It is possible to rule out, in addition to tetrahedral structures and structures containing bridging carbonyl oxygens, any structure which would significantly alter the chelate ring since the ultraviolet spectrum of this compound and that of bis(2,4-pentanedionato)copper(II), Figure 2, are identical except for intensity (the bands of the methoxide complex are approximately half as intense); the infrared absorptions of the 2,4-pentanedionato group are similar in the two compounds.

An X-ray investigation to confirm the suggested structure had been planned, but numerous attempts to obtain single crystals of the compound have failed.

Acknowledgment.—This work was supported by the Petroleum Research Fund of the American Chemical Society under Grant No. 1836-A1.

CONTRIBUTION FROM THE RESEARCH DEPARTMENT,
DOW CORNING CORPORATION, MIDLAND, MICHIGAN

Identification of Organosilanols by Nuclear Magnetic Resonance Spectroscopy

BY J. F. HAMPTON, C. W. LACEFIELD, AND J. F. HYDE

Received June 7, 1965

In a recent communication,[1] Chapman and King described the use of dimethyl sulfoxide (DMSO) in identifying alcohols by nuclear magnetic resonance spectroscopy. The classification of alcohols was determined by the degree of hydroxyl proton splitting. In a related investigation we have examined the n.m.r. spectra of various organosilanols in DMSO, and our preliminary results are reported herein.

In contrast to spectra recorded in common n.m.r. solvents sharp hydroxyl proton absorptions were obtained for all organosilanols examined. In addition, the use of DMSO allowed us to observe the first reported case of spin–spin splitting of the hydroxyl proton with an organosilanol. These latter two observations are illustrated by the spectra of diphenylsilanol determined in carbon tetrachloride (Figure 1) and DMSO (Figure 2). Thus, in DMSO solutions, extensive hydrogen bonding of the silanols to the solvent reduces the rate of proton exchange sufficiently to permit these observations. Hydroxyl proton exchange in DMSO is slow relative to the reciprocal of the doublet splitting ($1/J_{\mathrm{HSiOH}}$), but is still rapid enough to permit complete hydroxyl proton–deuterium exchange in phenyldimethylsilanol in less than a minute.

Application of DMSO has proved extremely useful in the analysis of silanols in the presence of other hydroxyl-containing species. The n.m.r. spectrum of a DMSO solution of a mixture of organosilanols, *t*-butyl alcohol, and water shows separate, sharp, resolvable hydroxyl proton absorptions for all species (Figure 3). Table I lists the various proton resonance assignments for this n.m.r. spectrum.

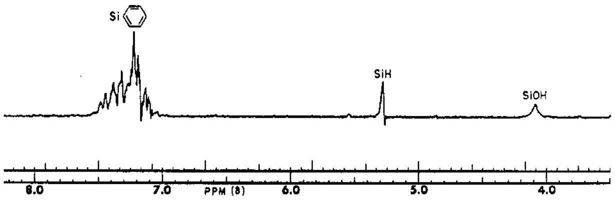

Figure 1.—N.m.r. spectrum of diphenylsilanol in carbon tetrachloride.

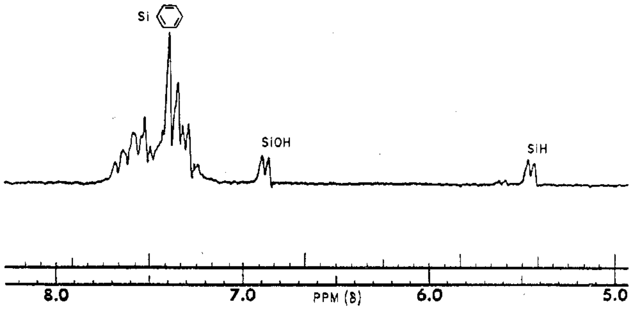

Figure 2.—N.m.r. spectrum of diphenylsilanol in DMSO showing the spin–spin splitting of the hydroxyl proton and silane proton resonances.

