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Kinetics and Mechanisms of Aquation of Some σ-Bonded Organochromium Complexes

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The study of the aquation of the organochromium complexes formed during reactions of chromous ion with 3- and 4-pyridineacrylic acids on one hand and maleic and fumaric acids on the other showed essential kinetic and mechanistic differences between the two groups. In the first group the rate of aquation has no acid-independent term, is accelerated by oxygen, but is unaffected by excess chromous ion. In the second group the rate of aquation has both an acid-dependent and an acid-independent term, it is not affected by oxygen, but it is considerably enhanced by chromous and vanadous ions. The aquation of the second group is also accelerated by carboxylic acids. Activation parameters of all the catalytic and noncatalytic paths studied are reported. For the organometallic complexes obtained from pyridineacrylic acids it is postulated that the first step toward aquation is an intramolecular transfer of the $Cr(OH_2)_5$ moiety from carbon to the carboxylic oxygen. For the organometallic complexes obtained from maleic and fumaric acids it is postulated that, in the chelate ring containing both a Cr–C and a Cr–O bond, the weaker link is the latter. An interpretation is also given for the observation that Cr^{2+} does not catalyze the aquation of *all* organochromium complexes, as it seems to do for the ordinary ones.

Introduction

The acidolysis of aqueous ethanol solutions of pentaaquobenzylchromium(III) ion to toluene was studied by Kochi and Buchanan.[2a] In the presence of nucleophilic species X^- it is proposed that the mechanism consists of a proton-assisted heterolytic rate-determining step, preceded by a fast preequilibrium (eq 1 and 2).

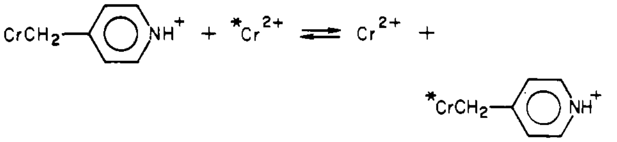
$$ArCH_2Cr^{2+} + X^- \xrightleftharpoons{fast} ArCH_2CrX^+ \qquad (1)$$

$$ArCH_2CrX^+ + H^+ \xrightarrow{slow} ArCH_3 + CrX^{2+} \qquad (2)$$

In contrast, the evidence obtained by Nohr and Espenson[2b] suggests that the reaction of this organochromium ion with six oxidizing agents, Fe^{3+}, Cu^{2+}, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, O_2, and H_2O_2, proceeds by homolytic rather than heterolytic rate-determining cleavage of the Cr–C σ bond (eq 3).

$$ArCH_2Cr^{2+} \rightarrow ArCH_2\cdot + Cr^{2+} \qquad (3)$$

A homolytic rate-determining step has also been postulated[2c] in the reactions of oxidizing agents with dimetallic organochromium cations containing two benzylchromium-like units per molecule. In the acid hydrolysis of pentaaquo(2-, -3-, and -4-pyridinomethyl)chromium(III) to the corresponding dipyridylethanes the rate-determining step is believed[3] to be homolytic. In this case too, however, a change in conditions may result in a change of mechanism. Thus, Espenson and Leslie[4] argue that the exchange reaction between (4-pyridinomethyl)chromium(III) and $^{51}Cr^{2+}$(aq) occurs primarily by a direct bimolecular path (eq 4) and not by intramolecular homolytic dissociation.



(4)

Schmidt, Swinehart, and Taube[5a] have studied the aquation rates of the pentaaquochromium(III) ion σ bonded to various acyclic anions. Additional experiments enriching the field were also reported by Hyde and Espenson[5b] and by Cohen and Meyerstein.[5c] The rate law in these cases has the general form

$$-\frac{d[RCr^{III}]}{dt} = [k_1 + k_2[H^+]][RCr^{III}] \qquad k_1, k_2 \neq 0 \qquad (5)$$

but again there are exceptions: for R = CH_3 or the radical derived from diethyl ether[5a] there is no acid-independent term, and for R = C(=O)NH_2 or $CH_2N(CH_3)CHO$ the acid dependence is complicated.[5c] Anyway, the acid-dependent term in the rate law is interpreted[6] as resulting from an electrophilic attack of H^+ at the α carbon and a subsequent heterolytic cleavage of the Cr^{III}–C bond. The acid-independent term is similarly thought[5a] to result from an activated complex containing a solvent molecule. In the hydrolysis of halogenated derivatives, it is believed[7] that the rate-determining activation act involves not only breaking of the chromium–carbon bond but also a simultaneous breaking of the neighboring carbon–halogen bond. It is also interesting that the rate law for $(H_2O)_5CrCF_3^{2+}$ contains both an acid-dependent and an acid independent term, whereas the rate laws for $(H_2O)_5CrCH_2X^{2+}$ (X = Cl, Br, I) have only acid-independent terms.

The complex $(H_2O)_5CrCH_2COOH^{2+}$ prepared by Ševčik and Jakubcova[8] does not have any halogens, yet its aquation proceeds by an acid-independent path only. It is also interesting that O_2 or Cr^{2+} have no effect on the aquation of $(H_2O)_5CrCCl_3^{2+}$,[7c] whereas the aquation of $(H_2O)_5CrCH_2COOH^{2+}$ is unaffected by O_2 but catalyzed by Cr^{2+}.[8]

The aquation of *ordinary* Cr^{III} complexes is catalyzed by Cr^{2+} via electron transfer.[9] An intriguing question arising then is why it does not also do so for *all* organochromium complexes.

