Reports

Identification of Hydroxymethanesulfonate in Fog Water

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Previous studies have suggested that hydroxymethanesulfonate ion (HMSA) can be an important species in fog and cloud water. Formation of HMSA explains observed excesses of sulfur in the S(IV) state (+4 oxidation state) and formaldehyde (CH_2O) in fogs and clouds. HMSA was determined in fog water by a novel ion-pairing chromatographic technique. Concentrations in samples collected in Bakersfield, California, within 5 kilometers of major sources of sulfur dioxide (SO_2), were as high as 300 micromoles per liter. Total CH_2O and S(IV) concentrations, which were measured independently, ranged from 10 to 200 and 5 to more than 300 micromoles per liter, respectively. Concentrations of CH_2O, S(IV), and HMSA at Buttonwillow, California, which is 15 kilometers from the nearest source of SO_2, were less than those at Bakersfield but not absent. These data confirm that HMSA forms in atmospheric water droplets and can reach appreciable concentrations. HMSA represents an important source of acidity for water droplets and may also play a role in long-distance transport and transformation of SO_2.

HYDROXYMETHANESULFONATE, THE HSO_3^- adduct of CH_2O, has been postulated as an important S(IV) species in fog and cloud water (*1*). We define $SO_{2(aq)}$ as the sum of $SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$; we define S(IV) as the sum of $SO_{2(aq)}$ plus all other species with sulfur in the +4 oxidation state (that is, aldehyde adducts, $HORHSO_3^-$, and metal complexes, $(Me)_n(SO_3)_m^{ny-2m}$). This sum is identical to the measured concentration of S(IV), [S(IV)]. The formation of hydroxymethanesulfonate (HMSA) allows an apparent excess of S(IV) and CH_2O compared to the amounts present in Henry's law equilibrium to exist in the droplet phase. Because HMSA is a strong acid, its formation will acidify droplets without S(IV) oxidation. Furthermore, the formation of HMSA allows S(IV) to coexist with oxidants such as H_2O_2 and O_3 (*2–4*).

The thermodynamics and kinetics of reaction between CH_2O and dissolved SO_2 to form HMSA have been determined. Kerp (*5*), Donally (*6*), Deister *et al.* (*7*), and Kok *et al.* (*4*) have all reported values near $10^7\ M^{-1}$ for the equilibrium constant (defined by $K = [HMSA]/[HSO_3^-][CH_2O]$. The stability of the $CH_2O{:}HSO_3^-$ adduct will be at a maximum in the *p*H range 3 to 5, where HSO_3^- is the dominant form of $SO_{2(aq)}$. The rate at which HMSA forms in a droplet can be calculated from the rate constants determined by Boyce and Hoffmann (*8*). For CH_2O and SO_2 partial pressures of 1×10^{-9} and 5×10^{-9} atm at *p*H 3, the HMSA formation rate is $1.6\ nM\ hour^{-1}$. It increases by about a factor of 100 for each unit increase in *p*H to $0.1M\ hour^{-1}$ at *p*H 7. The formation rate increases linearly with gas-phase concentration; lower temperatures also increase the formation rate somewhat because of increased gas solubility. The rate of HMSA decomposition increases with *p*H (*4, 7*); this can be expressed as $R = k_d[HMSA][OH^-]$. The value of k_d derived from the data of Kok *et al.* (*4*) and Deister *et al.* (*7*) between *p*H 4 and 5.6 is $3.6 \times 10^3 M^{-1}\ sec^{-1}$. The characteristic time for HMSA dissociation (time for a 1/*e* decrease in concentration) evaluated from this expression decreases from 579 to 25 hours as *p*H varies from 4 to 5.6. Dynamic models of fog and cloud-water chemistry (*9*) indicate that HMSA could be the major S(IV) species in droplets when *p*H exceeds 5. Appreciable [S(IV] would form in the droplet phase immediately after condensation. However, the suggestion by Richards *et al.* (*2*) that the presence of CH_2O prevents oxidation of S(IV) by H_2O_2 is not substantiated by model calculations (*9*) or experiments (*3, 4*). In an open system, SO_2 will continually dissolve in the droplet and be available as $SO_{2(aq)}$ to react with H_2O_2. High [HMSA] may be found in more acidic environments if HMSA is formed before droplet acidification. Prior formation is also indicated by the coexistence of HMSA and H_2O_2.

