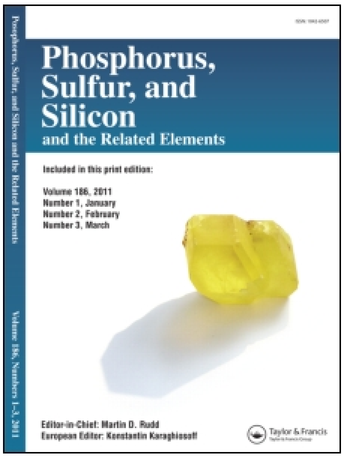

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TRIMETHYLAMMONIOMETHANESULFINATE AND TRIMETHYLAMMONIOMETHANESULFONATE, THE SIMPLEST SULFINIC AND SULFONIC ACID BETAINES. REVISION OF THE STRUCTURE OF THE TRIMETHYLAMINE OXIDE-SULFUR DIOXIDE PRODUCT

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TRIMETHYLAMMONIOMETHANESULFINATE AND TRIMETHYLAMMONIOMETHANESULFONATE, THE SIMPLEST SULFINIC AND SULFONIC ACID BETAINES. REVISION OF THE STRUCTURE OF THE TRIMETHYLAMINE OXIDE–SULFUR DIOXIDE PRODUCT[1]

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Bromomethanesulfinic acid (**1**) reacted with excess trimethylamine to give trimethylammoniomethanesulfinate (**3**) which was converted by aqueous chlorine into trimethylammoniomethanesulfonate (**4**). Compounds **3** and **4** are (a) the first examples of sulfino- and sulfo-betaines in which the sulfur and quaternary nitrogen are bound to the same carbon, and, at the same time, are (b) the parent compounds of the respective classes of the sulfinic and sulfonic acid betaines. Reaction of **1** with dimethylamine followed by aqueous chlorine yielded a compound which (a) proved to be identical to the product of the reaction of trimethylamine oxide with sulfur dioxide, and also to the formaldehyde-bisulfite-dimethylamine adduct, and (b) gave **4** on methylation with dimethyl sulfate. We conclude that the sulfur dioxide-trimethylamine oxide product, contrary to an earlier proposal, is dimethylammoniomethanesulfonate (**8**). The pK'_a of **8** and the equilibrium constant for the reaction $Me_2NCH_2SO_3^- + H_2O \rightleftharpoons Me_2NH + HOCH_2SO_3^-$ (in H_2O, ionic strength 0.5 M with NaCl), were found from ^{1}Hmr spectra to be 6.05 (at 19.2°C) and 1.20×10^{-4} M (at 20.8°C), respectively.

The Betaines

As part of a current mechanistic study we sought to generate sulfene (**2**) by the "abnormal route"[2] from an aqueous solution of bromomethanesulfinic acid (**1**) in the presence of tertiary amines. The reaction in the presence of triethylamine proceeded in the expected manner to give a mixture of the trialkylammonium methanesulfonate and bromide, but with trimethylamine an additional product was signalled by the appearance of ^{1}Hmr singlets at δ3.32 and 3.72. With excess trimethylamine this material became the major product and was readily obtained pure by the use of a deionizing resin followed by recrystallization. The following evidence showed it to be the simple but hitherto unknown sulfinobetaine trimethylammoniomethanesulfinate (**3**). Elemental analyses were consistent with the formula $C_4H_{11}NO_2S$ and the ir spectrum showed the characteristic sulfinate anion peaks[3] around 1060 and 990 cm^{-1}. Integration of the ^{1}Hmr signals gave the ratio 9 : 2, while the ^{13}Cmr spectrum showed peaks at δ57.4 and 89.2 in a roughly 3 : 1 ratio. Brief reaction with aqueous chlorine gave another crystalline product shown to be **4** by appropriate elemental analyses, ir peaks at 1230, 1195 and 1045 cm^{-1} consistent

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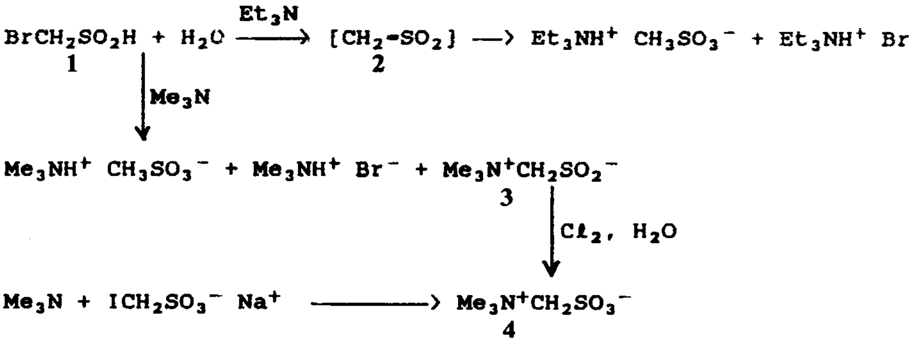
[a] On leave from the Technical University of Gdańsk, Poland



SCHEME 1

with the presence of the sulfonate anion,[3] and ^{1}Hmr and ^{13}Cmr absorption at 3.39 (s, 9 H) and 4.53 (s, 2 H) and 57.3 and 77.9 ppm, respectively. Independent synthesis of **4**, (a) by reaction of sodium iodomethanesulfonate and trimethylamine in aqueous solution (albeit in poor yield), and (b) also by the much more convenient route described in the next section, confirmed the identity of this compound. The reactions are summarized in Scheme 1.

