

Methanesulfinic Acid and Its Properties¹

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Abstract: Methanesulfinic acid has been isolated in crystalline form and characterized. All molecules within a particular crystal have been shown by X-ray analysis to have the same configuration about sulfur. Attempts to convert a single optically active crystal of the substance to optically active methyl methanesulfinate by reaction of diazomethane with the crystal failed. The production of racemate suggests that the molecules of acid left the crystal and became symmetric before reaction occurred. Mass spectra of the acid taken at various sample temperatures revealed that the molecule produces a CS₂ fragment before electron impact.

Although salts and derivatives of methanesulfinic acid have been known for some time,^{2a} the acid itself has never been isolated. Furthermore, the low molecular weight aliphatic sulfinic acids (below C₁₂) were described as viscous oils^{2b} which are subject to rapid decomposition.^{2a,c}

We wish to report the isolation of crystalline methanesulfinic acid (mp 40–42°, sealed tube). Although first obtained accidentally as a decomposition product of cedryl methanesulfinate, it was later conveniently prepared from its acid chloride. The compound was stored at 25° under nitrogen for only about 48 hr before decomposition was apparent (foul odor and formation of a pentane-insoluble oil). However, a sample has been kept for about 4 months under nitrogen at –10 to –15° without noticeable decomposition.

Chemical Properties. Conversion of methanesulfinic acid to its sodium salt and treatment with benzyl chloride in ethanol afforded methyl benzyl sulfone, a known, high-melting derivative.³

The mass spectrum of methanesulfinic acid (direct inlet system, source at room temperature) is depicted in Figure 1, and the relative peak intensities are tabulated in Table I. The presence of a prominent parent peak (*m/e* 80, 50% relative intensity) establishes the molecular weight of the substance. When spectra were determined using the heated inlet system (sample temperatures of 50 and 180°, source temperature 190–200°), the spectra depicted in Figures 2 and 3 were recorded.

An exact mass measurement of the *m/e* 76 peak in Figure 1 revealed that it is due to CS₂⁺. Moreover, its presence in spectra (Figures 2 and 3) exhibiting practically no *m/e* 80 peak, which is the parent ion peak of methanesulfinic acid, suggests that it originates substantially from thermal decomposition prior to electron impact. The thermal decomposition route also accounts in part, but apparently not completely, for the presence of such a peak in Figure 1.

An extrapolation of Kice's results⁴ on the decom-

position of arylsulfinic acids to our system would support the assumption that dimethyl disulfide is one of the decomposition products. Indeed, peaks of *m/e* 94, 79, and 45 appear in Figures 2 and 3, suggesting that a small amount of dimethyl disulfide was formed during decomposition of methanesulfinic acid at 50 and

Table I. Relative Peak Intensities Found in the Mass Spectrum of Methanesulfinic Acid (Source at Room Temperature, Direct Inlet System)

<i>m/e</i>	Rel abundance, ^a %	Assignment ^b
126	Trace	C ₂ H ₆ O ₂ S ₂
94	Trace	C ₂ H ₆ S ₂ , C ₂ H ₆ O ₂ S
82	4	
81	3	
80	50	CH ₄ O ₂ S
76	8	CS ₂ ^c
67	5.5	
66	4	
65	100	HO ₂ S
64	37	SO ₂
63	33	CH ₃ OS
62	10	CH ₂ OS
50	3	
49	4	
48	22.5	OS, CH ₄ S
46	10	CH ₂ S
45	19	CHS
44	11	CS, CO ₂ ^d
36	4	
34	14.5	H ₂ S
33	8	HS

^a Read-off ± 0.5%. ^b Tentative assignments unless stated otherwise. ^c Definite assignment from high-resolution mass measurement. ^d Not corrected for background (*e.g.*, H₂O, N₂, O₂).

180°. Moreover, the *m/e* 76 peak is much larger than the *m/e* 94 peak in Figures 2 and 3, but is much smaller than the *m/e* 94 peak in the mass spectrum of dimethyl disulfide (Figure 4). This implies that dimethyl disulfide is only a minor contributor to the *m/e* 76 peak. Some other decomposition intermediate must fragment more efficiently to yield CS₂.⁵

Preliminary results of an X-ray study⁶ indicated that a single crystal of methanesulfinic acid contains all molecules of one "chirality," *i.e.*, all left handed (S)

(5) The exact composition of *m/e* 76 in the mass spectrum of dimethyl disulfide has been determined to be CS₂: J. H. Bowie, S. O. Lawesson, J. O. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc., Sect. B*, 946 (1966).

(6) M. Meyers and K. N. Trueblood, private communication.

(1) This investigation was supported by Public Health Service Research Grant No. GM 12640-03 from the Department of Health, Education and Welfare.

