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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 12. Deuterium Solvent Isotope Effect on the Rate of Acid-Catalyzed Decarboxylation of the Carbonatobis(ethylenediamine)cobalt(III) Complex Ion. A Mechanistic Reappraisal

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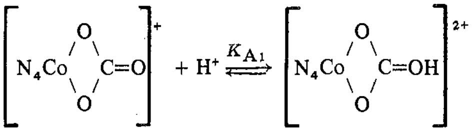
A recent study of the acid-catalyzed decarboxylation of the carbonatotetrakis(pyridine)cobalt(III) complex ion showed there to be rate acceleration in D_2O solvent, consistent with a proton-preequilibration mechanism. This observation directly contradicts the results of a similar study made some years ago of the analogous ion, carbonatobis(ethylenediamine)cobalt(III), for which there appeared to be deceleration in D_2O solvent. A reinvestigation of the latter reaction over a much wider acidity range has now shown the earlier work to be in error. The previously proposed generalized mechanism for aquation of chelated carbonato complex ions of the form $CoN_4CO_3^+$ ($N_4 \equiv$ various tetramine ligand groupings of uni-, bi-, or quadridentate type) has thus been revised to include a proton equilibration step. An unexpected complication arises in the interpretation of the data for the bis(ethylenediamine) complex ion in the acidity range $0.1 < [H^+] < 1.0$. Within these limits, the pseudo-first-order rate constant for carbonato chelate ring opening, which includes a $[H^+]$ term, overtakes and exceeds the true first-order rate constant for CO_2 release. The interesting implications of this unusual first-order successive reaction system are fully explored in the context of the present study.

Introduction

In a preceding paper in this series,[2] it was shown that the acid-catalyzed decarboxylation of the $Co(py)_4CO_3^+$ ion (py $\equiv$ pyridine) was best described by means of a proton preequilibration mechanism. Part of the evidence for this mechanism was the observed acceleration of the reaction in D_2O solvent. This observation contrasts with our earlier finding,[3] where an apparent *deceleration* of the corresponding reaction of the $Co(en)_2CO_3^+$ ion (en $\equiv$ ethylenediamine) in D_2O solvent was taken as evidence for proton transfer in the rate-determining step of the process. Specifically, the question involved is whether the first-order hydrogen ion concentration dependence of the catalyzed process arises from a carbonyl[4] preprotonation step (mechanism A) or a concerted proton-promoted carbonate dechelation (mechanism B) ($N_4 \equiv (py)_4$ or $(en)_2$).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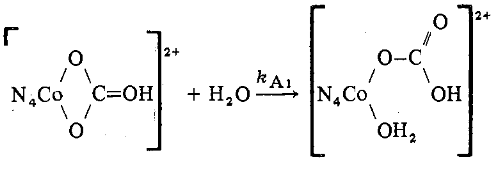
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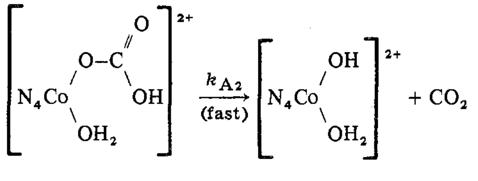
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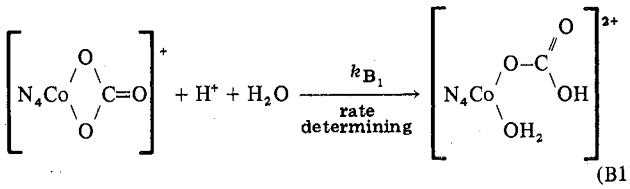
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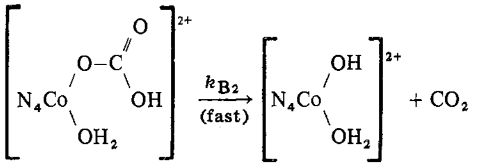
(B2)

Since K_{A1} is expected to be very small,[4] both mechanisms lead to pseudo-first-order observed rate constants at a fixed acidity (provided the final CO_2 release step is fast), viz.