Not only is **4** previously unreported, but, remarkably, it is the first example to our knowledge of a [1]betaine, i.e. a sulfobetaine in which the quaternary nitrogen and sulfur atoms are attached to the same carbon. The simple "parent" sulfobetaines of the general formula $(CH_3)_3N^+(CH_2)_nSO_3^-$ where $n = 0$ and 2, 3, 4, and 6, along with numerous compounds formally derived by replacing the *N*-methyl or methylene hydrogens by other groups, have been known for quite some time,[4,5] but we are unable to find any reports of either the parent or derived species in which $n = 1$. Preparation of **4** enables us to compare infrared and nmr spectra of the first five members of the simple trimethyl series (see Table I).

The Product of the Sulfur Dioxide–Trimethylamine Oxide Reaction

The above observations recalled the report by Craig and Purushothaman[6] on the product of the reaction of trimethylamine oxide and sulfur dioxide. These authors had noted that the presence of two peaks in the ^{1}Hmr spectrum (singlets at $\delta 3.10$ and 4.30 in a 3 : 1 ratio) was inconsistent with Burg's[7] sulfite–betaine formulation (**5**) and suggested instead a zwitterionic sulfite structure (**6**).

$$\underset{\mathbf{5}}{Me_3\overset{+}{N}\text{—}OSO_2^-} \qquad \underset{\mathbf{6}}{Me_2\overset{+}{N}HCH_2\text{—}OSO_2^-}$$

$$\underset{\mathbf{7}}{Me_2\overset{+}{N}{=}CH_2\ HSO_3^-} \qquad \underset{\mathbf{8}}{Me_2\overset{+}{N}HCH_2\text{—}SO_3^-}$$

Such a structure, however, is highly suspect, because if, as would appear likely,[8] the product arises by way of a Polonovski-type rearrangement of the initially-formed adduct (**5**) to give the iminium bisulfite (**7**) which then gives the product, the most probable structure for this product is **8**, i.e. that of an aldehyde–bisulfite–amine

TABLE I

Characterization of the trimethylammonioalkanesulfonates $Me_3N^+(CH_2)_nSO_3^-$

n	M.p.[a] (°C)	IR (KBr, cm^{-1})	^{1}Hmr (D_2O)[b] δ	^{13}Cmr (D_2O)[b] δ
0	254–255 (dec.)[c]	3040 (vw), 3030 (vw), 1480 (s), 1460 (s), 1295 (br, vs), 1250 (m), 1050 (vs), 965 (s), 790 (s)	3.23 (s)	51.8 (t, J 3 Hz)
1	320–322, (d. 310)[d]	3045 (w), 3015 (m), 2960 (vw), 1490 (m), 1480 (s), 1230 (br, vs), 1195(s), 1120 (s), 1055 (vs), 1045 (vs), 965 (s), 930 (w), 890 (w), 790 (m)	3.38 (s, 9 H), 4.52 (s, 2 H)	57.1 (t, J 4 Hz), 77.7 (t, J 0.8 Hz)
2	356–358, (d. 353)[d]	3030 (m), 1482 (vs), 1200 (br, vs), 1110 (w), 1025 (vs), 930 (w), 910 (w)	3.20 (s, 9 H), 3.41–3.77 (A_2B_2 mult., strongest peaks at 3.49 and 3.69 ppm, 4 H)	47.1 (s), 55.8 (t, J 3.8 Hz), 64.1 (t, J 3.2 Hz)
3	356–358, (d.348)[d]	3030 (m), 2980 (w), 1495 (m), 1485 (m), 1198 (br, vs), 1140 (m), 1035 (vs), 970–955 (br, m), 915 (m), 800 (w), 740 (m)	2.15–2.31 (m, 2 H), 2.97 (t, J 7.35 Hz), 3.15 (s, 9 H), 3.44–3.53 (m, 2 H)	21.1 (s), 49.8 (t, J 1.6 Hz), 55.4 (t, J 4.0 Hz), 67.2 (t, J 3.2 Hz)
4	355–356, (d. 349)[d]	3030 (m), 2970–2930 (br, w), 1485 (s), 1465 (m), 1185 (br, vs), 1030 (vs), 955 (m), 900 (m)	1.81 (quintet, J 7.2 Hz, 2 H), 1.87–2.04 (m, 2 H), 2.98 (t, J 7.3 Hz), 3.13 (s, 9 H), 3.38 (t, J 8.3 Hz, 2 H)	23.6 (t, J 1.7 Hz), 23.8 (s), 52.6 (s), 55.4 (t, J 4.1 Hz), 68.4 (t, J 3.0 Hz)