(2) (a) W. E. Truce and A. M. Murphy, *Chem. Rev.*, **48**, 69 (1951).

(b) Two recently reported exceptions are the solid *n*-butane- and *n*-octanesulfinic acids: H. Reinheckel and D. Jahnke, *Chem. Ber.*, **99**, 1718 (1966). (c) C. S. Marvel and N. A. Meinhardt, *J. Am. Chem. Soc.*, **73**, 859 (1951).

(3) H. J. Backer, *Rec. Trav. Chim.*, **70**, 260 (1951).

(4) (a) J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966); (b) J. L. Kice and G. Guaraldi, *ibid.*, **31**, 3568 (1966); (c) J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964).

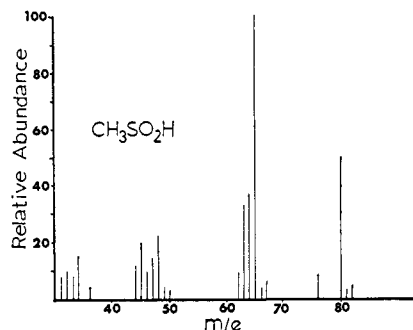


Figure 1. Mass spectrum of methanesulfonic acid (direct inlet, 25–50°).

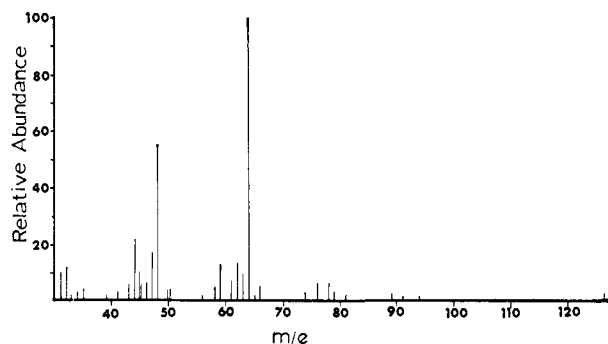


Figure 2. Mass spectrum of methanesulfonic acid (heated inlet, 50°).

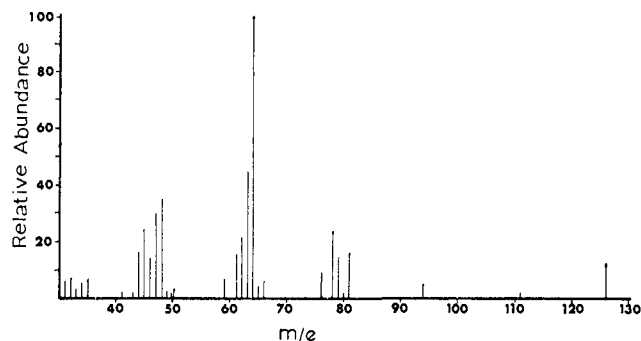


Figure 3. Mass spectrum of methanesulfonic acid (heated inlet, 180°).

or all right handed (*R*). This striking result suggested the possibility that if a reaction could be conducted at a single crystal–solvent interface, an optically active product capable of maintaining asymmetry around sulfur might be generated. Thus, the dissymmetry of the crystal might be transformed into molecular chirality. If the absolute configuration of the product could be determined, then the absolute configuration of the crystal could be inferred. Accordingly, the following scheme was devised. A single crystal of I suspended in pentane was allowed to react with diazomethane dissolved in pentane at 0°, and the methyl methanesulfinate produced was immediately treated with *p*-tolyl Grignard reagent. The absolute configuration of methyl *p*-tolyl sulfoxide (III) is well known,⁷ and the

(7) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

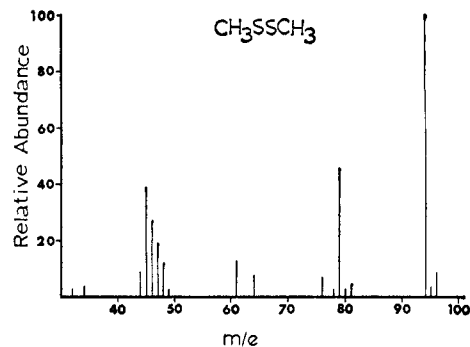
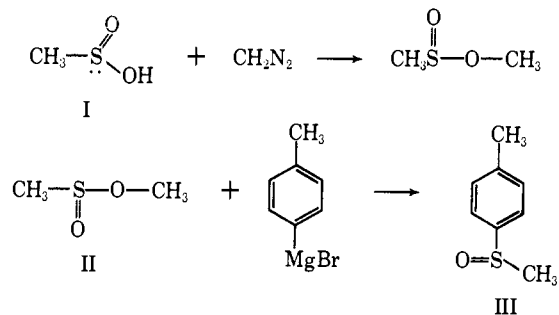
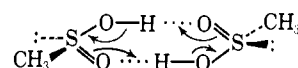


Figure 4. Mass spectrum of dimethyl disulfide (gas inlet, 25°).