TABLE I

PROTON RESONANCE ASSIGNMENTS FOR FIGURE 3

Ref. no.	Assignment
1	$(\mathit{CH}_3)_4\mathrm{Si}$
2	$(\mathit{CH}_3)_3\mathrm{SiOH}$
3	$\mathrm{C_6H_5}(\mathit{CH}_3)_2\mathrm{SiOH}$
4	$(\mathrm{C_6H_5})_2\mathit{CH}_3\mathrm{SiOH}$
5	$(\mathit{CH}_3)_3\mathrm{COH}$
6	DMSO–C^{13} high-field side band
7	High-field spinning side band
8	High-field spinning side band
9	$(\mathit{CH}_3)_2\mathrm{SO}$
10	Low-field spinning side band
11	Low-field spinning side band
12	$\mathit{H}_2\mathrm{O}$
13	DMSO–C^{13} low-field side band
14	$(\mathrm{CH_3})_3\mathrm{CO}\mathit{H}$
15	$(\mathrm{CH_3})_3\mathrm{SiO}\mathit{H}$
16	$\mathrm{C_6H_5(CH_3)_2SiO}\mathit{H}$
17	$(\mathrm{C_6H_5})_2\mathrm{CH_3SiO}\mathit{H}$
18	$(\mathrm{C_6H_5})_3\mathrm{SiO}\mathit{H}$
19	$(\mathit{C_6H_5})_3\mathrm{SiOH}$, $(\mathit{C_6H_5})_2\mathrm{CH_3SiOH}$, $\mathit{C_6H_5}(\mathrm{CH_3})_2\mathrm{SiOH}$

Chemical shift data for the hydroxyl proton resonance of a large variety of organosilicon compounds are given in Table II.

At present, the advantages of using DMSO in n.m.r. studies of organosilanols include: (1) sharp, resolved hydroxyl absorptions, (2) independence of concentration on the position of the silanol hydroxyl resonance below 20 mole %, (3) use as a criterion of purity, (4) quantitative analysis of silanol, alcohol, and water mixtures, (5) observation of hydroxyl spin–spin splitting of silanols, (6) resolution of unequivalent hydroxyl absorptions in polyhydroxyorganosilicon com-

---

[1] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

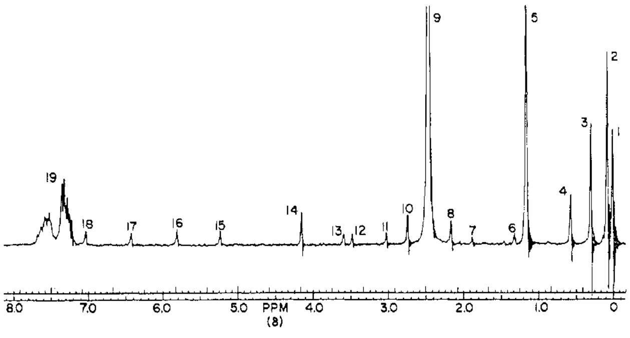

Figure 3.—N.m.r. spectrum of a triphenylsilanol (3.4 mole %), diphenylmethylsilanol (3.7 mole %), phenyldimethylsilanol (3.9 mole %), trimethylsilanol (4.1 mole %), trimethylcarbinol (6.3 mole %), and an unknown amount of water in DMSO showing the independence of the silanol, alcohol, and water hydroxyl proton resonances. Table I lists the individual proton resonance assignments.

TABLE II

HYDROXYL PROTON RESONANCES OF ORGANOSILANOLS IN DMSO[a]

Compound	Chemical shift,[b] p.p.m.	Multiplicity[c]
Ethyldimethylsilanol	4.83	s
Trimethylsilanol	4.80	s
3,3,3-Trifluoropropyldimethylsilanol	4.58	s
Vinyldimethylsilanol	4.50	s
Dimethylsilanol	4.42	d (J_{HSiOH} = 1.8 c.p.s.)
Phenyldimethylsilanol	4.22	s
Diphenylmethylsilanol	3.52	s
Diphenylsilanol	3.12	d (J_{HSiOH} = 2.0 c.p.s.)
unsym-Diphenyldimethyldisiloxane-1,3-diol	1-OH, 2.92; 3-OH, 3.85	s, s
Triphenylsilanol	2.90	s
Diphenylsilanediol	3.13	s
Phenylsilanetriol	3.74	s