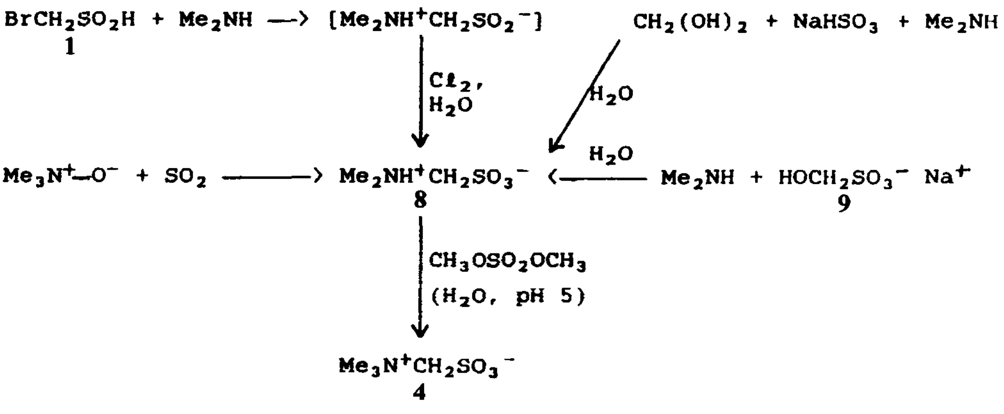
[a] Samples were placed on a preheated melting point apparatus at roughly 10 to 15°C below the lowest temperature reported.

[b] Determined with the XL300 spectrometer (300 MHz for ^{1}Hmr, 75.5 MHz for ^{13}C).

[c] A change in crystal form was observed at 238–9°C; melting accompanied by evolution of gas at 254–5°C gave a clear, colorless liquid.

[d] Samples first darkened at the lower temperature and then decomposed without melting at the higher temperature to give a black, solid residue.

adduct.[9] In fact, the aldehyde–bisulfite–amine adducts were in the early years of this century ascribed ammoniomethylsulfite structures like **6**, but the investigations of Backer and Mulder,[9] taken with the related work of Raschig on the hydroxy analogues,[10] provided a strong case for the aminomethanesulfonate formulae. This has subsequently been confirmed for two members of this class of compounds, isopropylammoniomethanesulfonate[11] and methylammoniomethanesulfonate,[12] by single crystal x-ray structure determination. In addition, Edward and Whiting[8] have, in fact, inferred an ammonioalkanesulfonate structure for the product of the reaction of benzyldimethylamine oxide with sulfur dioxide from "its analysis, ir spectrum,



SCHEME 2

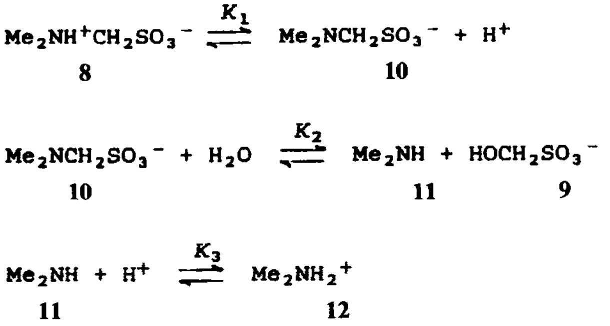
and decomposition to benzaldehyde... on attempts to crystallize it from water or 95% ethanol".

In our view these points argued against **6** and much in favour of **8** for the trimethylamine oxide–SO_2 product, but the fact that the Craig-Purushothaman picture had gained some acceptance,[13,14] taken with the consideration that these arguments can be regarded as not entirely conclusive, led us to perform the following experiments to put the matter to rest. Reaction of **1** with dimethylamine gave a fragile sulfinate which was treated directly with aqueous chlorine to yield a crystalline substance, identical in melting point, ir, ^{1}Hmr, and ^{13}Cmr spectra to the product of the reaction of trimethylamine oxide and sulfur dioxide. The same compound was also produced by the reaction in water of (a) formaldehyde hydrate, dimethylamine and sodium bisulfite, or (b) sodium hydroxymethanesulfonate (**9**) and dimethylamine. In addition, this material (a) on methylation with dimethyl sulfate in aqueous medium gave **4**, and (b) was only slowly affected by exposure to excess aqueous chlorine.[15]

Taken with the arguments already given above, the observations that (a) the compound is both formed from, and converted into, species with undoubted C—S bonds and (b) it is formed (and not immediately further transformed) in the presence of excess chlorine in water (a property inconsistent with any sulfite formula such as **6**),[16] clearly require that the sulfur dioxide–trimethylamine oxide product be formulated as dimethylammoniomethanesulfonate (**8**) (see Scheme 2).

