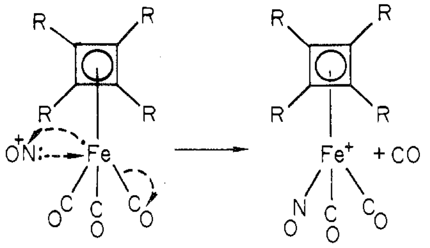
Previously, attempts to prepare cyclobutadienemetal nitrosyl complexes by a direct synthesis from cyclobutadienemetal derivatives and nitric oxide were unsuccessful.[24] Apparently, nitric oxide oxidatively displaces the cyclobutadiene ring from its complexes. These results are not unexpected since even mild oxidizing agents such as $FeCl_3$ and $(NH_4)_2Ce(NO_3)_6$ are known oxidatively to displace the cyclobutadiene ring from a relatively stable complex such as **2**, R = H.[5,20] Therefore, the preparation of cyclobutadienemetal nitrosyls should not be regarded a trivial extension of the related chemistry of cyclopentadienylmetal nitrosyl complexes. The nitrosonium ion, in spite of being a much stronger oxidizing agent than either Fe(III) or Ce(IV), does not oxidatively displace the cyclobutadiene ring under the present conditions. Unlike the reaction between **2**, R = H and Ce(IV) or Fe(III), which is believed to involve a free cyclobutadiene (singlet ground state) intermediate,[9] the reaction of the former with nitrosonium ion could best be explained in terms of a concerted oxidative substitution mechanism (eq 1). Such a process would involve an electronically and coordinatively saturated iron atom and therefore no substantial weakening of the cyclobutadiene–iron bond should occur.



1 **2** (1)

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Registry No. $[C_4H_4Fe(CO)_2NO]^+PF_6^-$, 43175-64-0; $[Me_4C_4Fe(CO)_2NO]^+PF_6^-$, 43218-57-1; $[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$, 43140-26-7; $[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$, 43140-27-8; $[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$, 43140-28-9; $[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$, 43140-29-0; $[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$, 43140-30-3; $[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$, 43140-31-4; $[Ph_4C_4Fe(NO)[(PhO)_3P]_2]^+PF_6^-$, 43140-32-5; $C_4H_4Fe(CO)_3$, 12078-17-0; $Me_4C_4Fe(CO)_3$, 12245-09-9; $Ph_4C_4Fe(CO)_3$, 31811-56-0; $NO^+PF_6^-$, 16921-91-8; Ph_3P, 603-35-0; $(PhO)_3P$, 101-02-0.

(24) A. Efraty, unpublished results.

Contribution from the Department of Chemistry,
Swarthmore College, Swarthmore, Pennsylvania 19081

Ligand Substitution at Five-Coordinate Centers. Reactions of Neutral Iron- and Cobalt-Dithiolene Complexes

D. A. SWEIGART,* D. E. COOPER,[1] and J. M. MILLICAN[1]

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The kinetics of the substitution reactions of the five-coordinate 1,2-dithiolene complexes $M(S_2C_2Ph_2)_2X$ (M = Fe, Co; X = a phosphine or phosphite) are reported. The X group is replaced by other phosphines or phosphites by an associative mechanism with a small dissociative contribution. The iron complexes react up to an order of magnitude faster than the analogous cobalt complexes. Steric effects are important in determining the relative rates of nucleophilic substitution.

Introduction

There has been a vast amount of work on the reactions of four- and six-coordinate transition metal complexes. In general it is found that the substitution reactions of six-coordinate complexes proceed by a predominantly dissociative pathway while four-coordinate planar complexes substitute their ligands *via* an associative mechanism. Except for a few isolated cases it is not known by what mechanism(s) substitutions at five-coordinate centers occur. Whether or not generalized pathways will emerge is unknown.

Until fairly recently five-coordination was only a curiosity and so a knowledge of the reaction mechanisms of these complexes was not, perhaps, necessary. Over the past few years it has become abundantly clear, however, that coordination number 5 is widespread; hundreds of examples are now known. In fact five-coordination can now be considered commonplace. It therefore is time that some detailed knowledge of the mechanisms by which five-coordinate complexes react be made available.