Grignard reaction leading to its formation occurs stereospecifically with inversion of configuration at sulfur.⁷



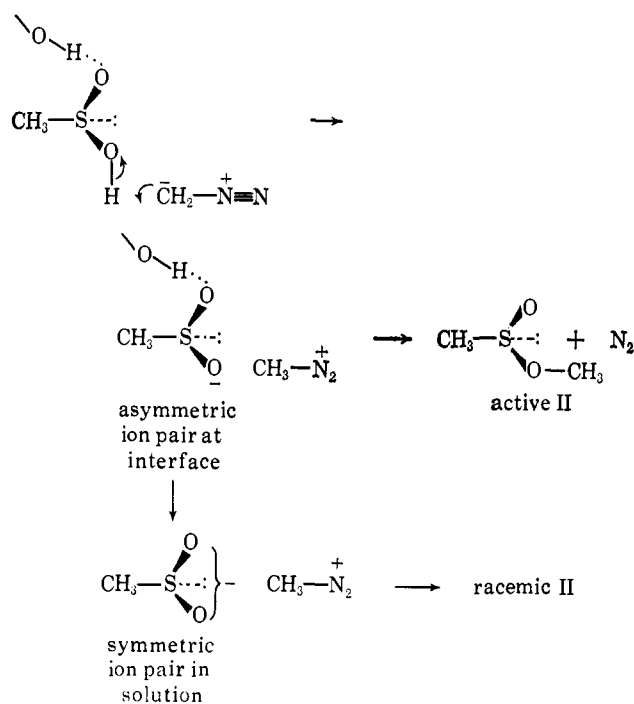
In practice, only racemic sulfoxide (III) was obtained, although bubbles of nitrogen gas were generated mainly near the pentane–crystal interface. The acid (I) was demonstrated to be very sparingly soluble in pentane, and possibly reaction took place only after racemizing proton transfers occurred in the solvent immediately surrounding the crystal. In fact, an osmometric molecular weight determination using 5–6 mM solutions of methanesulfonic acid in chloroform gave values of 132–135, suggesting a monomer–dimer equilibrium in solution.



A second possibility is that although an asymmetric ion pair was formed at the interface, the anion of the ion pair left its asymmetric environment before it collapsed to the covalent state.

Physical Properties. The pK_a of methanesulfonic acid (I) was determined in water at 25° and found to be 2.28 ± 0.04 . This value agrees well with that obtained for 4-phenylbutanesulfonic acid (2.23).⁸ The nmr spectrum of I in deuteriochloroform at 25° exhibited two sharp peaks at τ 7.3 and -0.4 of relative intensities of 3:1, respectively. With the possibility in mind that I exists as a tautomeric mixture in which one form has hydrogen attached to sulfur, the nmr spectrum of I was also taken at -62° in the same solvent. The only detectable change of spectrum with temperature was a slight change in chemical shift. The infrared spectrum of I in chloroform gave the following bands: 3000 (s), 2508 (s), 1410 (m), 1310 (m), 1235–1190 (m), 1075 (vs), 1025 (m, shoulder), 952 (m) cm^{-1} . Many of these

(8) P. Rumpf and J. Sadet, *Bull. Soc. Chim. France*, 450 (1958).



bands occur at frequencies similar to those exhibited by the arylsulfinic acids.⁹

Experimental Section

Methanesulfinic Acid (I). Exactly 3.6 ml (0.20 mole) of distilled water was added dropwise with stirring under a dry nitrogen atmosphere at -30° over *ca.* 5 min to 20 g (0.203 mole) of methanesulfinyl chloride.¹⁰ The hydrogen chloride generated was swept into a trap by a flow of dry (oxygen-free) nitrogen. A white solid precipitated about 5 min after the water addition had stopped. The mixture was stirred for 0.5 hr at -30° , 0.5 hr at 0° (at this temperature the solid disappears), and under vacuum (*ca.* 20 mm) for another 2.75 hr. By this time the reaction mixture consisted of a white semisolid (crystals and oil) or just a colorless oil. The semisolid (or oil) was mixed with *ca.* 7 ml of anhydrous ether and stored at -15° for 24 hr. Long, transparent, colorless needles (8–10 g) of the acid were obtained when the mother liquors were decanted, and the residual ether was evaporated under a stream of pure nitrogen. The acid crystallized well from ether, ether–pentane, and chloroform–pentane in the form of hygroscopic¹¹ needles. It was soluble in water, chloroform, and dichloromethane; slightly soluble in ether; and very sparingly soluble in pentane, heptane, and carbon tetrachloride.