[a] All spectra were recorded on dimethyl sulfoxide solutions with concentrations 10 mole % or less. All spectra were recorded at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.). [b] Tetramethylsilane was used as the internal reference. [c] s, singlet; d, doublet.

pounds, (7) characterization of polymeric hydroxyl-containing compounds, and (8) silanol stabilization.

Our work with DMSO in various areas of organosilicon chemistry including polymerization studies is continuing.

Acknowledgment.—We are grateful to Wanda Ratsek for securing the n.m.r. spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

The Monodentate Form of the Malonatochromium(III) Complex

BY D. H. HUCHITAL AND HENRY TAUBE

Received June 8, 1965

The kinetic stability of the ion $[(H_2O)_5CrO_2CCH_2CO_2H]^{2+}$ is important in understanding the mechanism of the reaction of Cr^{2+}(aq) with the acid malonatopentaamminecobalt(III) ion[1] and with the corresponding half-ester complex.[2] The subject, however, is of considerable interest in itself because the ion is unstable with respect to the chelate form, and the rate of ring closure in a system of this kind has to our knowledge not been measured. We have prepared the complex ion in connection with our studies on the reactions of metal ion reducing agents with the half-ester malonate complexes of pentaamminecobalt(III) and have studied some of its properties. We believe that the results are of interest quite apart from the oxidation–reduction work and are therefore describing them separately.

Procedure and Results

The monodentate acid malonate complex of Cr(III) is apparently formed in small yield in the oxidation of Cr^{2+}(aq) by Pb^{2+}(aq) in the presence of malonic acid. It can be separated from other chromium-containing components of the solution by ion-exchange techniques, taking advantage of the fact that it has a charge +2 while the chelate form has a charge of +1 and the hexaaquo ion or the "dimer" has a charge in excess of +2.

Our detailed procedure is herewith described. The reaction mixture was made up to contain 0.06 *M* Cr^{2+}, 0.03 *M* Pb^{2+}, 1 *M* H^+, 0.06 *M* malonic acid, and ClO_4^- as the only anion. After reaction was complete (*ca.* 10 min.) the product solution was passed through a cation-exchange column (Bio Rad AG 50W-X8, 50–100 mesh) in the sodium form. The column was eluted first with 0.2 *M* $NaClO_4$, which carries off the Cr(III) chelate, then when 1 *M* $NaClO_4$ was used a distinct band moved down the column and was collected. The elution behavior of the material suggests that the ion carries a charge of +2.

The following extinction coefficients were measured for the presumed monodentate malonato complex of chromium(III): λ_{max} 568 ± 1 mμ (ε 25.6 l. mole^{-1} cm.$^{-1}$), λ_{max} 412 ± 1 (ε 23.4 l. mole^{-1} cm.$^{-1}$). These values can be compared to those observed at the maxima for the methylmalonato complex (ε 24.0 at 568 mμ and ε 22.2 at 411 mμ). The maxima and the corresponding extinction coefficients for the chelate form are as follows: λ 559 mμ (ε 31.4), λ 415 mμ (ε 26.1). The comparisons strongly support the conclusion that the monodentate complex was isolated by the ion-exchange procedure. It is, however, possibly contaminated with a small amount of the chelate form.

The extinction coefficients of the chelate, monodentate complex, and hexaaquo complex are sufficiently different so that a spectrophotometric method of following the rate of ring closure or ligand dissociation can be and was used.

A second product mixture was prepared by the reaction of Cr^{2+}(aq) with Fe^{3+}(aq) in the presence of malonic acid in 0.1 *M* acid. The chromium-containing

---

(1) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

(2) D. H. Huchital and H. Taube, to be published.