A few kinetic studies of five-coordinate systems have been reported.[2-4] Most of these studies report dissociative-type mechanisms. We recently[3] reported kinetic studies of negatively charged five-coordinate iron- and cobalt-dithiolene systems

$$M(S_2C_2(CN)_2)_2PR_3^- + L \rightleftharpoons M(S_2C_2(CN)_2)_2L^- + PR_3 \qquad (1)$$

The 1,2-ditholene ligand in reaction 1 is maleonitriledithiolate (mnt). The nucleophile, L, in (1) is either unidentate or bidentate. We found that reaction 1 proceeded by both

(1) American Chemical Society–Petroleum Research Fund Scholars, summer 1973.

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dissociative and associative pathways, with the SN2 component predominating.

Herein we report kinetic studies of the substitution reactions of five-coordinate neutral dithiolene complexes according to

$$M(S_2C_2Ph_2)_2X + L \rightarrow M(S_2C_2Ph_2)_2L + X \qquad (2)$$

M is iron or cobalt; L and X are unidentate phosphines or phosphites. We will show that reaction 2 is predominantly associative.

The "unusual" behavior of transition metal–dithiolene complexes is well known. Thus the M in reaction 2 is formally M(IV), but formal oxidation states have little meaning with dithiolene complexes. Their reversible redox chemistry suggests them as models for biological redox catalysts.

It has been reported that a porphyrin or corrin ring around a metal greatly labilizes axial groups. Recent kinetic studies[5] on cobalamin complexes show this system to be astonishingly labile for cobalt(III). The usual model systems—the cobaloximes—do not mimic this "anomalous" behavior. Kinetic studies[6] of chromium(III), iron(III), and cobalt(III) porphyrins also show that axial group substitution occurs very rapidly. The rapidity of substitution reactions at a metal surrounded by a porphyrin or corrin group seems to be connected with π delocalization and a strong in-plane ligand field which is not present in "normal" complexes. Reactions 1 and 2 are very rapid and the dithiolene complexes therefore possess the "anomalous" behavior seen with porphyrins and corrins. This fact gives these studies added significance.

Experimental Section

The dimeric dithiolene precursors, $[M(S_2C_2Ph_2)_2]_2$, were synthesized by literature methods.[7] The five-coordinate triphenylphosphine adduct $Co(S_2C_2Ph_2)_2PPh_3$ was prepared *in situ* in benzene.[8] The iron analog was isolated. *Anal.* Calcd for $C_{46}H_{35}S_4PFe$: C, 68.8; H, 4.39. Found: C, 68.5; H, 4.49. The other phosphine and phosphite adducts were obtained by the addition of a stoichiometric amount of commercially available nucleophile to a solution of the PPh_3 adduct. The resulting spectra agreed with ones reported in the literature.[8]

The kinetics were followed at 25 ± 0.5° on a Durrum stopped-flow apparatus. The solvent was benzene which was fractionally distilled through a 3-ft column and used within a few days. The metal concentration was 10^{-4}–10^{-5} *M* and the nucleophile concentration was kept at least 10 times larger to ensure pseudo-first-order conditions.

A benzene solution of $Fe(S_2C_2Ph_2)_2PPh_3$ was found to be photochemically unstable, but decomposition over the course of several hours did not affect the kinetics. The cobalt analog, which was stored in the dark in benzene solution, decomposed very slowly (several weeks), but again the observed rate data for the substitution reactions were not affected; thus a fresh solution and one 1 week old gave the same k_{obsd} values, although the older solution contained somewhat less substrate.

Results

The principal results are summarized in Table I. Within error all k_{obsd} *vs.* concentration of nucleophile plots were linear. With $P(p\text{-tol})_3$ (tol = tolyl) attacking $Co(S_2C_2Ph_2)_2PPh_3$ the absorbance change observed decreased at low concentrations of nucleophile ($<5 \times 10^{-3}$). This indicates that this reaction did not go to completion in this range of nucleophile concentration and accounts for at least part of the nonzero intercept.