Anal. Calcd for $\text{CH}_4\text{O}_2\text{S}$: C, 14.99; H, 5.03; S, 39.93. Found: C, 15.19; H, 5.08; S, 40.30.

Mass Spectrometry. The mass spectra were determined with an AEI MS-9 mass spectrometer¹² operating with an ionizing voltage

(9) S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

(10) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).

(11) A few crystals of the acid will turn into a transparent, colorless oil within 15 min under normal atmospheric conditions but can be exposed to the atmosphere overnight without noticeable change in unusually dry weather (relative humidity below 20%).

of 70 ev. The methanesulfinic acid spectrum and high-resolution mass measurement were obtained by direct insertion (direct inlet system). The source temperature was 25° at the start of the operation and rose to *ca.* 50° by the time the spectrum was recorded. The sample of dimethyl disulfide was admitted to the ion source through a heated inlet system; the sample was at room temperature. The same procedure was used for recording the spectra corresponding to Figures 2 and 3, except that the methanesulfinic acid sample was heated to 50 and 180° , respectively.

Density Determination. The crystal density of I was determined by the flotation method in mixtures of carbon tetrachloride and heptane, and gave 1.52, 1.52, and 1.53. These values are in agreement with that calculated from the dimensions of the unit cell⁶ (1.54).

Potentiometric Titration. The detailed procedure described by Pecsok¹³ was employed for the potentiometric titration with a Beckman Model H2 pH meter. The residual ether from twice recrystallized methanesulfinic acid was removed under vacuum (0.08 mm) at 0° overnight. The sample concentration ranged from 0.0720 to 0.1544 g/30.0 ml of degassed (boiled) distilled water. Each sample was titrated with standard sodium hydroxide solution at 26° immediately after weighing and dilution.

Methyl *p*-Tolyl Sulfoxide. A single crystal ($\sim 1 \times 1 \times 15$ mm) of methanesulfinic acid was suspended in *ca.* 5 ml of dry pure pentane in a dry 8-in. test tube equipped with a magnetic stirring bar. The test tube was attached to a diazomethane generator which consisted of a 50-ml Claisen flask equipped with a 125-ml addition funnel (containing *ca.* 100 ml of dry pure pentane). The diazomethane generator was previously charged with a solution of 2.9 g of potassium hydroxide in 1.5 ml of water (the solution was carefully deposited on the bottom of the flask) followed *immediately* (to avoid vaporization of the water) by a layer of 5 ml of dry diethylene glycol. The test tube was attached by means of a two-hole rubber stopper to a train consisting of a calcium chloride drying tube and a diazomethane trap (anhydrous ether at 0°). The pentane suspension was immersed in an ice–water bath and stirred. Approximately 20 ml of pentane and *ca.* 0.5 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide were added to the generator. The Claisen flask was immersed in a 65° warm-water bath, and diazomethane–pentane was allowed to distil into the stirred sulfinic acid–pentane suspension until the suspension was definitely yellow (*ca.* 5 drops of distillate). The heating bath was removed and the methylation allowed to proceed until evolution of N_2 had stopped (for *ca.* 0.5 hr; the bubbles formed near the surface of the crystal). The test tube was then detached, sealed with a septum cap, and titrated at 0° (by means of a syringe) with a dilute solution of formic acid in ether followed by a large excess of *p*-tolylmagnesium bromide in tetrahydrofuran. An excess of saturated ammonium chloride solution was added, and the resulting pentane–tetrahydrofuran solution was decanted, dried, and evaporated. The residue was chromatographed on silica gel (15 g) with dichloromethane–ether mixtures (from 90% dichloromethane–10% ether to 50% dichloromethane–50% ether) as eluent. Thus, 31 mg of methyl *p*-tolyl sulfoxide (infrared spectrum and thin-layer chromatographic behavior identical with that of an authentic sample) was obtained. This compound was completely optically inactive although the wavelength of the light used was varied from 310 to 546μ .

Growth of Large Crystals. A modified method of Stedman and McCauley¹⁴ was employed. A temperature gradient of 9° (from 22 to 13°) was obtained by allowing acetone (technical grade) to evaporate in a fume hood. Crystals up to *ca.* $3 \times 2 \times 15$ mm were thus obtained.

(12) Purchased with funds made available by the National Science Foundation (GP 3672).

(13) R. L. Pecsok, *J. Chem. Educ.*, **28**, 252 (1951).

(14) M. Stedman and D. J. McCauley, *Chem. Ind. (London)*, 1883 (1966).