$$k_A = k_{A1}K_{A1}[H^+] \tag{1}$$

$$k_B = k_{B1}[H^+] \tag{2}$$

However, the D_2O solvent isotope effects should be completely different for such mechanisms,[5] with acceleration in heavy water according to A and deceleration according to B. There seems to be no strong reason why the two types of complex should differ so widely in their mechanisms of acid-catalyzed decarboxylation, though there are large differences in their rates. We have therefore repeated the study of the kinetics of $Co(en)_2CO_3^+$ aquation in acidified heavy water and have indeed shown that our earlier data for this system[3] are in error and that mechanism A is to be preferred. In our new study, it has been possible to examine the kinetics of the reaction to much higher acid concentrations than previously since we now

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have stopped-flow techniques available. These high acid data have provided an interesting corollary to the study in that the relative magnitudes of the first-order rate constants $k_1K_1[H^+]$ and k_2 (we will drop the added "A" designation for these constants in the remainder of this paper) for the $(en)_2$ complex undergoes reversal within the acidity range $0.1 < [H^+] < 1.0$ M. This introduces an unusual problem in the interpretation of consecutive first-order kinetics data which has been dealt with both in general terms and as specifically applied to the present experimental data.

Experimental Section

Carbonatobis(ethylenediamine)cobalt(III) chloride was prepared and purified according to established procedures.[6] Anal. Calcd for $[Co(en)_2CO_3]Cl$: C, 21.87; H, 5.87; N, 20.40. Found:[7] C, 21.81; H, 5.86; N, 20.30. The visible absorption spectrum (λ_{max} (ϵ) 511 (133), 359 (122); λ_{min} (ϵ) 426 (16), 321 (40)) is in good agreement with that reported.[6]

Carbonatobis(bipyridyl)cobalt(III) chloride trihydrate was prepared by adding bipyridine in a 2:1 molar ratio to a solution of $K_3Co(CO_3)_3$ obtained by the method of Mori et al.[8] On standing overnight orange crystals of $[Co(bpy)_2CO_3]Cl{\cdot}3H_2O$ settled out and were purified by recrystallization from water. The purity of the preparation was established by the almost exact identity of its spectrum with that previously published[9] for this compound.

Carbonatopentaamminecobalt(III) nitrate monohydrate was prepared according to the established method[10a] and its purity confirmed by spectral comparison with a known sample[10b] of $[Co(NH_3)_5CO_3]NO_3{\cdot}H_2O$.

McIlvaine buffers at unit ionic strength (NaCl) were used to ensure constant hydrogen ion concentration in the $2 < pH < 5$ region. At lower pH's, the acidity was established by additions of known amounts of $HClO_4$. All pH measurements were made by means of a Fisher Accumet Model 420 device with a standard Fisher combination electrode. Calibration was achieved by use of commerical buffers in the $2 < pH < 5$ range and at higher acidities by using solutions of known molar concentrations of $HClO_4$ in 1.0 M ionic strength medium (NaCl).

Rate measurements at the lower acidities (slower reactions) were made with a Cary Model 118C spectrophotometer by following the change in the absorbance maxima at 512 or 360 nm. Complete spectral scans during reaction were possible for $3 < pH < 4$ and showed two sharply fixed isosbestic points, and in these runs, the rate data derived from the spectral changes at either absorbance maximum were in very close agreement. Beyond pH 4, the isosbestic points drifted, indicative of a more complicated reaction pathway, so rate data were not recorded in this region. At higher acidities (faster rates), the aquation rate was determined by means of an automated Durrum Model 110 stopped-flow assembly as previously described.[11] Pseudo-first-order rate constants were derived in the conventional manner from semilogarithmic plots of $(A_t - A_\infty)$ vs. time, and these were reasonably linear over at least 3 half-times.[12] The complex concentration was typically $\sim 2.0 \times 10^{-3}$ M, but some runs were made at concentrations varied between 0.5×10^{-3} and 4.0×10^{-3} M with no effect on the derived rate constants, other conditions being unchanged.