Table I. Rate Data for Five-Coordinate $M(S_2C_2Ph_2)_2PR_3$ Substrates (M = Fe, Co)[a]

Substrate	Nucleophile[b]	$10^3 \times$ range of [nucl],[c] *M*	k_{obsd}, sec^{-1}
$Fe(S_2C_2Ph_2)_2PPh_3$	$P(p\text{-tol})_3$	1.5–18	116[nucl]
$Fe(S_2C_2Ph_2)_2PPh_3$	$P(OBu)_3$	1.0–13	445[nucl]
$Fe(S_2C_2Ph_2)_2PPh_3$	$P(OEt)_3$	1.0–13	472[nucl]
$Fe(S_2C_2Ph_2)_2PPh_3$	PBu_3	0.2–2.6	5.16×10^4[nucl]
$Fe(S_2C_2Ph_2)_2P(OBu)_3$	PBu_3	0.2–2.6	2.30×10^5[nucl]
$Co(S_2C_2Ph_2)_2PPh_3$	$P(p\text{-tol})_3$	5.0–30	0.07 + 11.8[nucl][d]
$Co(S_2C_2Ph_2)_2PPh_3$	$P(OEt)_3$	2.0–12	0.05 + 42.5[nucl]
$Co(S_2C_2Ph_2)_2PPh_3$	$P(OBu)_3$	2.0–13	0.03 + 44.0[nucl]
$Co(S_2C_2Ph_2)_2PPh_3$	PPh_2OMe	2.0–16	678[nucl]
$Co(S_2C_2Ph_2)_2PPh_3$	PBu_3	0.5–5.0	1.01×10^4[nucl]
$Co(S_2C_2Ph_2)_2P(OBu)_3$	PBu_3	0.5–3.0	8.27×10^4[nucl]

[a] Conditions are 25° and benzene solvent. [b] All butyl groups are *n*-Bu; tol = tolyl. [c] [nucl] is concentration of nucleophile. [d] See Discussion.

Nonzero intercepts of approximately 0.05 sec^{-1} were observed for the three slowest reactions in the cobalt series (Figure 1). We estimate the k_{obsd} values to be correct to ±10%. This means that intercepts of ~0.05 sec^{-1} would not have been detected for the other reactions in the cobalt series.

The reactions were also studied with excess leaving group (X) present, because this frequently gives one insight into the mechanism.[3,4] For the iron series excess leaving group had no effect except for the replacement of PPh_3 by $P(p\text{-tol})_3$ in which case the rate increases slightly as PPh_3 is added because the reaction does not go to completion. In the cobalt series the three slowest reactions showed a very slight decrease in rate when [nucleophile] = 2×10^{-3} *M* and [leaving group] = 5×10^{-3} *M*. With $P(OBu)_3$ and $P(OEt)_3$ as the leaving groups the decrease was 15–20% while with $P(p\text{-tol})_3$ it was ~10%. The decrease with $P(p\text{-tol})_3$ was partly balanced by an *increase* in rate because the reaction failed to go to completion. As the nucleophile concentration was increased, excess leaving group had less and less effect. With PBu_3 as the nucleophile there was no change when excess leaving group was added. We could not obtain conclusive results for the PPh_2OCH_3 reaction due to decomposition of the nucleophile. We shall show below that these small effects are probably significant.

Discussion

It is easy to show, as found for the $M[S_2C_2(CN)_2]_2PR_3^-$ series,[3] that a limiting SN1 mechanism is not operating here for reaction 2.

$$M(S_2C_2Ph_2)_2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(S_2C_2Ph_2)_2 + X \qquad (3)$$

$$M(S_2C_2Ph_2)_2 + L \xrightarrow{k_3} M(S_2C_2Ph_2)_2L \qquad (4)$$

Assuming $M(S_2C_2Ph_2)_2$ is in a steady state, this SN1 scheme predicts

$$k_{obsd} = \frac{k_1k_3[L]}{k_2[X] + k_3[L]} \qquad (5)$$

Equation 5 demands $k_{obsd} = k_1$ when excess X has no effect, *i.e.*, when $k_3[L] >> k_2[X]$. Likewise $k_{obsd} \propto 1/[X]$ when the reaction is first order in L. Table I and the comments in the Results show clearly that the data are completely incompatible with an SN1 mechanism. For example, in most cases