From the above brief analysis of the "state of the art" it is obvious that the problems related to the cleavage of the

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(1) (a) University of Athens. (b) Greek Atomic Energy Commission.

(2) (a) Kochi, J. K.; Buchanan, D. *J. Am. Chem. Soc.* **1965**, *87*, 853. (b) Nohr, R. S.; Espenson, J. H. *Ibid.* **1975**, *97*, 3392. (c) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235.

(3) (a) Coombes, R. G.; Johnson, M. D.; Winterton, N. *J. Chem. Soc. A* **1965**, 7029. (b) Coombes, R. G.; Johnson, M. D. *Ibid.* **1966**, 177. (c) Johnson, M. D. *Rec. Chem. Prog.* **1970**, *31*, 143. (d) Schmidt, A. R.; Swaddle, T. W. *J. Chem. Soc. A* **1970**, 1927.

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(6) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.

(7) (a) Malik, S. K.; Schmidt, W.; Spreer, L. O. *Inorg. Chem.* **1974**, *13*, 2986. (b) Byington, J. I.; Peters, R. D.; Spreer, L. O. *Ibid.* **1979**, *18*, 3324, 3327. (c) Ševčik, P. *Inorg. Chim. Acta* **1976**, *32*, L16.

(8) Ševčik, P.; Jakubcová, *Collect. Czech. Chem. Commun.* **1977**, *42*, 1776.

(9) (a) Ogard, A. E.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1084. (b) Pennington, D. E.; Haim, A. *Inorg. Chem.* **1966**, *5*, 1887. (c) Deutsch, E.; Taube, H. *Ibid.* **1968**, *7*, 1532. (d) De Chant, M. J.; Hunt, J. B. *J. Am. Chem. Soc.* **1968**, *90*, 3695. (e) Williams, T. J.; Garner, C. S. *Inorg. Chem.* **1970**, *9*, 2058. (f) Davis, R.; Jordan, R. B. *Ibid.* **1971**, *10*, 1102. (g) Cannon, R. D.; Stillman, J. S. *Ibid.* **1975**, *14*, 2202. One of the reviewers correctly pointed out that "electron transfer between Cr^{2+} and $CrCl^{2+}$ via a chloride-bridged transition state results in exchange of chromium between the two species, but aquation does not occur in this process". It can, however, be considered that in this case too, Cr^{2+} accelerates the aquation of the *original* Cr^{III} complex. The fact that in this process Cr^{2+} is transformed into a Cr^{III} species identical with the original and that there is no net chemical change does not essentially affect the point we want to make.

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Table I. λ_{max} and ϵ_{max} of Complex 1 and the Intermediate Product of Its Aquation (31 °C, 3 M $HClO_4$)

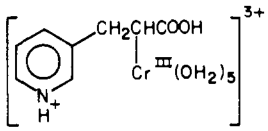
	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
organochromium complex (1)	287.5^a	13 260
	320^a	8 500
intermediate complex	260	13 000

^{a} The absorptivities of the intermediate complex at these wavelengths are 5120 and 2260 M^{-1} cm^{-1}, respectively.

Cr–C σ bond are by no means solved. The number of mechanistic studies made in this field so far is limited, and the issues are not all settled. The investigation of other systems seems therefore desirable. In this paper we study the new organochromium complexes, which have been prepared and characterized recently in our laboratory.[10]

Experimental Section

Abbreviations. The formulas of the organochromium complexes studied in this paper are as follows. Complexes **1** and **2**, in which Cr^{III} is σ bonded to a chain carbon of 3- and 4-pyridinepropionic acid, respectively, are abbreviated Cr-3-PPA and Cr-4-PPA. The dinuclear complexes **3** and **4**, in which one Cr^{III} is σ bonded to a carbon atom of succinic acid and to carboxylic oxygen, are abbreviated Cr-SA and (MA)Cr-SA, respectively.



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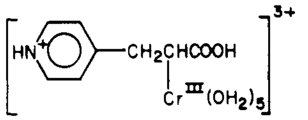

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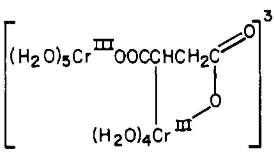

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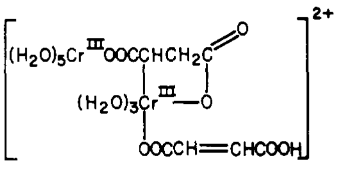

4

Preparations. The reagents used were of analytical grade. Cr^{2+} solutions in 0.2–2 M perchloric acid were prepared electrolytically, by reduction of Cr^{3+}(aq) on a mercury cathode. These solutions were mixed with the acidic ($HClO_4$) aqueous solutions of the organic acids. The concentrations of the reactants generally ranged from 0.1 to 1 M. A large excess of maleic or fumaric acids is necessary in order to obtain complex **4**. The mixtures containing Cr^{2+} and the unsaturated organic acid are allowed to react at room temperature. The time necessary for the formation of the organochromium complex ranges from a few minutes for maleic acid to a few days for 3-pyridineacrylic acid.

