CH_3\underset{O}{\overset{O}{S}}\overset{O}{S}CH_3\ [\text{or } \underset{\text{VIII}}{CH_3SOSO_2CH_3}] + CH_3S(O)Cl \rightarrow \underset{\text{II}}{CH_3SO_2Cl} + \underset{\text{IX}}{CH_3\overset{O}{S}\overset{O}{S}CH_3} \rightarrow \underset{\text{III}}{CH_3\underset{O}{\overset{O}{S}}SCH_3} \qquad (4)$$

The methanesulfonic acid (V) observed in this study may have had two origins: (1) from the hydrolysis of the sulfonyl chloride II, or (2) from the reaction of methanesulfinic acid (IV) with methylsulfinyl methyl sulfone (VII) or its rearranged product VIII, a step analogous to the behavior of arenesulfinic acids discovered by Kice and his co-workers[6] (eq 5).


(5)

$$2ArSO_2H + Ar\underset{O}{\overset{O}{S}}\overset{O}{S}Ar \rightarrow ArSO\underset{O}{\overset{O}{S}}Ar \xrightarrow{ArSO_2H} Ar\underset{O}{\overset{O}{S}}SAr + ArSO_3H \qquad (5)$$

The results of our study do not present unequivocal evidence, but the data shown in Table I indicates that the formation of sulfonyl chloride precedes the formation of sulfonic acid, suggesting that the latter is a simple hydrolysis product of the former.

An interesting aspect of the reaction between I and D_2O is that in mixtures (*e.g.*, $I:D_2O = 0.33$) in which the hydrolysis equilibrium of I (eq 2) is displaced well to the right giving mainly IV, the trace amounts of I are sufficient to decrease the concentration of IV with the passage of time as shown in Table I. In mixtures in which the equilibrium is shifted so far to the right that a pmr signal for I is no longer perceptible in CCl_4 extracts (*e.g.*, $I:D_2O = 0.25$), the sulfinic acid IV shows a high degree of stability.

The evidence that the sulfinyl chloride I is involved in the formation of II and III through reaction with a sulfinyl sulfone intermediate (VII) (eq 3 and 4) was provided by the pmr analysis of a solution resulting from the reaction of excess I with sodium methanesulfinate (CH_3SO_2Na). An unstable compound, obtained when the above reaction was carried out at −70°, showed two singlets in the pmr spectrum, one at $\delta = 3.23$ ppm [$CH_3S(O_2)$] and the other at $\delta = 2.87$ ppm [$CH_3S(O)$] with both having the same integration areas. Upon warming the reaction mixture to 30° the singlets at $\delta = 2.87$ and 3.23 ppm disappeared and were replaced by singlet peaks corresponding to II and III in equimolar quantities.

Experimental Section

Methanesulfinyl chloride (I) was prepared by a modification of the method previously described.[3] A mixture of freshly distilled methyl disulfide (28.6 g, 0.3 mole) and glacial acetic acid (36.0 g, 0.6 mole) was treated with chlorine (64 g, 0.9 mole) in a Dry-Ice bath. After completing the reaction and warming

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[4] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

[5] I. B. Douglass and B. S. Farah, *ibid.*, **24**, 973 (1959).

[6] J. L. Kice, G. Guaraldi and C. G. Venier, *ibid.*, **31**, 3561 (1966).

the mixture to room temperature, with stirring to facilitate the escape of hydrogen chloride, distillation was carried out under the reduced pressure of a water aspirator. The by-product acetyl chloride distilled at about 27° (50–70 mm); the removal of the last acetyl chloride being accompanied by an abrupt pressure drop to about 15 mm. Continued fractional distillation gave 52.1 g (88% yield) of colorless methanesulfinyl chloride boiling at 38–41° (15 mm) and having $n^{25}\text{D}$ 1.5000.