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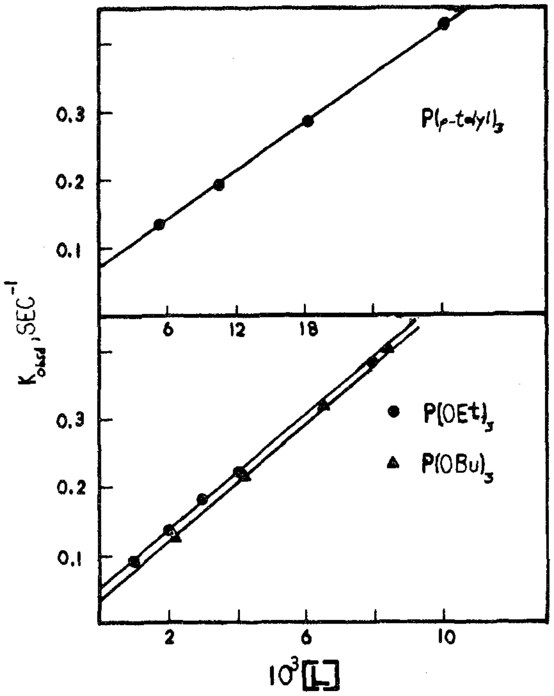

Figure 1. Results for the reaction $Co(S_2C_2Ph_2)_2PPh_3 + L \rightarrow Co(S_2C_2Ph_2)_2L + PPh_3$, where L is a phosphine or phosphite shown in the figure.

excess X had no effect, yet k_{obsd} was first order in L.

The mechanism followed by reaction 2 is probably mainly associative. However, the existence of nonzero intercepts for the cobalt series (Figure 1) suggests that a dissociative pathway does contribute a small amount. The intercepts are sufficiently close to suggest that they are within error identical and probably refer to dissociation of PPh_3. Part of the intercept when P(p-tol)$_3$ is the nucleophile is due to the reverse reaction; *i.e.*, the reaction does not go to completion at the conditions used. For those cobalt reactions for which no intercept is listed in Table I, an intercept of 0.05 sec^{-1} would not have been detected.

Since excess leaving group affects some of the cobalt reactions, competition for an intermediate appears to be occurring. This is why excess leaving group only has an effect at low concentrations of the weaker nucleophiles. These facts also suggest that a dissociative pathway exists. A purely associative mechanism predicts that excess leaving group will have no effect.

The following mechanism is consistant with all our data and is essentially the same as that proposed by us previously[3] for other dithiolene reactions. Let X be the leaving group, L the nucleophile, and omitting all other ligands:

$$\text{M-X} + \text{L} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{X-M-L} \xrightarrow{k_3} \text{M-L} + \text{X}$$

$$\text{M-X} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \text{M} + \text{X}$$

$$\text{M} + \text{L} \xrightarrow{k_6} \text{M-L}$$

This scheme predicts eq 6. The nonzero intercepts observed

$$k_{obsd} = \frac{k_1k_3[\text{L}]}{k_2 + k_3} + \frac{k_4k_6[\text{L}]}{k_5[\text{X}] + k_6[\text{L}]} \tag{6}$$

for some of the cobalt reactions are therefore k_4 and should be independent of nucleophile, as it is within error.

Table II. Relative Rates of Substitution of Iron and Cobalt Substrates

Leaving group	Nucleophile	k_{Fe}/k_{Co}	Leaving group	Nucleophile	k_{Fe}/k_{Co}
P(OBu)$_3$	PBu$_3$	2.8	PPh$_3$	P(OEt)$_3$	11.1
PPh$_3$	PBu$_3$	5.1	PPh$_3$	P(p-tol)$_3$	9.8
PPh$_3$	P(OBu)$_3$	10.1			

The first term in eq 6 is the SN2 pathway and is clearly dominant for the cobalt series. For the iron series, we have no evidence that the second term (SN1) contributes at all. This contrasts somewhat with the $M[S_2C_2(CN)_2]_2PR_3^-$ series where the intercepts were greater for M = Fe.[3]

The relative nucleophilic strengths with PPh_3 as the leaving group are given below.

