

Finally, the synthesis of these dinuclear carbyne complexes may be achieved alternatively and more directly in moderate yield, by treatment of the parent dimer [CpFe(CO)₂]₂ with alkyl- or aryllithium reagents, followed by acidification with HBF₄. In this manner complexes **13b** and **13c** are obtained as cis isomers and **13a** as a mixture of cis and trans isomers.

Further examination of these reactions and of the chemistry of the carbyne complexes is in progress.

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References and Notes

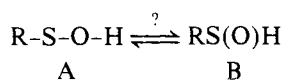
- J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972); C. P. Casey and C. A. Bunnell, *ibid.*, **98**, 436 (1976); J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *ibid.*, **99**, 2515 (1977); M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *ibid.*, **98**, 3127 (1976).
- W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Am. Chem. Soc.*, **94**, 7170 (1972); A. Cutler, D. Ehrnholz, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *ibid.*, **98**, 3495 (1976).
- P. Klemarczyk, T. Price, W. Priester, and M. Rosenblum, *J. Organomet. Chem.*, **139**, C25 (1977). See also W. H. Knoth, *Inorg. Chem.*, **14**, 1566 (1975), who has observed a similar reaction in analogous β -oxidoalkyltungsten and -molybdenum complexes.
- M. Nitay and M. Rosenblum, *J. Organomet. Chem.*, **136**, C23 (1977).
- (a) A satisfactory elemental analysis was obtained for this compound; (b) IR and NMR spectral data are in accord with this structure.
- Throughout, assignments of cis and trans isomers are made on the basis of the relative intensities of carbonyl stretching absorptions near 2000 cm⁻¹, which are expected to behave like A or B modes in [CpFe(CO)₂]₂: (a) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968); (b) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, **11**, 671 (1972).
- Resonances for bridging carbyne carbon atoms in M₂(CSiMe₃)(CH₂SiMe₃)₄ (M = W, Nb, Ta) have been reported at δ 354, 406, and 406, respectively: R. A. Andersen, A. L. Galyer, and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, **15**, 609 (1976).
- R. A. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, **13**, 1086 (1974); O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **98**, 5817 (1976).
- In contrast to salts derived from FpNa or FpLi and either acyclic epoxides or cyclohexene epoxide, which exhibit IR absorption at 1850 and 1530 cm⁻¹ (**2**), the product from cyclopentene epoxide shows two terminal carbonyl absorptions at 1995 and 1945 cm⁻¹.
- C. P. Casey, C. R. Cyr, R. L. Anderson, and D. F. Marten, *J. Am. Chem. Soc.*, **97**, 3053 (1975).
- However, Li ions do not enhance the rate of ligand transfer in the absence of a strong nucleophile since LiBF₄ is not observed to increase the rate of formation of FpCOCH₂Ph from FpCH₂Ph and CO.
- W. Priester and M. Rosenblum, *J. Chem. Soc., Chem. Commun.*, in press.
- The NMR spectrum of this substance in acetone-d₆ exhibits two cyclopentadienyl proton resonances below 18 °C at δ 4.72 and 4.57 of unequal intensity, which collapse to a single peak at room temperature. These changes may be associated with rapid transfer of the carbyne ligand between the two metal centers and a slower rate of cis-trans interconversion.

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Methanesulfenic Acid¹

Sir:

Sulfenic acids play a pivotal role in mechanistic organosulfur chemistry;² yet with rare exceptions these lowest members of the sulfur oxy acid family have defied isolation and structural characterization. The sulfenic acids that have been isolated in pure form³ are sufficiently encumbered with polar linkages to obscure key structural aspects such as the preferred position of hydrogen

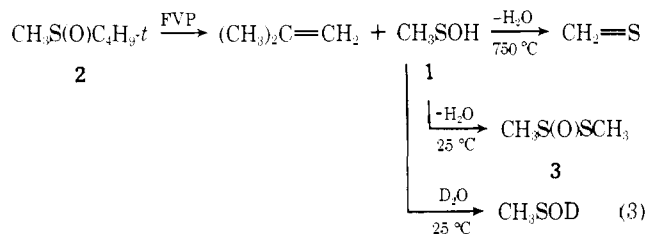


as well as conformational features of the singly bonded isomer (form A, eq 1). Simpler sulfenic acids have eluded isolation because of their high reactivity as either electrophiles or nucleophiles⁴ and because of their very facile conversion to thiosulfinate esters (eq 2; the mechanism shown^{2b} incorporates