Equilibrium Constants in the Dimethylammoniomethanesulfonate (8) System

Our initial ^{1}Hmr and ^{13}Cmr spectra (in D_2O solution) showed sufficient variation with the acidity of the medium that a more careful examination of the spectra was undertaken. Our observations, which are interpreted in terms of the equilibria shown in Scheme 3, may be summarized qualitatively as follows. In H_2O solution at low pH ($\leqslant 4$) the only species evident in the ^{1}H or ^{13}Cmr spectra is **8** and the equilibrium is essentially frozen (at room temperature); addition of **9** and **12** simply gives the extra signals due to the extra substances. At high pH ($\geqslant 10.5$) the only observed component is **10**, but the equilibrium is mobile, and addition of **9** and **11**



$$\underset{\mathbf{8}}{Me_2NH^+CH_2SO_3^-} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{10}}{Me_2NCH_2SO_3^-} + H^+ \tag{1}$$

$$\underset{\mathbf{10}}{Me_2NCH_2SO_3^-} + H_2O \overset{K_2}{\rightleftharpoons} \underset{\mathbf{11}}{Me_2NH} + \underset{\mathbf{9}}{HOCH_2SO_3^-} \tag{2}$$

$$\underset{\mathbf{11}}{Me_2NH} + H^+ \overset{K_3}{\rightleftharpoons} \underset{\mathbf{12}}{Me_2NH_2^+} \tag{3}$$

SCHEME 3

gives more **10** plus the signal appropriate to whichever compound (**9** or **11**) was added in the greater amount. As the pH is gradually lowered, **9** and **12** appear in the equilibrium mixture becoming the major components around pH 7.2. Just below pH 7 the peaks hitherto assigned to **10** start to shift towards the positions previously noted for its conjugate acid (**8**), and at pH 5 the shift is virtually complete. The variation of the chemical shifts of the two signals with pH (shown in Fig. 1) obviously has its origin in the acid–base equilibrium shown in eq. (1), and enables us to assign a pK'_a value of 6.05 ± 0.05 for **8** under these conditions (19.2°C, ionic strength 0.5 *M* with NaCl). As the pH of the medium is lowered in this range the concentration of **10** decreases and the rate of equilibration slows markedly until at pH 6, for example, a number of hours is required to achieve the equilibrium composition. From the relative amounts of **10** vs **9** and **12** in the pH range 7 to 9, K_2 was estimated from eq. (5), which is derived as follows.

From eq. (1) to (3)

$$K_1 = [Me_2NCH_2SO_3^-][H^+]/[Me_2NH^+CH_2SO_3^-]$$
$$K_2 = [Me_2NH][HOCH_2SO_3^-]/[Me_2NCH_2SO_3^-]$$

(taking the activity of water as unity) and

$$K_3 = [Me_2NH_2^+]/[Me_2NH][H^+].$$

Defining

$$A_T = [Me_2NH^+CH_2SO_3^-] + [Me_2NCH_2SO_3^-] \quad \text{and}$$
$$B_T = [Me_2NH_2^+] + [Me_2NH]$$

by making the usual substitutions, one may show that

$$K_2 = \frac{B_T^2(K_1 + [H^+])}{A_T K_1 (K_3[H^+] + 1)} \tag{4}$$

Further defining

A_0 = (total number of mmol of **8** added initially)/(total volume of the solution, in mL)