The organochromium complexes thus formed are isolated from the other chromium species present in the reaction mixture by ion exchange using a Dowex 50WX2 resin. Details of this separation are given elsewhere.[10]

Kinetics. The kinetics of acid hydrolysis of complexes **1** and **2** were mainly followed at 287.5 and 320 nm and for **3** and **4** at 278 nm. The absorptions are related to the Cr–C σ bond. Electronic spectra were taken on a Cary-14 and a Cary-17. The determination of the products has already been described.[10]

Results

Organochromium Complexes of 3- and 4-Pyridinepropionic Acids. The behaviors of the two complexes Cr-3-PPA (**1**) and Cr-4-PPA (**2**) are similar. Hence, only the 3-derivative was investigated systematically.

Acid hydrolysis of Cr-3-PPA proceeds in two stages. In the first stage the organochromium complex is transformed into another (regular) complex, which then hydrolyzes at a slower rate to Cr^{3+}(aq) and 3-pyridinepropionic acid. The spectra of the initial organochromium complex, the intermediate, and the saturated organic product are depicted in Figure 1. Table I contains the values for λ_{max} and ϵ_{max} of the initial and intermediate species. The values of ϵ_{max} depend on acid concentration (Figure 2). The qualitative characteristics of the spectra do not change with a change in hydrogen ion concentration; only the values of the absorptivities change. It must be pointed out in particular that there is no evidence for more than one intermediate product.

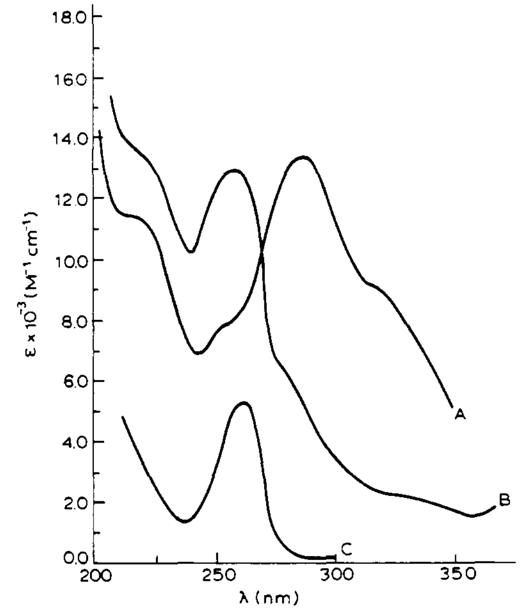

Figure 1. Spectra of (A) complex **1**, (B) the intermediate complex to which **1** is transformed, and (C) pyridinepropionic acid. The spectra were taken at 31 °C and 3 M $HClO_4$.

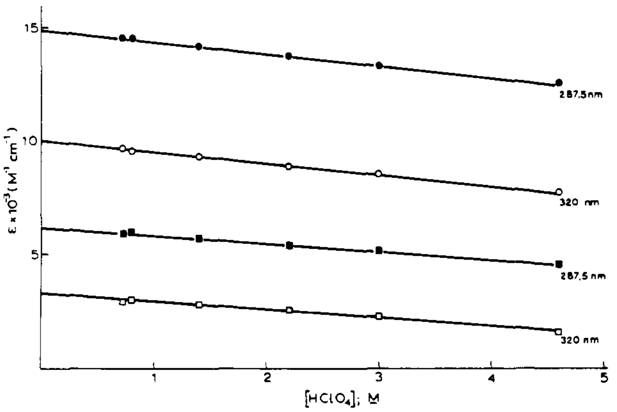

Figure 2. Dependence on acid concentration of the absorptivities at 31 °C. Complex **1**: ●, 287.5 nm; ○, 320 nm. Intermediate complex: ■, 287.5 nm; □, 320 nm.

The transformation of Cr-3-PPA to the intermediate complex follows first-order kinetics. Figure 3 gives the acid dependence on the first-order rate constant at various temperatures. It is noted that there is no acid-independent term ($k = k'[H^+]$) and that excess Cr^{2+} has no effect on the observed rate constants. From the data in Figure 3 we calculate k' and the Arrhenius parameters (Table II).

Organochromium Complexes of Succinic Acid. The decomposition of Cr-SA (**3**) and (MA)Cr-SA (**4**) were also studied in detail. The products in both cases are eventually Cr^{3+}(aq) and succinic acid. Complex **4** gives in addition maleic acid which is released from coordination. Ion-exchange experiments showed that in the course of the reaction (MA)-Cr-SA is to a small extent transformed into Cr-SA. It has also been shown[10] that in the presence of excess maleic acid Cr-SA is partially transformed into (MA)Cr-SA. Further-

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(10) Petrou, A.; Vrachnou-Astra, E.; Katakis, D. *Inorg. Chim. Acta* **1980**, *39*, 161.