Reaction of I with Water.—Distilled water (2.60 g, 0.144 mole) was added dropwise to freshly distilled I (31.06 g, 0.315 mole) at 0°. An exothermic reaction resulted and hydrogen chloride was slowly evolved during the addition of water and during the 30 min required for the solution to come to room temperature. The resulting clear, colorless solution after standing at room temperature for 7 days, was fractionally distilled and yielded 4.31 g (0.038 mole) of methanesulfonyl chloride (II) and 13.90 g (0.110 mole) of methyl methanethiosulfonate (III). Each sample was slightly contaminated by the other compound as evidenced by their pmr spectra.[7]

In order to confirm the stoichiometry, I (7.62 g, 0.0774 mole) was added in one portion to distilled water (0.46 g, 0.026 mole) at 0° and then stored at room temperature for 6 days. Pmr analysis of the reaction mixture dissolved in CCl_4 (in which it was miscible) indicated that it contained 49 mole % of II, 45 mole % of III, and 5 mole % of unreacted I.

In another experiment, distilled water (2.00 ml, 0.111 mole) was added in 0.20-ml portions at 15-min intervals to I (12.00 g, 0.122 mole) held at 0° by immersion in an ice bath. Before the second and each subsequent addition of water small samples of the reaction solution were removed, diluted to 10% concentration in CCl_4, and examined by pmr spectroscopy. At the end of 45 min (after three additions of water) the pmr spectrum showed a low-intensity broad band at $\delta = 2.71$ ppm and a large peak at $\delta = 3.37$ ppm corresponding to unreacted methanesulfinyl chloride. By the end of 2.5 hr all the water had been added and there were sharp peaks corresponding to trace amounts of II and III along with a considerable quantity of unreacted I. After holding the mixture at room temperature for 6 days, pmr analysis of a portion, diluted to 10% concentration in CCl_4, and integration of the peak areas indicated that the CCl_4 extract contained 45 mole % II, 48 mole % III, and 7 mole % of unreacted I. Because water and sulfinyl chloride had been mixed in approximately equimolar quantities, the unreacted water separated as an upper phase when samples were diluted.

Reaction of I with Deuterium Oxide.—Deuterium oxide (0.23 ml, 0.013 mole) was added to I (1.18 g, 0.012 mole) maintained at approximately 0° by immersion in an ice bath. The mixture was allowed to warm slowly to room temperature and the course of the reaction was followed by periodically removing samples and obtaining pmr spectra of the neat solutions. Simultaneously, samples were withdrawn and their CCl_4 extracts examined by pmr spectroscopy. The results are shown in Table I.

The same procedure was followed in studying the reaction of I with deuterium oxide in the molar proportions of $I:D_2O = 0.5$, 0.33, and 0.25. Results of these experiments are also shown in Table I. In all cases the mole percentages of components in the reaction mixtures were determined by integration of the peak areas of the pmr spectra.

Formation of I in the Reaction between Methanesulfinic Acid and Hydrogen Chloride.—Methyl methanesulfinate[8] (4.10 g, 0.0435 mole) was dissolved in 20 ml of water and treated with about 10 ml of solution containing sodium hydroxide (1.74 g, 0.0435 mole). Water and methanol were removed under reduced pressure in a rotary evaporator and colorless solid residue of sodium methanesulfinate was taken up in 3.2 ml of deuterium oxide. A pmr spectrum of the solution, using an external TMS standard showed a singlet at δ 2.33 for the $C\mathit{H}_3SO_2^-$ ion.

Gaseous hydrogen chloride was passed into the solution and caused the immediate precipitation of sodium chloride. After filtering the solution and continuing the passage of HCl for about 1 hr, the solution was extracted with carbon tetrachloride containing TMS. Pmr analysis showed a sharp singlet peak for I at δ 3.37.

The Disproportionation of I.—A slightly impure sample of I (5.1 g, 95% I, 5% II) was stored in a sealed vial and exposed to the daily sunlight on a window ledge for 23 days. The vial was cooled in Dry Ice and opened, and the solution was diluted with CCl_4 containing TMS. Pmr analysis indicated that the solution still contained 76 mole % of unchanged I, 13 mole % of II, 2 mole % of methyl chloride, and smaller amounts of other characteristic decomposition products of methanesulfenyl chloride.[9]

Reaction of I with Sodium Methanesulfinate (Evidence for the Formation of Methylsulfinyl Methyl Sulfone).—Methyl methanesulfinate (18.8 g, 0.20 mole) was added to a solution of sodium hydroxide (8.0 g, 0.20 mole) in 50 ml of water. The ensuing reaction was moderately exothermic and after 2 hr at 30°, 500 ml of benzene was added, and 40 ml of water was removed by azeotropic distillation. The viscous oil which remained after decanting the remaining benzene was dried in a rotary evaporator to a moist powder which was further dried at 120° for 12 hr.

