Hydration and Isomerization of Coordinated Maleate[1]

Sir:

We report here the hydration and isomerization of maleic acid when coordinated to Cr(III). The hydration reaction is a new example of a nucleophilic ligand reaction, perhaps mechanistically related to the reactions recently reported which involve nucleophilic attack at the carbonyl carbon of a coordinated ligand.[2–4]

In experiments on the inner-sphere chromium(II)–maleatopentaamminecobalt(III) electron transfer reaction, we have observed that the Cr(III) product is a mixture of the 2+ monodentate and the 1+ chelated 1:1 maleate complexes of Cr(III).[5] Although kinetically stable toward interconversion or aquation at room temperature in dilute perchloric acid, the complexes aquate under the conditions of the experiments summarized in Table I. In this table, the stoichiometry of the aquation reactions is reported.

Table I. Organic Aquation Products from Mixtures of the Monodentate and Chelated Maleate Complexes of Cr(III)

Expt	Chelate/ Monodentate[a]	Aquation[b] conditions	% aquation	%[c] as Maleic	Malic	Fumaric
I	54/46	20 hr $[H^+] = 0.78\ M$	95	79	19	2
II	47/53	11 hr $[H^+] = 4.2\ M$	99	98	1	1
III	~30/70	45 hr $[H^+] = 0.12\ M$	72	28	58	14

[a] The ratio of % of Cr(III) product of charge 1+ to that of charge 2+ as formed in the electron transfer reaction. [b] Temperature = 60°. Solutions contained also Co(II), Zn(II), and a small amount of residual Co(II). [c] Based on the amount of ligand found which was always within 10% of the amount expected. The liberated carboxylic acids were analyzed by anion exchange chromatography.

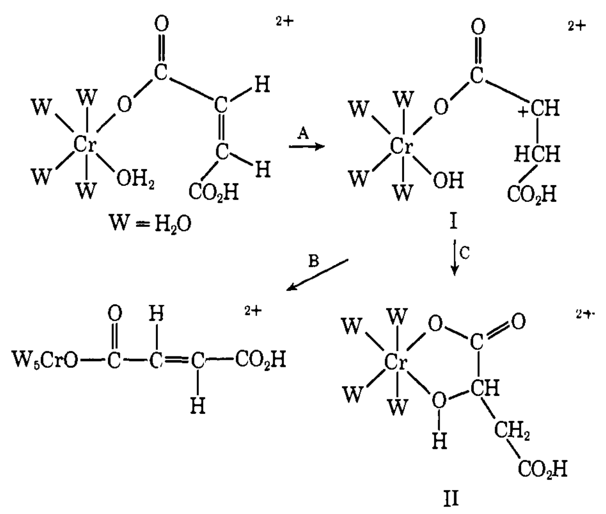
When equivalent amounts of hexaaquochromium(III) and maleic acid were subjected to the aquation conditions of experiment I for like periods of time, the organic products recovered analyzed as 98% maleic acid.[4a] This result, together with those reported in Table I, shows that the conversion of maleate to malate occurs in the first coordination sphere of Cr(III). An experiment with maleatopentaamminecobalt(III) under similar conditions showed that the organic acid liberated on 77% aquation contained 98% maleic acid.

The hydration reactions were observed also with Cr(III)-maleate complexes prepared independently of the redox reaction. A solution 50 ml in volume containing 2.5 mmol of perchloric acid, 2.5 mmol of hexaaquochromium(III), and 5.0 mmol of maleic acid was heated for 115 hr at 40°. The product mixture was separated by cation exchange chromatography, yielding three bands ahead of hexaaquochromium(III). The leading band, containing 0.16 mmol of Cr(III), had the same ion exchange behavior and visible spectrum as those of the chelated maleate complex. On aquation for 20 hr at 60° in 0.94 *M* perchloric acid (conditions similar to experiment I, Table I) it gave 76% maleic, 22% malic, and 1% fumaric acid. The tailing band was similarly identified as the monodentate maleate complex. Under the same aquation conditions it gave 87% maleic, 10% malic, and 3% fumaric acid. When the two complexes had been prepared *via* the redox reaction and separated before aquation, they exhibited similar individual stoichiometries.