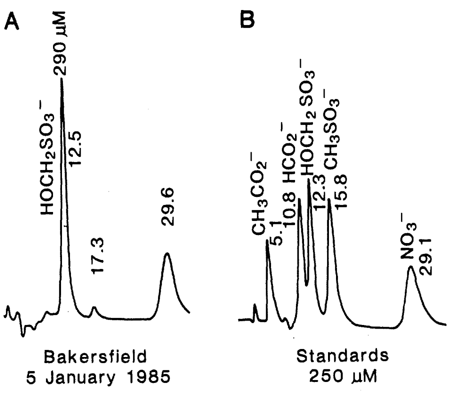

Fig. 1. Representative chromatograms for (A) a sample of fog water collected in Bakersfield, California, and (B) a solution containing formate, acetate, HMSA, methanesulfonate, and nitrate. The numbers indicate retention times in minutes. Neither methanesulfonate nor hydroxyethanesulfonate was present in the fog water samples. The peak at 17.3 minutes was present in many samples.

An interesting feature of HMSA chemistry is that the conditions most conducive to the production of HMSA are not suitable for its preservation. It forms most rapidly above *p*H 5 but will not be preserved unless the droplets are subsequently acidified. High concentrations of oxidant will compete for $SO_{2(aq)}$, but, once HMSA forms, it is fairly resistant to oxidation by H_2O_2 and O_3 (*3, 4*). We suggest that a likely environment for rapid HMSA formation is in SO_2 source plumes, where concentrations of the precursor species are high, *p*H is near neutral, and oxidant concentrations are low. As the plume is diluted, equilibrium between HMSA and its precursors may not be maintained because of the slow dissociation kinetics, especially if continued $SO_{2(aq)}$ oxidation generates additional acidity in the droplet. Equilibrium will be maintained only between gaseous SO_2 and $SO_{2(aq)}$.

The presence of HMSA in a variety of environments is indicated by circumstantial evidence. Analyses of Los Angeles fog and cloud water, which had *p*H in the range 2 to 4, indicated that total S(IV) and CH_2O were supersaturated with respect to Henry's law equilibrium with $SO_{2(g)}$ and $CH_2O_{(g)}$ (*1, 2*). Similar observations were made in the San Joaquin Valley (*1*). Warneck *et al.* (*10*) observed that $[CH_2O]$ in aerosol over Germany was supersaturated with respect to the gas phase and postulated that HMSA was present. Snider and Dawson (*11*) suggested that enhanced concentrations of carbonyls in Arizona rainwater compared to the gas phase may indicate aqueous-phase production of carbonyl. Their observations may also be accounted for by the formation of sulfonic acids. No analyses were per-

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formed in these earlier studies to confirm the presence of HMSA.

The southern San Joaquin Valley of California offers an amenable environment for studying aqueous-phase atmospheric chemistry. Oil field operations supply a major source of SO_2, hydrocarbons, and NO_x, while extensive agricultural activity produces large amounts of NH_3; thus *p*H is maintained near neutral in aerosol and fog droplets. During the winter the valley is frequently capped by a temperature inversion, leading to persistent atmospheric stagnation with widespread fogs or low clouds (*12*). This combination of high concentrations of precursors, humid conditions, sufficient NH_3 to neutralize acidity, and stagnation is conducive to the formation of HMSA.

In earlier studies of fog in the San Joaquin Valley during the winters of 1982–83 and 1983–84 (*1, 12*) we have observed [S(IV)] up to $3 \times 10^{-3}M$ and [CH_2O] up to $7 \times 10^{-4}M$. These values were far in excess of the Henry's law equilibrium for dissolution of SO_2 at the ambient levels of 0 to 50 parts per billion (1 ppb = 1×10^{-9} atm).