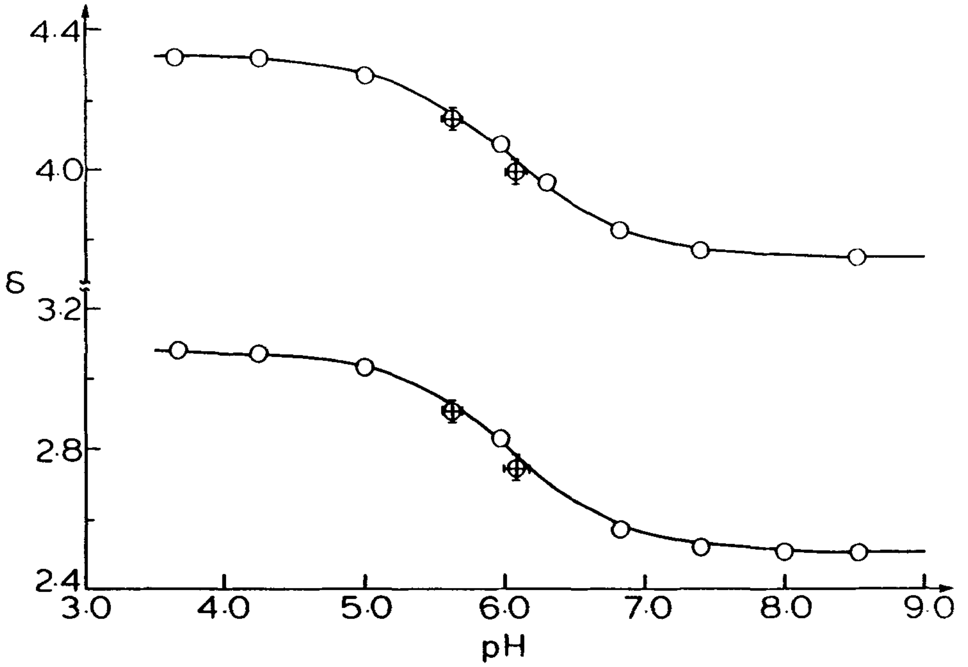


FIGURE 1. ^{1}Hmr chemical shifts vs pH of **8** (initially) in H_2O (ionic strength 0.5 M with NaCl). The plain circles are experimental values from fully equilibrated samples; the circles with error bars show measurements with non-equilibrated samples in which the pH change during the running of the spectrum and the uncertainty in δ are indicated by the bars. The upper line corresponds to the equation $\delta = (3.75 + 4.33e^a)/(1 + e^a)$ and the lower to $\delta = (2.50 + 3.08e^a)/(1 + e^a)$ where $a = 2.303(6.05 - \text{pH})$, equations obtained by simple transformation of eq. (6).

and r = (integral of a signal due to **8** and (or) **10**)/(integral of the corresponding signal due to **11** and (or) **12**, or to **9**)

and noting that $A_0 = A_T + B_T$ and $r = A_T/B_T$, we obtain (5) after appropriate substitution in (4)

$$K_2 = \frac{A_0(K_1 + [H^+])}{K_1 r(r + 1)(K_3[H^+] + 1)} \tag{5}$$

From a series of ^{1}Hmr spectra (at 20.8°C) with a known amount of **8** dissolved in known volumes of H_2O (ionic strength 0.5 M with NaCl) at a range of pH values (see Table II), and knowing K_1 and K_3, eq. (5) yields $K_2 = (1.20 \pm 0.04) \times 10^{-4}$ M. If we define a further equilibrium constant,

$$K_4 = [Me_2NH_2^+][HOCH_2SO_3^-]/[Me_2NH^+CH_2SO_3^-]$$

it may be shown also that $K_4 = K_1K_2K_3 = 9.8 \pm 0.4$ M.

The only reports of related equilibrium constants that we are aware of are the early value for the pK_a of ammoniomethanesulfonate ($NH_3^+CH_2SO_3^-$) obtained by potentiometric titration by Rumpf,[17] and the approximate values for the pK_a and the equilibrium constant corresponding to K_2 for butylammoniomethanesulfonate, obtained from ^{1}Hmr spectra of D_2O solutions by McMillan and Pattison.[18] The

TABLE II

^{1}Hmr peaks and integrals over the pH range 7.20 to 9.09 of the equilibrium mixture from hydrolysis of **8**, and derived equilibrium constants[a]

		Peaks from **10**		Peak from **12**			
pH	A_0^b	δ(integral)	δ(integral)	δ(integral)[c]	r^d	K_2 (M) ($\times 10^4$)	K_4 (M)
7.20	0.189	3.78 (5)	2.53 (15)	2.72 (65.5)	0.23	1.25	10.2
7.60	0.181	3.76 (8)	2.51 (24)	2.72 (53.5)	0.45	1.25	10.2
8.11	0.167	3.75 (7.5)	2.50 (22.5)	2.72 (22.5)	1.00	1.19	9.7
8.55	0.158	3.75 (16)	2.50 (48)	2.72 (25.5)	1.86	1.16	9.4
9.09	0.151	3.75 (27.5)	2.50 (82.5)	2.71 (22.5)	3.67	1.17	9.5
	Mean and standard deviation: $K_2 = (1.20 \pm 0.04) \times 10^{-4}$ M						
	$K_4 = 9.8 \pm 0.4$ M						

[a] In H_2O, ionic strength 0.5 M with NaCl at 20.6°C, DSS standard.

[b] A_0 = (total number of mmol of **8** added initially)/(total volume of solution in mL).

[c] Authentic dimethylammonium chloride shows a singlet at 2.72 ppm. In addition a singlet at 4.40 ppm was observed but could not be reliably integrated owing to interference by the nearby H_2O signal; authentic **9** shows a singlet at 4.40 ppm.