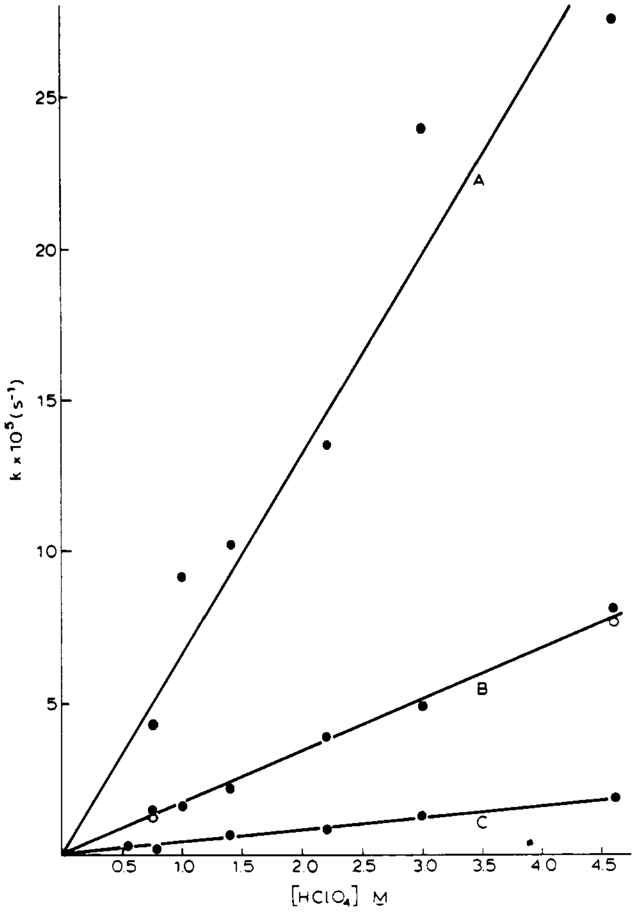


Figure 3. First-order rate constants for the transformation of complex **1** to the intermediate complex as a function of acid concentration: A, 41 °C; B, 31 °C; C, 21 °C; ●, without Cr^{2+}; ○, with excess Cr^{2+} (5×10^{-4} M).

Table II. Apparent Activation Parameters

complex	*E*, kcal mol^{-1}	ln *A*
Cr-3-PPA (1)[a]	25.4 ± 0.6	30.7 ± 0.9
Cr-SA (3), acid-dependent term[b]	18.8 ± 0.9	17.8 ± 1.35
Cr-SA (3), acid-independent term[b]	24.2 ± 1.6	26.9 ± 2.5
(MA)Cr-SA (4), acid-dependent term[c]	19.1 ± 1.3	19.6 ± 2
(MA)Cr-SA (4), acid-independent term[c]	24.2 ± 3.2	26.7 ± 5.3
Cr-SA (3), Cr^{2+}-catalyzed, acid-independent term[b]	10.7 ± 0.5	12.7 ± 0.9
Cr-SA (3), Cr^{2+}-catalyzed, inverse in acid term[b]	15.2 ± 0.7	18.3 ± 1.3
(MA)Cr-SA (4), maleic acid catalyzed term[c]	17.7 ± 0.1	20.4 ± 0.2

[a] $k_{obsd} = k'[H^+]$; activation parameters are calculated from the values of k'. [b] $k_{obsd} = k_1 + k_2[H^+] + k_3[Cr^{2+}] + k_4[Cr^{2+}]/[H^+]$; activation parameters are calculated from the values of k_1, k_2, k_3, and k_4. [c] $k'_{obsd} = k'_1 + k'_2[H^+] + k'_3[MA]$; activation parameters parameters are calculated from the values of k'_1, k'_2, and k'_3.

Table III. Observed Rate Constants of Hydrolysis of Complex **3**[a-c]

[H$^+$], M	[Cr^{2+}]$_0$, M	temp, °C	$10^5 k_{obsd}$, s^{-1}
0.33	0	22	0.09 ± 0.01
0.33	0	36	0.39 ± 0.03
0.33	0	45	1.64 ± 0.01
0.33	0	54.5	5.11 ± 0.03
1.33	0	22	0.16 ± 0.01
1.33	0	36	0.67 ± 0.06
1.33	0	45	2.28 ± 0.10
1.33	0	54.5	6.94 ± 0.52
0.50	0	45	1.71 ± 0.12
1.70	0	45	2.42 ± 0.18
1.00	0.0088	23	3.33 ± 0.30
1.00	0.0130	23	4.86 ± 0.42
1.00	0.0208	23	9.17 ± 0.08
1.00	0.0147	26	8.40 ± 0.23
1.00	0.0147	34	14.31 ± 0.82
1.00	0.0147	42	23.89 ± 1.83
1.00	0.0147	48	34.44 ± 2.86
0.035	0.0033	10.5	1.81 ± 0.09
0.035	0.0033	22.5	6.39 ± 0.39
0.035	0.0033	34.5	16.02 ± 1.24
0.33	0.0090	34.5	9.72 ± 0.54

[a] The initial concentrations of complex **3** were between 10^{-3} and 10^{-4} M. [b] At H^+ concentrations lower than 1.0 M the ionic strength was kept constant at $\mu = 1$, by addition of $NaClO_4$. [c] 20–25 experiments were performed at each set of concentration conditions.

Table IV. Observed Rate Constants of Hydrolysis of Complex **4**[a-d]

[H$^+$], M	[MA]$_0$,[d] M	temp, °C	$10^5 k_{obsd}$, s^{-1}
0.11	0	22	0.119 ± 0.01
0.11	0	36	0.35 ± 0.03
0.11	0	45	1.67 ± 0.09
0.11	0	54.5	5.47 ± 0.37
1.00	0	22	0.41 ± 0.03
1.00	0	36	1.29 ± 0.11
1.00	0	45	4.44 ± 0.41
1.00	0	54.5	13.11 ± 0.91
0.50	0	45	2.75 ± 0.18
1.70	0	45	6.55 ± 0.28
0.46	0.182	32	5.21 ± 0.49
0.46	0.364	32	10.72 ± 1.03
0.46	0.727	32	20.45 ± 0.98
0.46	1.000	32	29.31 ± 2.42
1.00	0.017	48.5	8.75 ± 0.82
1.00	0.050	48.5	13.06 ± 1.21
1.00	0.083	48.5	16.25 ± 1.42
1.00	0.050	23	0.78 ± 0.04
1.00	0.050	35	2.68 ± 0.18
1.00	0.050	54	16.80 ± 0.93

[a] The initial concentrations of complex **4** were between 10^{-3} and 10^{-4} M. [b] At H^+ concentrations lower than 1.0 M the ionic strength was kept constant at $\mu = 1$, by addition of $NaClO_4$. [c] 20–25 experiments were performed at each set of concentration conditions. [d] MA = maleic acid.

more, an ordinary blue complex is formed during hydrolysis.

