

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<sup>a</sup>

Compound	Chemical shift, <sup>b</sup> p.p.m.	Multiplicity <sup>c</sup>
Ethyldimethylsilanol	4.83	s
Trimethylsilanol	4.80	s
3,3,3-Trifluoropropyl-dimethylsilanol	4.58	s
Vinyldimethylsilanol	4.50	s
Dimethylsilanol	4.42	d ( $J_{\text{HSiOH}} = 1.8$ c.p.s.)
Phenyldimethylsilanol	4.22	s
Diphenylmethylsilanol	3.52	s
Diphenylsilanol	3.12	d ( $J_{\text{HSiOH}} = 2.0$ c.p.s.)
<i>unsym</i> -Diphenyldimethylsiloxane-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

<sup>a</sup> 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.). <sup>b</sup> Tetramethylsilane was used as the internal reference. <sup>c</sup> 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.

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## The Monodentate Form of the Malonatochromium(III) Complex

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The kinetic stability of the ion  $[(\text{H}_2\text{O})_5\text{CrO}_2\text{CCH}_2\text{CO}_2\text{H}]^{2+}$  is important in understanding the mechanism

of the reaction of  $\text{Cr}^{2+}(\text{aq})$  with the acid malonato-pentaamminecobalt(III) ion<sup>1</sup> and with the corresponding half-ester complex.<sup>2</sup> 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  $\text{Cr}^{2+}(\text{aq})$  by  $\text{Pb}^{2+}(\text{aq})$  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 hexa-aquo 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*  $\text{Cr}^{2+}$ , 0.03 *M*  $\text{Pb}^{2+}$ , 1 *M*  $\text{H}^+$ , 0.06 *M* malonic acid, and  $\text{ClO}_4^-$  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*  $\text{NaClO}_4$ , which carries off the Cr(III) chelate, then when 1 *M*  $\text{NaClO}_4$  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):  $\lambda_{\text{max}} 568 \pm 1 \text{ m}\mu$  ( $\epsilon 25.6 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ ),  $\lambda_{\text{max}} 412 \pm 1$  ( $\epsilon 23.4 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ ). These values can be compared to those observed at the maxima for the methylmalonato complex ( $\epsilon 24.0$  at 568 *m* $\mu$  and  $\epsilon 22.2$  at 411 *m* $\mu$ ). The maxima and the corresponding extinction coefficients for the chelate form are as follows:  $\lambda 559 \text{ m}\mu$  ( $\epsilon 31.4$ ),  $\lambda 415 \text{ m}\mu$  ( $\epsilon 26.1$ ). 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 hexa-aquo 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  $\text{Cr}^{2+}(\text{aq})$  with  $\text{Fe}^{3+}(\text{aq})$  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.

species in this mixture are the chelate, the monodentate, and the hexaquo in *ca.* 65, 15, and 20% yield. Over a short time period the changes in extinction can be accounted for entirely by ring closure for the monodentate form, and at low acid with, in addition, a small amount of dissociation, and therefore the spectrophotometric measurements were made without separating the monodentate form.

The results obtained in the spectrophotometric studies are summarized in Table I.

TABLE I  
CHELATION STUDIES ON  $(\text{H}_2\text{O})_6\text{Cr}-\text{O}_2\text{CCH}_2\text{CO}_2\text{H}^{2+}$   
(25°,  $\mu = 1.0 M$ )

Concn. of complex, <i>M</i>	$\text{H}^+$ , <i>M</i>	% chelation <sup>a</sup>	$k_{\text{chelation}}$ , sec. <sup>-1</sup>
0.00140 <sup>b</sup>	0.1	74	$6.2 \times 10^{-6}$
0.00185 <sup>c</sup>	0.2	88	$8.0 \times 10^{-6}$
0.00174	0.5	100	$1.58 \times 10^{-5}$
0.00140	1.0	100	$2.60 \times 10^{-5}$

<sup>a</sup> The hydrolysis to the aquo complex accounts for the remainder. <sup>b</sup> Prepared from  $\text{Pb}^{2+}-\text{Cr}^{2+}$ -malonic acid reaction. <sup>c</sup> Prepared from  $\text{Fe}^{3+}-\text{Cr}^{2+}$ -malonic acid reaction.