	PBu$_3$	PPh$_2$OCH$_3$	P(OBu)$_3$	P(OEt)$_3$	P(p-tol)$_3$
M = Fe	445		4.3	4.4	(1)
M = Co	855	57.5	3.7	3.6	(1)

These series simply parallel the adduct stability series.

It is interesting to observe (Table I) that P(OBu)$_3$ is more easily replaced than is PPh$_3$ although the P(OBu)$_3$ adducts are more stable than the PPh$_3$ adducts. Thus the better nucleophile (P(OBu)$_3$) is the better leaving group. Models reveal that there is significant crowding in the six-coordinate intermediate when PPh$_3$ is present. This crowding is much less with P(OBu)$_3$ and we believe this accounts for the reversal in the expected rates for these leaving groups. Similar steric considerations have been noted by Stephenson[9] concerning $Pd(S_2PPh_2)_2PR_3$ complexes.

The observed increase in rate in going from PPh$_3$ replacement to P(OBu)$_3$ replacement when the adduct stabilities are P(OBu)$_3$ > PPh$_3$ is good evidence for a primarily associative mode of activation. A dissociative process would predict PPh$_3$ > P(OBu)$_3$ in rate. An associative mode, on the other hand, nicely explains the observed rate pattern when considering the steric crowding most likely occurring in the transition state with the PPh$_3$ adduct. The fact that the order is seen with both cobalt and iron shows that this is not due to some "anomalous" electronic factor.

Table II contains data on the relative rates of analogous iron and cobalt complexes. The iron complexes are all substantially more reactive. This was also observed with the $M[S_2C_2(CN)_2]_2PR_3^-$ series.[3]

We[4] recently studied reaction 7 in which the replacement

$$\text{Ni}[\text{S}_2\text{P}(\text{OEt})_2]_2\text{PBu}_3 + \text{L-L} \rightarrow \text{Ni}[\text{S}_2\text{P}(\text{OEt})_2]_2(\text{L-L}) + \text{PBu}_3 \tag{7}$$

of PBu$_3$ on a five-coordinate nickel(II) complex was exclusively SN1. Yet the work reported here shows an almost exclusive SN2 mechanism for a reaction that is rather similar to (7). Thus it is not at all clear at this time exactly what controls the reaction mechanisms at five-coordinate centers. We suggested previously[4] that low-spin d^8 systems will always be SN1 because a spin change would be necessary to form the six-coordinate intermediate needed for a SN2 pathway. We expect that most any other five-coordinate system can substitute by both associative and dissociative pathways unless some special steric factor prevails.

Conclusion

The five-coordinate dithiolene complexes $M(S_2C_2Ph_2)_2PR_3$ (M = Fe, Co) substitute the PR$_3$ group by a mechanism that

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(9) T. A. Stephenson and B. D. Faithful, *J. Chem. Soc. A*, 1504 (1970).

is almost exclusively associative. Most previous studies of five-coordinate systems report dissociative mechanisms.

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Registry No. $Fe(S_2C_2Ph_2)_2 \cdot PPh_3$, 14375-89-4; $Fe(S_2C_2Ph_2)_2 \cdot P(OBu)_3$, 51108-62-4; $Co(S_2C_2Ph_2)_2 \cdot PPh_3$, 15636-21-2; $Co(S_2C_2Ph_2)_2P(OBu)_3$, 51154-94-0; P(*p*-tolyl)$_3$, 1038-95-5; $P(OBu)_3$, 102-85-2; $P(OEt)_3$, 122-52-1; PBu_3, 998-40-3; PPh_2OMe, 4020-99-9.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. VII. Acid-Catalyzed Aquation of Carbonato(nitrilotriacetato)cobaltate(III) Ion[1,2]