During December 1984 and January 1985 we sampled fog in Bakersfield and Buttonwillow, California; the sampling sites (*13*) and fog collection procedure (*14*) have been described. Immediately after collection, the *p*H was determined with a combination electrode and individual aliquots were preserved for later determination of [S(IV)] and [CH_2O] (*15, 16*). The analytical procedures are designed to measure total species. However, our results suggest that the efficiency of the Nash method for CH_2O determination is less than 100 percent when HMSA is present. HMSA was determined by ion-pairing chromatography and identified by retention time (*17*). Standards containing hydroxyethanesulfonic acid and methanesulfonic acid were also analyzed to determine their retention times. A representative chromatogram is given in Fig. 1. The difference between standard and sample retention times was less than 2 percent. We recognize that identification based on retention time is not definitive; however, other species such as formate and acetate, likely to be present in fog water, elute separately. The instability of HMSA and the difficulty of obtaining large sample volumes preclude the use of mass spectrometry for confirmation. In samples with high *p*H, some of the HMSA could have decomposed between sampling and analysis; the results presented here should be considered lower bounds for [HMSA].

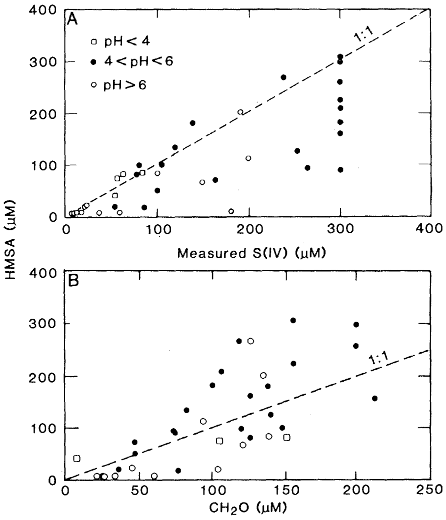

Fig. 2. (A) [HMSA] at Bakersfield plotted against measured [S(IV)]; [S(IV)] greater than 300 μ*M* saturated the reagents used. Points plotted at 300 μ*M* had [S(IV)] in excess of the saturation level. (B) [HMSA] at Bakersfield plotted against measured [CH_2O].

Table 1. Volume-weighted average of concentrations for various species in fog water samples.

Date*	Sample *p*H	Concentration of species (μ*M*) S(IV)	CH₂O	HMSA	*n*†
		Bakersfield, California			
12/28/84	5.9	150	98	140	6
1/3/85	5.2	130	78	76	10
1/4/85	6.9	18	32	0	5
1/5/85	4.6	≥230	110	120	13
1/8/85	7.4	16	27	0	1
1/10/85	6.1	180	‡		2
1/14/85	5.9	150	120	65	3
1/19/85	4.1	89	150	79	10
1/20/85	3.0	84	160		2
		Buttonwillow, California			
1/3/85	5.1	36	55		6
1/4/85	6.2	9	28		7
1/5/85	6.1	22	33	0	11

*The date given is that of the morning on which the fog event ended. †Number of consecutive samples collected over the course of each fog event. The sampling period was generally 1 hour. ‡Not analyzed because of insufficient sample volume.

Table 1 presents the volume-weighted mean and ranges of [S(IV)], [CH_2O], and [HMSA] and *p*H for each fog event sampled. Figure 2A shows the apparently linear relation between HMSA and S(IV) at Bakersfield ($r^2 = 0.65$). The residual variance is due to the presence of free $SO_{2(aq)}$ in high *p*H samples and possibly some HMSA decomposition before analysis. The highest [HMSA] was found in samples with moderate *p*H (5.5 to 6.5). Samples with higher or lower *p*H had lower [HMSA]. Low *p*H will retard the formation of adduct, while high *p*H will prevent its preservation in the atmosphere and in sample bottles.

There is also an apparently linear relation between [HMSA] and [CH_2O] ($r^2 = 0.54$) (Fig. 2B). The appearance of excess HMSA as compared to total CH_2O in many samples indicates that I_2, added in order to prevent the interference of S(IV) in CH_2O analysis, is not totally effective. Appreciable concentrations of free CH_2O should exist in the droplet because of the high effective Henry's law constant.