[d] r = (integral of δ2.5 signal)/(integral of δ2.7 signal).

latter authors assign a pK$_a$ of "roughly 7.1" to $BuNH_2^+CH_2SO_3^-$ and give two roughly similar values (1.38×10^{-3} and 0.68×10^{-3}, from experiments at different pH's) for the equilibrium constant for hydrolysis of $BuNHCH_2SO_3^-$. They point out that "the accuracy of these equilibrium constants is limited by the accuracy of the pH and NMR integral determinations, [and] the validity of transposing data... from an aqueous to a deuterium oxide system..."; in addition a "second singlet... assigned to n-$BuND_2CH_2OD$..." (in the ^{1}Hmr spectrum in D_2O) and the appearance of 1,3,5-tributylhexahydro-s-triazine as a second liquid phase increase the complexity of the system and the difficulty in making accurate estimates of the equilibrium constants. Potentiometric titration is not entirely straightforward either because, as was noted by Rumpf,[17] above pH 5.5 the acid ($NH_3^+CH_2SO_3^-$) "decomposes more or less rapidly". In our hands titration of **8** shows a change in pH with addition of base which looks much like a true titration but which shows the jump in pH around pH ~ 6 with a titre well below that predicted by theory for a simple titration; the pK$'_a$ calculated from this apparent end point is 5.7, whereas that obtained using the theoretical end point is 6.1, in good agreement with that from the nmr experiments. In the light of the nmr evidence for hydrolysis around pH 6, it is clear that the pH jump cannot be ascribed to a true end point and hence that pK$_a$ estimates based on such an assumption would be in error; unfortunately, since we do not know exactly how Rumpf obtained his value of 5.75 for the pK$_a$ of $NH_3^+CH_2SO_3^-$, we cannot be sure of its reliability. We conclude that, in comparison with the limited earlier data on aminomethanesulfonates, the pK$_a$ and K_2 values derived in the present study have fewer uncertainties and comparable or greater accuracy.

EXPERIMENTAL

Proton magnetic resonance spectra (^{1}Hmr) spectra were recorded using Varian T60, XL100, XL200, and XL300 spectrometers with all δ values from spectra obtained on the XL instruments; ^{13}Cmr spectra were obtained using Varian XL200 and XL300 spectrometers. Spectra of $CDCl_3$ (Merck, Sharp and Dohme

Ltd.) and CD_3NO_2 solutions were calibrated with tetramethylsilane, those in D_2O with sodium 3-(trimethylsilyl)propionate (TSP), where unspecified, or sodium 3-(trimethylsilyl)propanesulfonate (DSS). Infrared (ir) spectra were recorded on a Beckman 4250 spectrometer using sodium chloride cells; all ir spectra were calibrated with a polystyrene reference film. All melting points were obtained on a Kofler Hot Stage apparatus, and are uncorrected; pH was determined with a Radiometer Model 25 pH meter using a Radiometer combined (GK2301C or GK2401C) electrode. All reagents and solvents were reagent grade and used as supplied unless otherwise specified.

Bromomethanesulfinic acid (**1**). Bromomethanesulfonyl bromide[19] (1.84 g, 7.7 mmol) was added slowly to an ice-cold solution of sodium sulfite (1.6 g, 12.7 mmol) and sodium bicarbonate (1.0 g, 12 mmol) in H_2O (15 mL) and the mixture stirred at room temperature for 1 h. The solution was then extracted twice with CH_2Cl_2 (25 mL portions), acidified with cold diluted H_2SO_4 (pH < 1) and extracted with ether (4 × 50 mL); the ether layer was dried over $MgSO_4$ and the solvent evaporated giving about 1 g (80%) of the product. Bromomethanesulfinic acid (**1**) is unstable (even at −10°C) and should be used within 1 h; ir ($CHCl_3$) ν_{max}: 3000–2840 (br, s), 2490 (br, s), 1380 (m), 1340 (m), 1140–1050 (br, vs), 850–830 (br, s) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 4.21 (s, 2 H) plus variable singlet at 6.5–7.5 (1.5 to 2 H); ^{13}Cmr ($CDCl_3$) δ: 48.1.

Trimethylammoniomethanesulfinate (**3**). A solution of bromomethanesulfinic acid (**1**) (0.8 g, 5 mmol) in H_2O (10 mL) was cooled in an ice bath and trimethylamine (6 g, 0.1 mol) was added in small portions with stirring so that the solution warmed only slightly; the reaction mixture was then left at room temperature for 3 days. The excess trimethylamine was evaporated under reduced pressure, and the solution concentrated to about 5 mL and passed through a short column of deionizing resin (Rexyn 300 (H—OH)). The water was evaporated to give fine, white crystals (450 mg, 65%) which were recrystallized from absolute ethanol (275 mg, 40%) and dried in a vacuum desiccator, mp 239–240°C (dec.); ir (KBr) ν_{max}: 3020 (s), 1480 (vs), 1105 (s), 1070–1050 (vs), 1000–980 (vs), 960–950 (s), 925 (s) cm^{-1}; ^{1}Hmr (D_2O) δ: 3.32 (s, 9 H), 3.72 (s, 2 H); ^{13}Cmr (D_2O) δ: 57.4, 89.2. Anal. Calcd. for $C_4H_{11}O_2S$: C, 35.02; H, 8.08; N, 10.21; S, 23.37. Found: C, 35.12; H, 8.21; N, 10.16; S, 23.24.