All these observations indicate that the first stage in the aquation of complexes **3** and **4** is the destruction of the chelate ring, which includes the Cr–C bond. The kinetics were therefore followed at the characteristic peak of this bond at 278 nm, and they were found to be first order in the organochromium species. Representative results of the kinetics experiments are given in Tables III and IV. The rate law has two terms: an acid-independent and an acid-catalyzed one. Within this context it is also important to emphasize that what we actually observe is the overall decrease in the concentration of *all* organochromium species that may be simultaneously present in the system. Thus, in the aquation of complex **4** and in view of the small conversion **4** → **3**, the results may have some systematic error due to the presence of some **3**. This error is, however, expected to be rather small, because the extent **4** transformed into **3** is also small, but it is nevertheless important to establish that the rate constants for these two complexes are indeed significantly different. From Table III it is seen that the rate of aquation of complex **4** is faster than that of complex **3**, which makes the expected systematic error even smaller. The difference in rates is mainly due to the acid-catalyzed term (Tables III and IV).

The Arrhenius plots do not deviate from linearity. The values of the apparent activation parameters are given in Table II. It can be seen that the acid-independent paths for the two complexes have nearly the same activation parameters. The same is true for the acid-catalyzed paths. In fact, the ex-

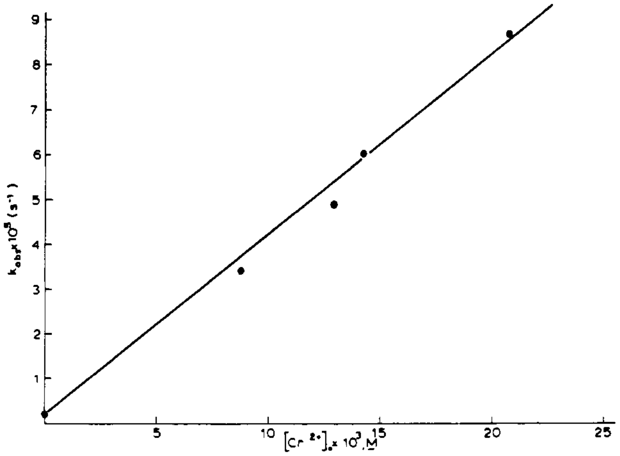


Figure 4. Acceleration of the decomposition of complex **3**, in the presence of chromous ion (1 M $HClO_4$, 23 °C).

Table V. Comparison of the Effects Various Carboxylic Acids Have on the Rate Constant of Aquation of Complex **4**[a]

acid	$10^4 k_{obsd}$, s^{-1}
maleic	1.7
fumaric	1.4
succinic	2.2
acetic	1.7

[a] 54 °C, 1 M $HClO_4$, 0.05 M organic acid, 2.5×10^{-4} M organochromium complex.

perimental error blurs the relatively small differences expected on the basis of the data in Tables III and IV.

Table II also includes the observed activation parameters for two chromous-catalyzed paths in the aquation of Cr-SA (Figure 4). One of these paths is inverse in the concentration of hydrogen ion; the other is independent of acid. It is interesting that the frequency factors are small, indicating that we may be dealing with composite rather than elementary reactions.

None of the four paths in the aquation of complex **3** mentioned above is influenced by chloride ion at a concentration up to 0.5 M and at constant ionic strength. The rate constants for the acid-independent, the acid-assisted, and the Cr^{2+}-catalyzed paths are the same whether chloride ion is added at zero time or not.

The aquation of complex **3** is also catalyzed by V^{2+}. The observed pseudo-first-order constant at 35 °C, $[HClO_4]$ = 0.335 M, and $\mu = 1$, in the presence of 9×10^{-3} M V^{2+} is 1.75×10^{-3} s^{-1}. The corresponding value with the same concentration of Cr^{2+} (9×10^{-3} M) is only 9.72×10^{-5} s^{-1}.

The Cr^{2+}-assisted aquation of complex (MA)Cr-SA is accompanied by reduction of the coordinated unsaturated ligand, and it will be reported separately.

Finally, the aquation of complex **4** is accelerated by maleic acid (Figure 5) and by other carboxylic acids, even saturated ones (Table V). It is worth mentioning within this context that, in mixtures containing complex **4** and excess maleic acid, ion-exchange separation revealed the formation of a new pink band of low charge, lower than that of (MA)Cr-SA. Under these conditions a second maleate presumably enters the coordination sphere of the carbon-bound Cr^{III}.

Figure 5 includes data for two acidities. Within this acid range the maleic acid catalyzed path is independent of hydrogen ion concentration.

Fumaric acid gives with chromous ion two organochromium species similar to **3** and **4**. The high-charge complex obtained from fumaric acid is in fact identical with **3** and hydrolyzes with the same rate. The low-charge complex from fumaric acid differs from the corresponding complex from maleic acid (**4**) only in that it contains fumarate rather than maleate and the rates of hydrolysis are within experimental error the same. The high-charge complex from fumaric acid is also partially transformed into complex **4**, by addition of excess maleic acid.