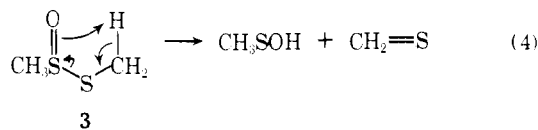


the dual electrophilic/nucleophilic character of sulfenic acids). Thus information on these intriguing molecules is based for the most part on kinetic and trapping studies.^{2,5} Structural characterization of sulfenic acids takes on added importance with the recent demonstration that specific sulfhydryl groups in some enzymes can be oxidized to stable sulfenic acids and that these modified enzymes show altered catalytic activity.⁷ We now wish to report that we have succeeded in generating by flash vacuum pyrolysis (FVP) the simplest organic sulfenic acid, methanesulfenic acid (**1**), and have fully characterized it by microwave spectroscopy. We report herein aspects of the structure and chemistry of this elusive molecule.

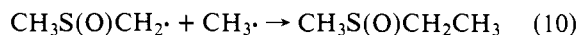
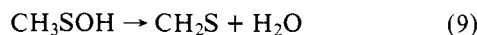
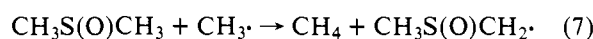
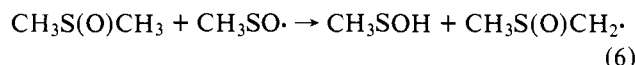
FVP-mass spectrometric examination^{1b,8} of *tert*-butyl methyl sulfoxide (**2**), a likely precursor to methanesulfenic acid,^{9,10} indicated the conversion of **2** above 250 °C to species with molecular ions of *m/e* 56 and 64. Definitive evidence for the formation of methanesulfenic acid and 2-methylpropene (*m/e* 64 and 56, respectively) from **2** under FVP conditions was obtained by following the decomposition of **2** by microwave spectroscopy. When **2** at its vapor pressure of 0.1–0.2 Torr was evaporated through a pyrolysis tube into a microwave absorption cell, generation of methanesulfenic acid and 2-methylpropene (whose microwave spectrum is known¹¹) was detected first at a pyrolysis temperature of 240 °C and was complete above 400 °C; above 750 °C the microwave spectrum of methanesulfenic acid had been replaced by that of thioformaldehyde. A tandem pyrolysis experiment confirmed the gas phase dehydration of methanesulfenic acid to thioformaldehyde.¹² When condensed at –196 °C methanesulfenic acid could not be recovered on warming in vacuum. Analysis of the condensate warmed to room temperature revealed the presence of methyl methanethiosulfinate (**3**), water, 2-methylpropene, and traces of dimethyl disulfide (a known disproportionation product of **3**).¹³ It was also shown that methanesulfenic acid readily exchanges with D₂O in the wave guide affording methanesulfenic acid-*hydroxy-d*₁. The several reactions of methanesulfenic acid are summarized in eq 3.



A number of other thermal sources of methanesulfenic acid were found using FVP-microwave techniques, although none of these sources were as efficient as **2**. Methyl methanethiosulfinate (**3**) at 250 °C afforded methanesulfenic acid and thioformaldehyde presumably by a mechanism previously described by one of us (eq 4).^{2b} Dimethyl sulfoxide also provided



to be a source of methanesulfenic acid at 500–650 °C. We have previously established the formation of sulfine in the FVP of dimethyl sulfoxide⁸ and can readily amend our mechanism to account for formation of the sulfenic acid via a hydrogen atom abstraction step (eq 6) or less likely by way of ethyl methyl sulfoxide (eq 10, 11) which we also find to be a thermal source of methanesulfenic acid. Thioformaldehyde is also detected in the pyrolysis of dimethyl sulfoxide at 600–800 °C and presumably arises from dehydration of methanesulfenic acid. It is clear that dimethyl sulfoxide, in addition to being a key organosulfur reagent and valuable solvent with an extensive chemistry^{2a,14} is also a remarkably rich thermal source of reactive molecules. Yet another thermal source of methanesulfenic acid is allyl methyl sulfoxide, which affords both the sulfenic acid and sulfine at temperatures above 250 °C. It is likely that allyl methyl sulfoxide decomposes by a radical mechanism similar to that indicated in eq 5–8 (a competing retro-ene^{1b} route to sulfine cannot be excluded).