Trimethylammoniomethanesulfonate (**4**). (a) *From trimethylammoniomethanesulfinate* (**3**). A sample of trimethylammoniomethanesulfinate (**3**) (1.37 g, 10 mmol) was dissolved in H_2O (15 mL) and chlorine was bubbled for *ca.* 1 min. The water was then evaporated to give white crystals (1.53 g, 100%) which were recrystallized from absolute ethanol/ether (1.26 g, 82%) and dried in a vacuum desiccator; mp and spectra are listed in Table I. Anal. Calcd. for $C_4H_{11}NO_3S$: C, 31.36; H, 7.24; N, 9.14; S, 20.93. Found: C, 31.48; H, 7.41; N, 9.22; S 20.99.

(b) *From sodium iodomethanesulfonate and trimethylamine.* Sodium iodomethanesulfonate (1.75 g, 7.17 mmol) was dissolved in H_2O (ca. 10 mL) and placed in a Carius tube which was then cooled in dry ice. Trimethylamine (ca. 11 g) was then added, the tube sealed, allowed to warm up slowly and then heated at about 100°C for 2 days, whereupon the solution was concentrated and passed through the Rexyn 300 (H—OH) resin to give a white crystalline product (42 mg, 4%) with ^{1}Hmr, ^{13}Cmr, and ir spectra identical to those of **4** obtained as above.

Dimethylammoniomethanesulfonate (**8**). (a) *From trimethylamine oxide and sulfur dioxide.* Sulfur dioxide was bubbled into a suspension of trimethylamine oxide[20] (1.5 g, 20 mmol) dry methylene chloride (ca. 5 mL) cooled in dry ice until a vigorous reaction was observed (approximately 2–3 mL of SO_2 was added to this point). The solvent and excess of sulfur dioxide were evaporated under reduced pressure and the residual white solid (3.2 g) recrystallized from absolute ethanol–ether to give **8** as white crystals (1.9 g, 44%), mp 160–161°C; ir (Nujol) ν_{max}: 1460 (s), 1375 (m), 1265 (s), 1230 (vs), 1200 (vs), 1165 (s), 1130 (s), 1060 (s), 1025 (s) cm^{-1}; ^{1}Hmr (D_2O + DCl) δ: 3.10 (s, 6 H), 4.35 (s, 2 H); ^{13}Cmr (D_2O) δ: 46.9, 72.1.

(b) *From bromomethanesulfinic acid* (**1**) *and dimethylamine.* Dimethylamine (2.25 g, 50 mmol) was added slowly to a solution of bromomethanesulfinic acid (**1**) (1.6 g, 10 mmol) in water (10 mL) cooled in an ice bath. The mixture was left at room temperature for three days and then saturated with chlorine and passed through deionizing resin (Rexyn 300 (H—OH)) to give **8** (0.4 g, 30% after recrystallization from absolute ethanol–ether); mp 161–162°C, ^{1}Hmr spectrum identical to that of **8** prepared as in (a). In a separate experiment authentic **8** (50 mg) was dissolved in D_2O saturated with Cl_2 (resultant solution pH 0.7); the ^{1}Hmr spectrum showed initial loss of **8** of less than 5%, with subsequent slow ($t_{1/2} \sim 6$ h) disappearance of **8**.

(c) *From formaldehyde, sodium bisulfite, and dimethylamine.* Aqueous dimethylamine (25%) was added in a small excess to a mixture of aqueous formaldehyde (37.3%, 1.61 g, 20 mmol) and sodium bisulfite dissolved in H_2O (5 mL) until the pH was roughly 11. The mixture was stirred for 20 min at room temperature, the solution then acidified to pH ~ 1.5 with concentrated hydrochloric acid, and the water evaporated under reduced pressure. The residue was triturated with hot absolute ethanol, the extract concentrated, and ether added, whereupon compound **8** crystallized and was collected by filtration (yield 2.2 g, 80%); 160–161°C, ^{1}Hmr δ (D_2O + DCl, DSS) 3.08 and 4.33.

(d) *From sodium hydroxymethanesulfonate* (**9**) *and dimethylamine.* Sodium hydroxymethanesulfonate (**9**) was prepared[21] by mixing sodium bisulfite (4.16) g, 40 mmol) in H_2O (10 mL) and aqueous formaldehyde (37.3%, 3.22 g, 40 mmol), stirring for 10 min, evaporating the water under reduced pressure, and recrystallizing the product from aqueous ethanol; ^{1}Hmr (H_2O) δ: 4.41, ^{13}Cmr (H_2O) δ: 76.03. This salt (**9**) (2.6 g, 20 mmol) was dissolved in water (10 mL) and cooled in an ice bath, and dimethylamine (1.0 g, 23 mmol) added. The water and excess dimethylamine were evaporated under reduced pressure and the white residue recrystallized from absolute ethanol–ether giving **8** (1.68 g, 70%); mp 160–162°C; ^{1}Hmr δ (D_2O + DCl, DSS) 3.08 and 4.33.