Pmr examination of a 10% (by weight) solution of the sodium methanesulfinate in D_2O showed a singlet at $\delta = 2.34$ ppm ($CH_3S(O)O^-Na^+$) and a small singlet at $\delta = 2.08$ ppm ($C\mathit{H}_3SC\mathit{H}_3$).[10] Acidification of the D_2O solution with gaseous hydrogen chloride gave a solution which showed a major pmr singlet at $\delta = 2.93$ ppm ($C\mathit{H}_3S(O)OH$) and a minor singlet at $\delta = 2.08$ ppm ($C\mathit{H}_3SC\mathit{H}_3$). Integrations of the two spectra showed that the $CH_3SO_2Na:CH_3SCH_3$ and the $CH_3SO_2H:CH_3SCH_3$ ratios were the same.

A small sample of sodium methanesulfinate was placed in a test tube immersed in a Dry Ice bath at −70° and I was slowly added. After extracting the cold slurry with CCl_4 containing TMS the pmr spectrum indicated that the solution contained two known compounds, I ($\delta = 3.36$ ppm, 50-mm integration height) and II ($\delta = 3.69$ ppm, 1-mm integration height), and an unknown compound presumed to be methylsulfinyl methyl sulfone, $CH_3S(O)S(O_2)CH_3$, ($C\mathit{H}_3SO_2^-$, $\delta = 3.23$ ppm, 10-mm integration height; $C\mathit{H}_3SO^-$, $\delta = 2.87$ ppm, 10-mm integration height).

Pmr analysis of the solution after it had been kept for 1 hr at 30° indicated that it contained only I ($\delta = 3.37$ ppm, 40-mm integration height), II ($\delta = 3.69$ ppm, 11-mm integration height), and III ($C\mathit{H}_3SO_2$, $\delta = 3.28$ ppm, 10-mm integration height; $C\mathit{H}_3S$, $\delta = 2.69$ ppm, 10-mm integration height).

Registry No.—I, 676-85-7; II, 124-63-0; VII, 14128-56-4; water, 7732-18-5; deuterium oxide, 7789-20-0.

Acknowledgment.—This work was supported by a grant (AP 00383) from the Research Grants Branch, National Center for Air Pollution Control. We wish to thank Dr. R. E. Hill for determining some of the pmr spectra.

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[7] The pmr spectra were determined on a Varian A-60 analytical spectrometer at ambient probe temperature. The chart was calibrated frequently using the chloroform ($CHCl_3$) and tetramethylsilane (TMS) signals. Using this procedure chemical shifts determined in CCl_4 solution on the pure compounds were $C\mathit{H}_3S(O)Cl$, $\delta = 3.37$ ppm; $C\mathit{H}_3S(O_2)Cl$, $\delta = 3.61$ ppm; $C\mathit{H}_3S(O_2)SCH_3$, $\delta = 3.28$ ppm; $CH_3S(O_2)SC\mathit{H}_3$, $\delta = 2.69$ ppm. Compare G. R. Pettit, I. B. Douglass, and R. E. Hill, *Can. J. Chem.*, **42**, 2357 (1964). In the spectra of the neat solutions, the peaks relative to TMS were variable, depending on the composition of the systems. For example, the δ values of $C\mathit{H}_3SO_2Cl$ in the reactions of I with D_2O in various ratios varied from 3.83 to 4.06 ppm. In individual mixtures, however, the positions of characteristic peaks with respect to each other remained practically constant in all cases, thus facilitating identification of the compounds present.

[8] I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965).

[9] The spontaneous decomposition of methanesulfenyl chloride, which occurs with formation of methyl chloride, methyl polysulfides, and other products is currently under investigation and will be reported in the near future.

[10] H. G. Houlton and H. V. Tartar [*J. Am. Chem. Soc.*, **60**, 544 (1938)] reported that sodium alkanesulfinates decompose on standing in a concentrated aqueous solution: $2RS(O)ONa \rightarrow RSR + Na_2SO_4$.