Interpretation of the aquation stoichiometries must take into account the complexity of the aquation processes for the two maleate complexes. The monodentate complex must occur as an intermediate in the aquation of the chelated complex. Therefore, some of the ligand hydration and all the isomerization observed for initially chelated complex are expected to occur during the monodentate stage of aquation. There is, however, no such ambiguity about the ligand reactions observed for the initially monodentate complex, since our measurements of the equilibrium constant for ring opening show that very little ring closing can accompany aquation of the monodentate complex in 1 *M* acid.

The intermediate band (0.04 mmol of chromium) is an unknown complex with absorption maxima at 417 nm (ϵ 36.3 M^{-1} cm^{-1}). Its elution behavior is more like that of a 1+ than a 2+ complex, but it nevertheless moves substantially behind the chelated maleate complex. On aquation under the conditions used for the other bands, it gave 28% maleic, 69% malic, and 3% fumaric acid.

Two key observations concerning the ligand reactions are that they become more extensive the lower the acid concentration, and that they are not observed in the course of the aquation of maleatopentaamminecobalt-



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(1) Abstracted from the Ph.D. Thesis of M. V. Olson, Stanford University, 1969.

(2) J. P. Collman, *Transition Metal Chem.*, **2**, 1 (1966).

(3) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **91**, 3451 (1969).

(4) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 4102 (1969).

(4a) Note Added in Proof. The specific rate for the hydration of maleic acid is given as 0.08 M^{-1} in 0.92 *M* HCl at 125° (L. Rozelle, Ph.D. Dissertation, University of Wisconsin, 1960). From the data of expt 1, a value of 0.03 hr^{-1} is calculated for complexed maleate in 0.78 *M* HCl at 60°.

(III). Both observations can be understood in terms of the preceding mechanism, written for the monodentate complex.

Step A would probably be rate determining. The intermediate I could then isomerize to the fumarato complex as in (B) or undergo intramolecular nucleophilic attack as in (C) to produce the novel chelated maleate complex (II). Step C is analogous to the mechanism of a recently reported amidolysis of glycine ethyl ester by a coordinate amide.[3]

In terms of the above mechanism, the failure of maleatopentaamminecobalt(III) to undergo the ligand reactions is explained by the absence of a coordinated water molecule. Furthermore, the greater prevalence of the observed ligand reactions in the Cr(III) system at lower acidities is readily explicable in view of the fact that the rate of ligand release from the complexes is acid catalyzed. Therefore, at lower acidity the lifetime of maleate in the first coordination sphere is longer and the extent of hydration and isomerization is correspondingly greater.

The nature of the unknown complex resulting from the direct reaction between maleic acid and hexaaquochromium(III) is not understood. Since it is neither the monodentate nor chelated form of the maleate complex, it seems necessary to assume that the ligand in the complex is hydrated. A striking aspect of the chemistry of the unknown complex is that it yields substantial amounts of maleic acid on aquation. This behavior is unexpected since ΔF° for free maleic acid going to malic acid in acidic solution is about -7 kcal/mol. Only a malate complex with substantial instability relative to hexaaquochromium(III) and free malic acid could exhibit the observed behavior. Intermediate II would not seem to have the requisite instability; tridentate attachment of malate would be more likely to satisfy the energy requirement.

Many of the experimental details are described elsewhere.[1,5] The analysis for the organic anions is, however, particularly germane to the results just reported and, accordingly, is described herewith.

The reaction mixture was charged onto a lithium-form cation exchange column which was then rinsed with water until all the carboxylic acids had been washed through. The eluent solution was charged onto a 18-mm diameter column containing 15 ml of AG1-X2, 200–400 mesh chloride-form resin.[6] Separation followed the scheme developed by Blaedel and Todd[7] for mixtures of maleic and fumaric acids. Elution of the column with $0.073\ M$ HCl gave quantitative separation of the three acids, malic, fumaric, and maleic, appearing at the fractions 20–40, 75–125, and 150–300 ml, respectively (the actual volumes depend on the particular experimental arrangement, but are reported as support for the claim that separation was complete).