T. P. DASGUPTA and G. M. HARRIS*

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The aquation of the title compound has been studied over the range $-0.03 < \mathrm{pH} < 4.8$ and $15° < T < 30°$ at $I = 2\,M$ by means of stopped-flow technique. The pseudo-first-order rate constants are directly proportional to $[H^+]$ for $1 < \mathrm{pH} < 2.5$, above which pH the rate tends to independence of acidity. The results have been interpreted in terms of a duality of mechanism involving both water- and acid-catalyzed dechelation which leads to a rate expression $k_{\mathrm{obsd}} = k_0 + k_1[H^+]$. At high acid concentration ($[H^+] > 1.5\,M$) the observed pseudo-first-order rate constant readily attains the limiting condition $k_{\mathrm{obsd}} = k_2$, where k_2 is the decarboxylation rate of the aquobicarbonato ring-opened intermediate species. At 25°, $k_0 = 3.0 \times 10^{-3}\ \mathrm{sec}^{-1}$, $k_1 = 41.9\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_2 = 57.1\ \mathrm{sec}^{-1}$, and the temperature-variation parameters describing these constants are respectively $\Delta H^{\ddagger} = 12.6 \pm 2.7$, 15.8 ± 0.5, and 15.3 ± 1.0 kcal/mol and $\Delta S^{\ddagger} = 28.1 \pm 9.0$, -1.5 ± 1.5, and -0.8 ± 3.2 cal/deg mol. The high reactivity of this anionic carbonato complex relative to the cationic carbonato complexes reported upon earlier is explained in terms of charge and entropy differences.

Introduction

It is now firmly established[3-5] that the cationic carbonatotetramine complexes of cobalt(III) undergo aquation *via* a mechanism consisting of ring opening of the chelated carbonato group catalyzed both by water and by hydronium ion, followed by a rapid decarboxylation of the monodentate intermediate, as shown in the reaction sequence (1)-(5).

$$CoN_4CO_3^+ + H_2O \xrightarrow{k_0} CoN_4(OH)(CO_3H)^+ \tag{1}$$

$$CoN_4CO_3^+ + H_3O^+ \xrightarrow{k_1} CoN_4(OH_2)(CO_3H)^{2+} \tag{2}$$

$$CoN_4(OH_2)(CO_3H)^{2+} + H_2O \overset{K_1}{\rightleftharpoons} CoN_4(OH)(CO_3H)^+ + H_3O^+ \tag{3}$$

$$CoN_4(OH_2)(CO_3H)^{2+} \xrightarrow{k_2} CoN_4(OH_2)(OH)^{2+} + CO_2 \tag{4}$$

$$CoN_4(OH_2)_2{}^{3+} + H_2O \rightleftarrows CoN_4(OH_2)(OH)^{2+} + H_3O^+ \tag{5}$$

The corresponding rate law which describes the variation of the observed pseudo-first-order rate constant with acidity is given by (6). This rate law fits the data well at acidities

$$k_{\mathrm{obsd}} = k_0 + k_1[H^+] \tag{6}$$

above pH 2, where k_2 greatly exceeds $k_1[H^+]$. There is, however, evidence that at high acid concentrations[5] k_{obsd} approaches a limiting value, indicative of the situation in which $k_1[H^+] > k_2$, and $k_{\mathrm{obsd}} \rightarrow k_2 = $ constant. Also, recent photochemical studies[6] further support the proposed appearance of the dechelated aquobicarbonato intermediate, which is the actual species involved in the decarboxylation step (reaction 4). There are, however, no data concerning the decarboxylation of anionic carbonatocobalt(III) complexes with the exception of some as yet unpublished studies of carbonato(ethylenediaminediacetato)cobalt(III) complexes.[7] The role that charge plays in the substitution reactions of amine complexes of cobalt(III) is not easily predictable,[8] but generally the rates observed increase as charge decreases. As is apparent from this work as well as from Garnett's study, the reactivity of anionic carbonatocobalt(III) complexes is considerably greater than that of cationic complexes.

This paper now reports in detail the kinetic investigation of the acid-catalyzed aquation of $Co(NTA)CO_3^{2-}$ (NTA ≡ nitrilotriacetate ion) and offers a possible explanation for the high lability of the complex. Also presented is evidence that at high acid concentration the pseudo-first-order rate constant for the acid hydrolysis of $Co(NTA)CO_3^{2-}$ readily reaches the limiting condition where $k_{\mathrm{obsd}} = k_2$. This enables accurate evaluation of the decarboxylation rate constant k_2 completely independent of the ring-opening rate constant k_1, an aim which we were only partially successful in accomplishing in our earlier studies of cationic carbonatocobalt(III) species.[5]

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