Microwave spectroscopic study of the thermolysis products of several isotopic modifications of *tert*-butyl methyl sulfoxide allows spectral assignments to be made for the ¹³C, ³⁴S, ¹⁸O, hydroxy-*d*₁, methyl-*d*₃, and methyl-*d*₃ ³⁴S modifications of methanesulfenic acid.¹⁵ These and the normal species assignments result in the following “substitution” structure for methanesulfenic acid: C–S = 1.806 (2) Å, S–O = 1.658 (2) Å, O–H = 0.957 (10) Å, ∠CSO = 100.1 (1)°, ∠SOH = 107.7 (4)°, dihedral angle (displacement from “eclipsed” *cis*) ∠CSOH = 93.9 (1)°; dipole moment = 1.87 (7) D.^{17,19} Methanesulfenic acid has thus been found to contain dicoordinate rather than tricoordinate sulfur (form A rather than B, eq 1); we find no evidence for the presence of the isomeric form of methanesulfenic acid containing tricoordinate sulfur with hydrogen bonded to sulfur.

A number of overall rotational transitions are found to be split into “quartets” by the internal rotation of the methyl and hydroxyl groups. Analysis of these splittings gives a 2.4 (1) kcal mol⁻¹ threefold potential barrier to internal rotation about the C–S bond and 5.4 (2) and 4.1 (2) kcal mol⁻¹ *cis* and *trans* potential barriers to internal rotation about the S–O bond. Compared with the internal rotation in H₂O₂ and H₂S₂, the hindering potential for rotation about the S–O bond in methanesulfenic acid bears much more resemblance to the latter.²⁰ The half-life of methanesulfenic acid in the gas phase at 0.1 Torr and 25 °C is ~1 min. We shall report elsewhere on a photoelectron spectroscopic study of methanesulfenic acid.