Maleic and fumaric acids were determined by direct measurement of the uv absorbance at 220 nm on the appropriate eluent fraction. Extinction coefficients of $4.5 \times 10^3\ M^{-1}\ \text{cm}^{-1}$ for maleic acid and $1.03 \times 10^4\ M^{-1}\ \text{cm}^{-1}$ for fumaric acid were measured in $0.073\ M$ HCl. Malic acid was determined colorimetrically by the method of Goodban and Stark.[8] Samples containing 10–80 μg of malic acid in 1 ml could be determined with a precision of somewhat better than ±10%. Blank corrections were found necessary for each run.

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[5] M. V. Olson and H. Taube, submitted for publication.

[6] In some instances the resin could be used after only cursory preliminary rinsing. Other batches required prolonged rinsing with $6\ M$ HCl before the effluent gave negligible uv absorbance at 220 nm.

[7] W. J. Blaedel and J. W. Todd, *Anal. Chem.*, **30**, 1821 (1958).

[8] A. E. Goodban and J. B. Stark, *ibid.*, **29**, 283 (1957).

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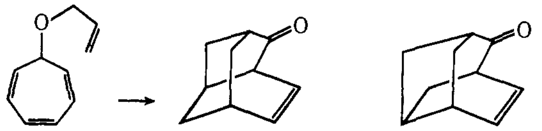
Multiple Thermal Rearrangements. The Pyrolysis of 7-Allyloxycycloheptatriene

Sir:

Cycloheptatriene and its derivatives have been found to undergo a variety of thermal unimolecular processes: (1) conformational ring inversion;[1] (2) valence tautomerization;[2] (3) [1,5]-hydrogen shift(s);[3] (4) [1,5]-carbon shifts(s).[4,5] One aspect of the thermal chemistry of cycloheptatriene which we felt had considerable synthetic potential was to examine the behavior of certain 7-substituted tropilidenes in which the substituent itself could undergo further reaction(s) with the ring double bonds of the tropilidene by virtue of hybridization changes (isomerization) attending [1,5]-sigmatropic hydrogen shift(s). We illustrate how multiple thermal rearrangements in the cycloheptatriene series may provide a facile entry to new polycyclic systems by the one-step high-yield synthesis (83%) of two unique tricyclic ketones from the pyrolysis of 7-allyloxycycloheptatriene (**1**; eq 1).



1 **10** **11** (1)

There are four possible tricyclic products **8–11** which could arise from **1** as a result of two sequential sigmatropic reactions[3a,6] followed by intramolecular cycloaddition reactions. That is, thermal rearrangement of **1** would first generate, *via* [1,5]-hydrogen shifts,

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[1] W. E. Heyd and C. A. Cupas, *J. Amer. Chem. Soc.*, **91**, 1559 (1969), and references therein cited.

[2] (a) For a review see G. Maier, *Angew, Chem. Int. Ed. Engl.*, **6**, 402 (1967); (b) M. Goerlitz and H. Gunther, *Tetrahedron*, **25**, 4467 (1969); (c) J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968); (d) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967), and previous papers; (e) D. Schoenleber, *Angew. Chem. Int. Ed. Engl.*, **8**, 76 (1969); (f) M. Jones Jr., *ibid.*, **8**, 76 (1969).

[3] (a) For a review see G. B. Gill, *Quart. Rev., Chem. Soc.*, **22**, 338 (1968); (b) A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 266 (1969), and previous papers; (c) K. W. Egger, *J. Amer. Chem. Soc.*, **90**, 1 (1968).

[4] J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

[5] For examples of thermal migration of other groups, see R. W. Hoffmann, K. R. Eicken, H. F. Luthardt, and B. Dittrich, *Tetrahedron Lett.*, 3789 (1969); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); ref 2d.

[6] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); K. Fukui and H. Fujimoto in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1969, pp 117–190.