Methylation of dimethylammoniomethanesulfonate (**8**). Dimethyl sulfate (800 mg, 6.8 mmol) was added to a solution of dimethylammoniomethanesulfonate (**8**) (380 mg, 2.73 mmol) in dilute aqueous HCl (4 mL, pH ~ 4); the suspension was stirred vigorously while 0.5 *M* aqueous sodium hydroxide was added dropwise at such a rate as to keep the pH of the reaction mixture in the range 5.0 to 5.2. When the dimethyl sulfate layer had disappeared (ca. 20 min) the pH was brought to 7 with NaOH; the solution was concentrated and passed through deionizing resin (Rexyn 300 (H—OH)) and the water evaporated giving **4** as white crystals (348 mg, 83%) with the same mp, ir, ^{1}Hmr and ^{13}Cmr spectra as those listed in Table I above.

NMR studies of the dimethylaminomethanesulfonate equilibria in H_2O. Dimethylammoniomethanesulfonate (**8**) (596 mg, 4 mmol) was added to a solution of sodium chloride (350 mg, 6 mmol) in H_2O (20 mL) acidified with aqueous HCl to pH ~ 2.5 and the ^{1}Hmr spectrum (XL100) of a sample run immediately. The remaining solution was basified with 0.5 *M* NaOH and samples for nmr taken at about every 0.5 pH units till pH ~ 6. Solutions at pH above 6.30 are unstable and undergo spontaneous hydrolysis accompanied by an increase in pH of about 2 units. Another solution of **8** was therefore prepared as above, 0.5 *M* NaOH added to obtain solution of pH 4.6 and left at room temperature for 3 days (the pH increased in the meantime, first very slowly, then faster, and finally more slowly, stabilizing on the third day at pH 5.97). A sample of this solution was taken for nmr, and 0.5 *M* NaOH added to the remainder taking samples about every 0.5 pH units. Chemical shifts (at 19.2°C) of the peaks due to **8**, **10**, or **8** ⇄ **10** vs pH for the range 3.6 to 8.5 are plotted in Fig. 1; pK$'_a$ values were calculated from δ's from the pH range 5.0 to 6.8 from eq. (6),

$$\mathrm{pK}'_a = \mathrm{pH} + \log[(\delta - \delta_{10})/(\delta_8 - \delta)] \qquad (6)$$

where for one set of peaks $\delta_8 = 4.33$ and $\delta_{10} = 3.75$ and for the other set $\delta_8 = 3.08$ and $\delta_{10} = 2.50$, and δ is the observed chemical shift at that pH for the equilibrium mixture; mean pK$'_a$ 6.05, standard deviation ±0.05. In a similar separate experiment (at 20.8°C) the integrals of the signals due to **10** (at δ 3.75–3.78 and 2.50–2.53) and that due to **12** (at δ 2.71–2.72) were determined at a series of pH values; the signal at 4.40 due to **9** was also clearly in evidence but could not be separated from the H_2O signal well enough to be integrated satisfactorily. These taken with A_0 (see above and footnote b, Table II), K_1 (from $-\log K_1 = 6.05$, the pK$'_a$ of **8**), and K_3 (from $\log K_3 = 10.95$ the pK$'_a$ of **12**, see below), were used to calculate K_2 and K_4 (see Table II) from eq. (5) and the relation $K_4 = K_1K_2K_3$ (above). The pK$'_a$ of **12** (in H_2O, ionic strength 0.5 *M* with NaCl, 20.8°C) was found to be 10.95 ± 0.05 by the method of Parke and Davis.[22]

^{13}Cmr spectra in H_2O display essentially the same pattern. At low pH the two signals of **8** are seen at δ 72.0 and 47.0, and high pH those due to **10** appear at 76.3 and 46.3, with the change in δ occurring from pH 5 to 7. In the pH range 7 to 9 the signals due to **10** are accompanied by those of **9** (at 77.0) and **12** (at 37.5) with the relative intensities showing the pattern displayed by the ^{1}Hmr spectra in Table II. Authentic samples of **9** and **12** each show a single peak, at 76.8 and 37.4 ppm from DSS, respectively. The ^{1}Hmr spectra in D_2O show a similar behavior except that the δ value corresponding to equimolar concentrations of **8** and **10** appears at a "pH" = 6.3 (i.e. the meter reading of the D_2O solution determined after calibration with ordinary aqueous buffer).

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