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References and Notes

- (1) (a) Flash Vacuum Pyrolysis Studies. 5. (b) Part 4: E. Block and L. K. Revelle, *J. Am. Chem. Soc.*, **100**, 1630 (1978).
- (2) See (a) E. Block, “Reactions of Organosulfur Compounds”, Academic Press, New York, N.Y., 1978; (b) E. Block and J. O’Connor, *J. Am. Chem. Soc.*, **96**, 3929 (1974); (c) B. M. Trost, T. N. Salzmann, and K. Hiroi, *ibid.*, **98**, 4887 (1976); (d) J. W. A. M. Janssen and H. Kwart, *J. Org. Chem.*, **42**, 1530 (1977); (e) D. N. Jones, D. R. Hill, D. A. Lewton, and C. Sheppard, *J. Chem. Soc., Perkin Trans. 1*, 1574 (1977), and references therein.
- (3) (a) Anthraquinonesulfenic acid: K. Fries, *Chem. Ber.*, **45**, 2965 (1912); T. C. Bruice and P. T. Markiw, *J. Am. Chem. Soc.*, **79**, 3150 (1957); W. Jenny, *Helv. Chim. Acta*, **41**, 317, 326 (1958); T. C. Bruice and A. B. Sayih, *J. Am. Chem. Soc.*, **81**, 3416 (1959). (b) Pyrimidinesulfenic acids: B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *J. Am. Chem. Soc.*, **91**, 3634 (1969). (c) Penicillin- (azetidinone-) sulfenic acids: T. S. Chou, J. R. Burgtof, A. L. Ellis, S. R. Lammert, and S. P. Kukoljia, *J. Am. Chem. Soc.*, **96**, 1609 (1974). (d) Aryloxyiminomethanesulfenic acids: K. Kato, *Acta Crystallogr., Sect. B*, **28**, 55 (1972).
- (4) J. L. Kice and J. P. Cleveland, *J. Am. Chem. Soc.*, **95**, 104 (1973).
- (5) 2-Methyl-2-propanesulfenic acid has been detected in solution but isolation or full structural characterization has not proven possible.⁶
- (6) J. R. Shelton and K. E. Davis, *J. Am. Chem. Soc.*, **89**, 718 (1967); *Int. J. Sulfur Chem.*, **8**, 205 (1973).
- (7) W. S. Allison, *Acc. Chem. Res.*, **9**, 293 (1976), and references therein.
- (8) E. Block, R. E. Penn, R. J. Olsen, and P. F. Sherwin, *J. Am. Chem. Soc.*, **98**, 1264 (1976).
- (9) J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, **8**, 197 (1973).
- (10) F. A. Davis, S. G. Yocklovich, and G. S. Baker, *Tetrahedron Lett.*, 97 (1978).
- (11) V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961).
- (12) Two adjacent electrically heated pyrolysis tubes were connected to the microwave spectrometer. Conversion of **2** into **1** was complete at 450 °C, while thioformaldehyde was absent at this temperature. Passage of **1** through the second pyrolysis tube heated to 800 °C led to complete disappearance of **1** and appearance of characteristic thioformaldehyde lines.⁸ The intensity of isobutylene lines were unchanged by passage through the second pyrolysis tube.
- (13) FVP–mass spectrometric analysis of **2** also indicated the formation of **3** and dimethyl disulfide as well as methyl methanethiosulfonate.
- (14) D. Martin and H. G. Hauthal, “Dimethyl Sulfoxide”, Van Nostrand–Reinhold, Princeton, N.J., 1975.
- (15) The preparation of isotopic modifications of **2** followed standard procedures. *tert*-Butyl methyl-¹³C sulfoxide was prepared through reaction of methyl-¹³C iodide with *tert*-butylthiol followed by oxidation (H₂O₂–*t*-BuOH–V₂O₅ at 10 °C). *tert*-Butyl methyl-*d*₃ sulfoxide was prepared analogously from methyl-*d*₃ iodide. *tert*-Butyl methyl-¹⁸O sulfoxide was prepared by oxidation of *tert*-butyl methyl sulfide with iodobenzene dichloride in the presence of H₂¹⁸O and triethylamine in acetonitrile.¹⁶ *tert*-Butyl-*d*₉ methyl sulfoxide (a source of CH₃SOD) was prepared as described by Kwart.^{2d}
- (16) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc.*, 659 (1968).
- (17) An x-ray structural study of a sulfenic acid of type ArN=C(SO)OAr’ indicated an S–O bond distance of 1.624 (5) Å, ∠CSO = 104.4 (3)°, and ∠SOH = 105 (3)°.^{3d} An x-ray study of methyl *o*-nitrobenzenesulfonate, ArSOCH₃, indicated an S–O bond distance of 1.648 (12) Å and ∠CSO = 100°.¹⁸
- (18) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964).
- (19) Professor Saul Wolfe has informed us of an unpublished computational study of methanesulfenic acid at the STO-3G level (F. Bernardi, B. H. Schlegel, and S. Wolfe) with predictions in good agreement with our structural results.
- (20) For H₂O₂ dihedral ∠HOOH ≈ 118°, *V*_{cis} = 7.0 and *V*_{trans} = 1.1 kcal mol⁻¹;²¹ for H₂S₂ dihedral ∠HSSH = 90.6°, *V*_{cis} = 7.2 and *V*_{trans} = 6.8 kcal mol⁻¹.²²
- (21) R. H. Hunt, R. A. Leacock, C. W. Peters and K. T. Hecht, *J. Chem. Phys.*, **42**, 1931 (1965).
- (22) G. Winnewisser, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, **49**, 3465 (1968); W. C. Oelfke and W. Gordy, *J. Chem. Phys.*, **51**, 5336 (1969).

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Catalysis of Carbon Monoxide Hydrogenation by Soluble Mononuclear Complexes

Sir:

We report the homogeneous hydrogenation of carbon monoxide to methanol, higher primary alcohols, and their formate esters in the presence of soluble, mononuclear catalysts. In the course of an investigation of the proposed¹ free-radical mechanism for the cobalt–carbonyl catalyzed homogeneous hydrogenation of arenes, we decided to verify the predicted slow reduction of benzene. Accordingly, 160 mL of