### Discussion

The data of Table I show that the rate of chelation increases with the concentration of acid. When the values of the specific rate  $k$  in Table I are plotted against  $(\text{H}^+)$ , they are found to conform well to the relation

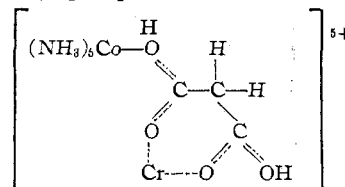
$$k = 4.0 \times 10^{-6} + 2.2 \times 10^{-7}(\text{H}^+) \text{ (units: } M \text{ and sec.)}$$

The existence of the second term in the rate law, though at first surprising, becomes less so if the possibility of ring closure by substitution at carbon rather than at chromium is entertained. For substitution at carbon, a rate term first order in  $(\text{H}^+)$  is to be expected as in ester hydrolysis or oxygen exchange between a carboxylic acid and solvent. The rate corresponding to the first term of the rate law is several times slower than is the rate of water exchange between  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and the solvent, and this term may correspond to substitution at Cr(III); in any case, the specific rate for the term sets an upper limit on the rate of substitution at Cr(III). It is interesting to note that the substitution is as slow as it is, particularly because the local concentration of the free carboxylate end is high. The observation suggests that the displacement of water is not greatly assisted by the incoming carboxyl which, it must be remembered, is protonated. At low  $(\text{H}^+)$ , a term inverse in this variable is expected but our measurements were not extended enough to reveal this effect.

The aquation is less sensitive to  $(\text{H}^+)$  in the range we investigated than is the rate of ring closure. This may mean that for aquation the acid-independent term relative to the acid-dependent one is greater than is the case for ring closure, or it may mean that the term inverse in  $(\text{H}^+)$  is to some extent featured in the rate law for aquation under the conditions of our experiments.

Comparison of the work described here with that reported by Svatos and Taube<sup>1</sup> shows that, at ordinary concentrations, the oxidation-reduction reaction of

$\text{Cr}^{2+}(\text{aq})$  with malonatopentaamminecobalt(III) is much more rapid than ring closure of the chelate. This being so, important features of the mechanism can be settled by examining the nature of the Cr(III) product formed by the reaction. Experiments were done making up two reaction mixtures, each at  $\mu \sim 2.5 M$ , but the first at  $0.2 M \text{H}^+$  and the second at  $2.4 M \text{H}^+$ . For the first solution, more than 90% of the reaction proceeds by the path which is inverse in  $(\text{H}^+)$  (corresponding to reaction of the complexed dinegative anion); for the second, approximately 75% by the path first order in  $(\text{H}^+)$ . Analysis of the reaction mixture using the ion-exchange technique showed that well in excess of 85% of the product by each path is the chelate. This observation together with our present observations on rate of ring closure proves that by each path the chelate ring is formed before  $\text{Cr}^{2+}(\text{aq})$  is oxidized and requires a re-examination of the mechanism for the path corresponding to the term first order in  $(\text{H}^+)$ . Specifically the conclusion<sup>1</sup> that this path corresponds to remote attack is incorrect. An activated complex along the following lines is indicated rather than one in which chromium attacks only the remote carboxyl group.



The conclusion<sup>1</sup> that a methylene proton is lost in the activation process is neither proven nor disproven by the current findings.

Since the chelate is formed directly by the reaction of  $\text{Cr}^{2+}(\text{aq})$  by the path inverse in  $(\text{H}^+)$ , it is reasonable to attribute the high second-order specific rate observed by this path compared to that for the acid malonate complex to the chelation, rather than simply to a decrease in electrostatic repulsion. This conclusion was by no means clear on the basis of the earlier work.

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### $\pi$ Bonding in the $\text{M}(\text{CO})_3$ Group

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It is generally accepted that an important feature of the bonding of terminal carbonyl groups to a metal