During the sampling program, [SO_2] was always less than 30 ppb and usually less than 10 ppb (*18*). This partial pressure of SO_2 was sufficient to account for all the S(IV) observed during most of the sampling periods when fog water *p*H values varied from 5 to 7. Nevertheless, HMSA was an important fraction of the S(IV) measured. In the two fog events that were in the low *p*H domain, the equilibrium of $SO_{2(aq)}$ with ambient $SO_{2(g)}$ was not sufficient to account for all the measured S(IV). During an 8-hour period in the middle of the fog event on 5 January 1985, when the *p*H varied from 5.5 to 4.8, the measured [S(IV)] was continually above the upper detection limit (250 μ*M*). The concentration of free $SO_{2(aq)}$, as calculated from the sample *p*H and SO_2 partial pressure = 10 ppb (an upper limit for the period), was less than half the measured [S(IV)]. In terms of the Henry's law dissolution, S(IV) was supersaturated by a factor of 10 during the fog event of 19 January. The *p*H during this event was 3.7 to 4.9; [HMSA] and [S(IV)] were about 60 to 80 μ*M*, with higher values at the beginning and end of the fog event when the liquid water content was lower. [CH_2O] during this event was generally higher than [HMSA], suggesting the presence of free CH_2O.

At Buttonwillow, [S(IV)] and [CH_2O] were considerably less than at Bakersfield. This is consistent with the greater distance between major pollution sources and Buttonwillow as compared to Bakersfield; [SO_4^{2-}] and [NO_3^-] were lower at Buttonwillow as well (13). The pH was usually in the range 5.5 to 7, although two samples had $p\text{H} < 5$ with [S(IV)] less than 10 μM. HMSA was not determined in all the samples from Buttonwillow, but little or none was observed in the samples that were analyzed. As noted above, the lifetime of HMSA at pH 5.6 is 25 hours and should decrease further as pH rises. Thus HMSA may decompose during advection from SO_2 source areas to Buttonwillow. More HMSA and S(IV) is observed at Bakersfield because of its proximity to the oil fields in Oildale. If the atmosphere in the valley were not buffered by NH_3 emissions, then HMSA would have a longer residence time.

The results of this study support the hypothesis that HMSA may be an important species in fog and cloud water. The pattern of [HMSA] in the fog samples is consistent with the formation of HMSA during favorable conditions of high SO_2 and intermediate pH and preservation by subsequent acidification. Over the pH range of 5.5 to 7, which is typical of the samples from the San Joaquin Valley, the chemical lifetime of HMSA is shorter than the time for atmospheric transport within the valley (19). Appreciable [HMSA] or [S(IV)] was not observed at Buttonwillow. Observations of excess [S(IV)] and [CH_2O] in fog and cloud water from the more acidic Los Angeles basin indicate that other conditions may also allow the formation of HMSA.

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8. The initial formation of HMSA can be expressed in terms of gas-phase concentrations as

$$\frac{d[\text{HMSA}]}{dt} = H_s H_f P_{SO_2} P_{CH_2O} \frac{1}{(1 + K_h)} \times \left(\frac{k_1 K_{a1}}{[H^+]} + \frac{k_2 K_{a1} K_{a2}}{[H^+]^2} \right)$$