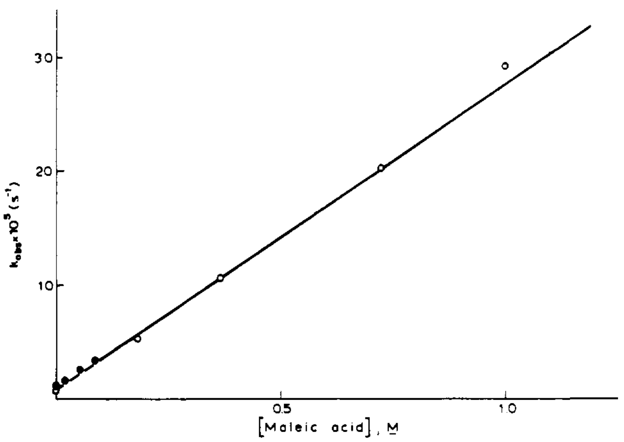
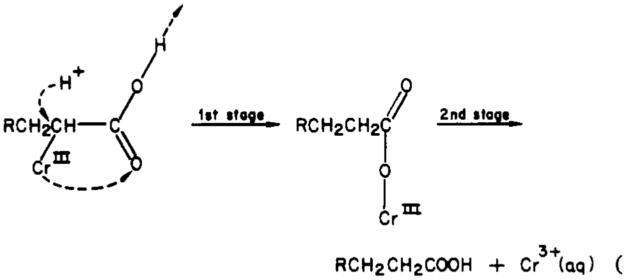


Figure 5. Effect of maleic acid on the rate of hydrolysis of complex **4** at 32 °C: ●, 1 M $HClO_4$; ○, 0.46 M $HClO_4$.

Discussion

The first-order kinetics of the organochromium species and the absence of dimeric organic products in the aquation reactions studied in this paper suggest mechanisms of heterolytic nature.

For the aquation of complexes **1** and **2** we propose mechanism[11] 6.



(6)

The intermediate complex was isolated, and its spectrum is given in Figure 1. The second stage is an ordinary aquation reaction, very slow compared to the first, and it was not studied further. The first stage is an intramolecular transfer of $Cr(OH_2)_5^{3+}$ from carbon to oxygen, assisted by a proton. Even for this hydrogen-catalyzed path, however, the activation energy is quite high (Table II). It is then perhaps not surprising that we have not detected an acid-independent path, which is expected to be even slower.

Space-filling models show that in Cr-3-PPA the carbonyl or hydroxyl oxygen can come pretty close to Cr^{III}, in a way that does not allow formation of a chelated ring but makes easy the intramolecular transfer of the $Cr(OH_2)_5$ moiety from carbon to oxygen. The pyridine ring could conceivably assist in giving to the hydroxyl group a favorable orientation toward Cr^{III} and keeping this orientation by inhibiting rotation. It is also possible that the crowding around Cr^{III} does not allow approach of a solvent molecule, protonated or not, and that this is the reason for the absence of a solvent-assisted, acid-independent path. For the same reason close approach of H_3O^+ seems unlikely and acid catalysis probably involves a concerted transfer to Cr–C of a proton. This interpretation is also consistent with the higher value (zero) for the entropy of activation in the aquation of Cr-3-PPA, as compared to the entropies of activation in cases where solvent involvement was

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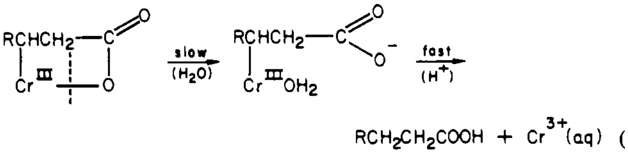
(11) In this and in the subsequent reactions only the relevant skeletons of the molecules are depicted.

postulated.[5a,8] The higher value of ΔS^* can be attributed to loss of order in the solvation of H^+.

The organochromium complexes of succinic acid (**3** and **4**) are more labile than those of pyridinepropionic acid (**1** and **2**). Moreover, the rate law contains both an acid-independent and an acid-dependent term. We suggest that these differences are not merely quantitative but that they reflect qualitative differences in the mechanisms as well. In complexes **3** and **4** transfer of the corresponding aquochromium group from carbon to oxygen has already been partially accomplished because of chelation, and there is no evidence that the five-membered ring opens in a way that Cr^{III} remains bound to oxygen only. In fact, it seems that the opening of the ring is accompanied or followed quickly by a removal of Cr^{III} and that it is the breaking of the Cr–O bond which probably determines the rate of this process. For one thing, the aquation of a binuclear intermediate complex having one Cr^{III} on each carboxyl group is not expected to be fast. Yet, we were unable to determine such a complex. Another important clue is that the aquation of complex **3** is remarkably similar to the aquation of the (acetato)pentaaquochromium(III) ion.[9c] As in that case, the reaction proceeds by two parallel paths, one of them catalyzed by a proton. The activation energies for these paths (Table II) are closer to the values reported by Deutsch and Taube ($\Delta H^* = 18.6$ kcal mol^{-1} for the acid-catalyzed path), rather than to the value 25.4 kcal mol^{-1} given here for Cr-3-PPA. The reaction is also catalyzed by Cr^{2+} and even more efficiently by V^{2+}. The catalysis by Cr^{2+} includes a term inverse in hydrogen ion concentration, in analogy with the acetato complex.