9. Values for the Henry's law constants for SO_2 and CH_2O at 298 K are $H_s = 1.245M$ atm^{-1} and $H_f = 6.3 \times 10^3 M$ atm^{-1} (in terms of hydrated CH_2O). P_i is the partial pressure of species i. The acidity constants for S(IV) are $K_{a1} = 1.29 \times 10^{-2} M$ and $K_{a2} = 6.01 \times 10^8 M$. The hydration constant for CH_2O is $K_h = 2.53 \times 10^3$. The original references and enthalpy data are given by Munger *et al.* (1). The rate constants are $k_1 = 7.9 \times 10^2 M^{-1}$ sec^{-1} (activation energy = 5.9 kcal mol^{-1}); $k_2 = 2.48 \times 10^7 M$ sec^{-1} (activation energy = 4.8 kcal mol^{-1}) [S. D. Boyce and M. R. Hoffmann, *J. Phys. Chem.* **88**, 4740 (1984)].
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13. During December 1984 and January 1985 fog water was collected at a site adjacent to the Bakersfield Airport and in Buttonwillow. Sampling commenced at the onset of fog formation and continued until the fog dissipated. Major oil fields are located within 5 km of the Bakersfield Airport in the northeast quadrant. Buttonwillow is located near the center of the valley, at least 15 km southeast of oil fields on the west side of the valley. Complete results and site descriptions are given by J. M. Waldman [thesis, California Institute of Technology, Pasadena (1985)].
14. The collector is described in D. J. Jacob, R.-F. T. Wang, R. C. Flagan, *Environ. Sci. Technol.* **18**, 827 (1984).
15. Total S(IV) was determined in an aliquot of sample that was preserved with CH_2O immediately after collection. Analysis was by the pararosaniline method [P. K. Dasgupta, K. DeCesare, J. C. Ullrey, *Anal. Chem.* **52**, 1912 (1980); P. K. Dasgupta, *ibid.* **53**, 2084 (1981)]. Standards made from Na_2SO_3 or $NaCH_2OHSO_3$ gave identical results. Analysis was complete within a week of collection; no loss of S(IV) was observed in preserved aliquots or standard solutions. Analytical error was within 5 percent.
16. Total CH_2O was determined in a separate aliquot of sample to which Nash reagent was added immediately after collection [T. Nash, *Biochem J.* **55**, 416 (1953)]. Prior to color determination, I_2 was added to destroy the S(IV) in the sample [R. V. Smith and P. W. Erhardt, *Anal. Chem.* **47**, 2462 (1975)]. Recovery of $NaCH_2OHSO_3$ standards was 90 to 100 percent compared to CH_2O standards. Minimal losses of CH_2O were observed during storage. Analytical error was less than 5 percent.
17. HMSA was determined by ion-pairing chromatography on a polystyrene divinylbenzene column (Dionex MPIC) followed by a suppressor column containing cation-exchange resin in the Ag^+ form (Dionex ISR), and a conductivity detector. The mobile phase contained 2 mM tetrabutylammonium chloride, 5 percent (by volume) CH_3OH, and $2 \times 10^{-5} M$ HCl. Analytical error was less than 5 percent. Samples to be analyzed for sulfonic acids were refrigerated, but no preservatives were used.
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Geomorphic Evidence for the Distribution of Ground Ice on Mars

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High-resolution Viking orbiter images show evidence for quasi-viscous relaxation of topography. The relaxation is believed to be due to creep deformation of ice in near-surface materials. The global distribution of the inferred ground ice shows a pronounced latitudinal dependence. The equatorial regions of Mars appear to be ice-poor, while the heavily cratered terrain poleward of ±30° latitude appears to be ice-rich. The style of creep poleward of ±30° varies with latitude, possibly due to variations in ice rheology with temperature. The distribution suggests that ice at low latitudes, which is not in equilibrium with the present atmosphere, has been lost via sublimation and diffusion through the regolith, thereby causing a net poleward transport of ice over martian history.

DETERMINATION OF THE DISTRIBUTION of subsurface ice on Mars is critical for understanding the planet's volatile inventory and will be a major concern for future martian exploration. Many martian landforms suggest the former presence of ground ice or water, including fretted and chaotic terrain (1), valley systems (2), outflow channels (3), and, with less certainty, various types of patterned ground (4) and rampart craters (5). None of these landforms provides strong evidence for the present distribution, however. If sufficient ice is present now, the regolith should undergo quasi-viscous flow due to creep deformation of the ice. Accordingly, to determine where ice may be present, we have examined the approximately 24,000 Viking Orbiter images taken within 5,000 km of the surface (6) and mapped the distribution of three types of features—lobate debris aprons, concentric crater fill, and terrain softening—that may indicate creep of near-surface materials.

Lobate debris aprons are accumulations of erosional debris at the base of steep escarpments (7). Surface lineations and compressional ridges adjacent to obstacles indicate that the constituent materials have flowed away from the escarpment. Distinct convex-upward topographic profiles suggest creep deformation throughout the entire thickness of the debris apron. They are morphologically similar to terrestrial rock

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