Accordingly, for the aquation of complexes **3** and **4** we propose a mechanism of stepwise dissociation (eq 7). In this mechanism we indicate fission of the metal to oxygen bond[12] to be rate determining. The substantial effect by carboxylic acids in accelerating aquation of complex **4** is better understood if it is assumed that coordination of these acids affects directly the atoms involved in the bond rupture. It therefore provides additional support for the suggestion that it is the Cr–O rather than the C–O bond that breaks. Our value for the activation energy of the acid-independent path agrees with the literature values for breaking the Cr–O bond.[9c,13] The "one-ended" intermediate is postulated to undergo fast decomposition. The higher rate of decomposition of this intermediate as compared to the remarkably stable Cr^{III}–C bond in Cr-3-PPA can at least partly be attributed to the presence of the second Cr^{III} and the resulting tendency to release the accumulated high positive charge. It should also be recalled that what we actually measure is the overall decrease in the concentration of Cr–C bonds. Any accumulation, therefore, of the "one-ended" binuclear organometallic species should result in a decrease in the measured rate. Yet, Cr-SA and (MA)Cr-SA are much more labile than Cr-3-PPA.



(7)

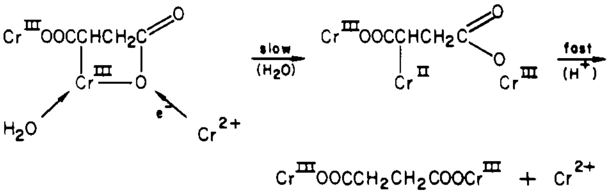
Acid catalysis in the rate-determining step of mechanism 2 probably involves attack of H_3O^+ on the oxygen bound to Cr^{III}.

The differences in rates between complex **3** and complex **4** can simply be attributed to the effect of the coordinated carboxylic acids on the strength of the Cr–O bond. Regarding this effect in general, it is interesting that the rate constants (Table IV) for maleic, fumaric, and acetic acids are nearly the same, whereas the rate constant for succinic acid is almost double; this is perhaps because succinic acid, in contrast to the other acids, can form a new chelate ring. Catalysis by these acids probably involves translabilization and substitution into the labilized site followed by loss of the labilized ligand.[14] It is also interesting that catalysis by carboxylic acids is not affected by hydrogen ion concentration. Hydrogen ion may accelerate the reaction, but the rate-determining step is preceded by the equilibrium of formation of the complex with the additional carboxylic ligand, which involves a term inverse in $[H^+]$. Thus, the two terms cancel out, and the carboxylic acid catalyzed path appears to be independent of hydrogen ion.

It is a well-known fact[9] that the aquation of ordinary Cr^{III} complexes is catalyzed by Cr^{2+} via electron transfer. Yet, among all σ-bonded organochromium complexes known, only **3** and **4** and the acetic acid derivative[8] are reported to exhibit such catalysis. Ordinary Cr^{III} complexes undergo reaction with Cr^{2+} principally through halide, hydroxide, azide, and other bridging ligands. The carboxylic group has also been postulated[9c] to participate in a double bridge with HO^-. The lack of a Cr^{2+}-catalyzed path in the aquation of organochromium complexes could then be attributed to a lack of the appropriate bridging group and the absence of an effective outer-shere path—at least under the conditions in which the studies were made. Such an interpretation, however, does not explain why, for example, $Cr^{III}CH_2COOH$ exhibits such catalysis, whereas $Cr^{III}CH(R)COOH$, where R = $(py)CH_2$, does not.

The driving force for the transfer of the electron is partly provided by the difference in energy between the HOMO of Cr^{2+} and the LUMO of the Cr^{III} complex. With organochromium complexes, *Dq* values are larger and the $e_g{}^*$ LUMO orbitals are in general higher than in ordinary complexes, which makes electron transfer less favorable. This is perhaps one reason that, only with highly electron-withdrawing ligands, which stabilize the LUMO's, reaction of organochromium(III) complexes with Cr^{2+} has been observed.

The inverse acid term in the reaction of Cr^{2+} with Cr^{III}-SA indicates bridging by hydroxide and the acid-independent-term attack on the carboxyl oxygen (eq 8).



(8)

Attack on the carbonyl oxygen is unlikely. Because of chelation this group is remote in respect to the metal ion center, and there is no conjugation for effective intramolecular "conduction". Thus, in mechanism 8 we postulate attack of Cr^{2+} on the oxygen bound to Cr^{III}. Yet, symmetries of donor and acceptor orbitals do not seem to be matching well, and it is very likely that the activated complex is gaining some stabilization by a combination of σ and π overlap, depending critically on the orientation of the attack. In that case Cr^{III}- and Cr^{2+}-centered orbitals overlap directly; in other words, an incipient metal–metal bond is formed. The expansion in Cr-SA of the Cr^{III} orbitals, which is reflected in the smaller Racah parameter[10] is certainly a favorable factor for an effective overlap of that sort. It is also interesting that the electrostatic interaction parameter for Cr-SA is smaller compared to other σ-bonded organochromium complexes, for which spectral data are available.

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The reactions in mechanisms 6–8 were essentially represented as concerted reactions. Preequilibria involving Cr^{2+} or protons are not depicted explicitly. This is of course arbitrary and cannot be justified on kinetic grounds alone. The only excuse we may have for ommitting such preequilibria is that we obtained no evidence for them.

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Registry No. 1, 76156-52-0; 1, intermediate complex, 76136-72-6; 2, 76136-73-7; 3, 76156-53-1; 4, 76136-74-8; maleic acid, 110-16-7; fumaric acid, 110-17-8; succinic acid, 110-15-6; acetic acid, 64-19-7; V^{2+}, 15121-26-3.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 5. Reactions of Diphenylzinc with Lithium Aluminum Hydride in Diethyl Ether and Tetrahydrofuran. Preparation of $PhZn_2H_3$

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The reactions of diphenylzinc with lithium aluminum hydride in diethyl ether and THF have been studied in detail. Although ZnH_2 as an insoluble solid and $LiAlPh_nH_{4-n}$ in solution are formed when the Ph_2Zn:$LiAlH_4$ ratio is 2:1, 3:2, 1:1, and 1:2 in ether, no ZnH_2 is formed when Ph_2Zn is allowed to react with $LiAlH_4$ in THF in ratios varying from 4:1 to 1:2. Instead, $PhZn_2H_3$ is formed which is insoluble in THF. This compound is reported for the first time, and its existence is supported by IR, X-ray powder diffraction, and DTA–TGA studies. When ZnH_2, prepared by the reaction of Ph_2Zn with $LiAlH_4$ in ether, was allowed to react with Ph_2Zn and cyclopentadiene independently in THF, the insoluble products $PhZn_2H_3$ and $CpZn_2H_3$ formed. Reaction of cyclohexanol with ZnH_2 is also discussed.

Introduction

In 1951, Schlesinger and co-workers[1] reported the formation of ZnH_2 in the reaction of $LiAlH_4$ with Me_2Zn in ether solution. Recently, we have reported the formation of triple metal complexes of the types $LiZnMe_2AlH_4$ and $LiZn_2Me_4AlH_4$[2,3] by the reaction of $LiAlH_4$ with Me_2Zn in THF. The reaction of Ph_2Zn with $LiAlH_4$ in THF was considered of interest in order to determine if similar triple metal complexes containing a phenyl group could possibly be prepared or whether this reaction would lead to PhZnH in a manner similar to the reaction of $LiAlH_4$ with Ph_2Mg in THF which produced PhMgH.[4,5] We have prepared a number of RMgH compounds,[4,5] and other workers have prepared several RBeH compounds.[6,8] More recently we reported the first stable organozinc hydride[9] followed by a report of the preparation of RZnH·py complexes.[10] Herein we wish to report the preparation of $PhZn_2H_3$ and the details of the reaction of $LiAlH_4$ and Ph_2Zn in ether and THF.

Experimental Section

Apparatus. Reactions were performed under dry nitrogen at the bench or in a glovebox equipped with a recirculating system using manganese oxide to remove oxygen.[11] Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded on a Varian-A-60. The X-ray powder diffraction pattern data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu $K\alpha$ radiation. "*d*" spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually. DTA–TGA data were obtained under vacuum with the use of a modified Mettler Thermoanalyzer II.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[11] Lithium was determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc in the absence of other metals was determined by EDTA titration. Phenyl groups present in the complexes were determined as benzene by hydrolysis of the samples with water and analyzing the filtrate by GLC using a SE 30 column at 70 °C. Mesitylene was used as the solvent, and hexanol was used as the internal standard.

Materials. Solutions of $LiAlH_4$ (Ventron, Metal Hydrides Division) were prepared in ether and THF in the usual manner. Dimethylzinc was prepared by the procedure of Noller.[12] Methyl iodide was obtained from Fisher Scientific. The iodide was dried over anhydrous $MgSO_4$ and distilled prior to use. The zinc–copper couple was obtained from Alfa Inorganics. The reactions of the zinc–copper couple with methyl iodide were allowed to proceed overnight. Dimethylzinc was distilled from the reaction mixture under nitrogen. Diethyl ether and tetrahydrofuran (Fisher Centrified reagent grade) were distilled under nitrogen over $LiAlH_4$ and $NaAlH_4$, respectively. Diphenylzinc was prepared by the reaction Ph_2Hg with a 100% excess of zinc metal at 130–140 °C.

Lithium tetraphenylaluminate ($LiAlPh_4$) was prepared by the addition of PhLi solution in ether to Ph_3Al in ether with continuous stirring. A viscous insoluble layer separated from the ether and crystallized from solution overnight. The white solid is soluble in THF but insoluble in diethyl ether. Analysis of the white solid gave the following results. Anal. Calcd for $LiAl(C_6H_5)_4$: Li:Al:Ph = 1.0:1.0:4.0. Found: 1.00:1.06:4.10.

X-ray powder diffraction data for $LiAlPh_4$ showed the following lines (Å): 8.5 s, 6.8 w, 6.0 w–m, 5.4 vw, 4.8 vw, 4.4 vs, 4.15 s, 3.8 w, 3.25 m–s, 2.95 m, 2.82 w, 2.76 w, 2.63 w, 2.55 w, 2.43 w, 2.30 vw, 2.25 vs, 2.13 vs, 2.05 vs, 2.00 vw, 1.90 w, 1.78 w, 1.58 w.

Infrared Study of the Reaction of $LiAlH_4$ with Ph_2Zn. (a) In Diethyl Ether. A 100-mL portion of a 0.10 M solution of Ph_2Zn in diethyl

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