The heavy water experiments were carried out in the manner just described, except that 99.7% D_2O was used as solvent. For all but the most acidic solutions the quantity of light water introduced by addition of reagents was less than 1%, mostly from the $HClO_4$ addition. In 1.0 M acid, the light water contamination is estimated to be not more than 3% by weight. Acidity measurements in the D_2O systems were made by means of the pH meter already mentioned, making the recommended addition of 0.41 pH units to correct the electrode readings in heavy water.[13] The electrode was immersed in H_2O between measurements but was rinsed several times with D_2O before a pD determination was made.

Results and Discussion

Table I. Deuterium Solvent Isotope Effect on the Decarboxylation of $Co(en)_2CO_3^+$ Ion in Aqueous Acidic Solution[e]

A. Low-acid runs[a]			B. High-acid runs[b]		
[Acid], 10^3M	10^3k^H, s^{-1}	10^3k^D, s^{-1}	[Acid], M	k^H, s^{-1}	k^D, s^{-1}
50.0	40	92	(2.50)	(0.42)[c]	(0.44)[c,d]
10.0	7.8	20	1.00	0.37	0.53
6.2	4.9		0.60	0.33	
2.9		7.6	0.50	0.31	0.49
2.6		7.3	0.40	0.27	0.45
2.0		4.6	0.40	0.26[a]	
1.7	1.64		0.30	0.23	0.40
0.86	0.81		0.20	0.16	0.32
0.66		1.39	0.10	0.088	0.19
0.30		0.91	0.10	0.083[a]	0.16[a]
0.21	0.25		0.05	0.046	0.10
0.091	0.20				
0.063		0.24			

[a] Runs made by Cary 118C technique. [b] Runs made by Durrum 110 technique. [c] Runs at $I = 2.5$ M (excluded from calculations). [d] D_2O content ~85%. [e] Temperature = 25 °C; $I = 1.0$ M ($NaCl + HClO_4$).

The values obtained for the observed rate constants, k, of decarboxylation of $Co(en)_2CO_3^+$ ion are collected in Table I. Those determined by means of the Cary 118C procedure are the average of two or more runs at a given acidity and agree within the limits of about ±5%. The Durrum 110 determinations are the average of four or more separate runs and have error limits of about ±2%. Plots of the "low acidity" ($[H^+]$ or $[D^+] \leq 0.05$ M) observed rate constants k^H (or k^D) vs. $[H^+]$ (or $[D^+]$) yield good straight lines. The rate constants for the uncatalyzed and acid-catalyzed reactions as determined from the least-squares intercepts and slopes of these plots are $10^4k_u^H = 1 \pm 1\ s^{-1}$, $k_c^H = 0.79 \pm 0.01\ M^{-1}\ s^{-1}$, $10^4k_u^D = 12 \pm 4\ s^{-1}$, and $k_c^D = 1.83 \pm 0.02\ M^{-1}\ s^{-1}$. The k_u values are seen to be subject to such large errors as to be essentially meaningless, but the acid-catalyzed constants k_c^H and k_c^D are quite precise and indicate a k_c^H/k_c^D ratio of 0.43 over the experimental acidity range. This value is consistent only with a proton preequilibration mechanism such as A above and is of the order of magnitude to be expected for acid-catalyzed hydrolysis of a carboxylic species.[5] The ratio k_1^H/k_1^D refers to the rate-determining ring-opening of chelated carbonato species in light and heavy water, respectively. Since this may be assumed to involve mainly Co–O bond fission in the rate-determining step,[14] the reaction rates k_1^H and k_1^D should differ but little. One can thus ascribe most of the observed isotope effect to the ratio K_1^H/K_1^D, for which a value of ~ 0.4 is quite reasonable.[5]

Referring to our previous study, it is seen that we are quite consistent with respect to the $[H^+]$ data in this same acidity range, our previous values[3] for the two rate constants being $10^4k_u^H = 1.2 \pm 0.2\ s^{-1}$ and $k_c^H = 0.6 \pm 0.05\ M^{-1}\ s^{-1}$. However, our previous solvent isotope effect data (ref 3a, Table III) suggest a k_c^H/k_c^D ratio of between 2 and 3, a complete reversal of our new observation. We have reexamined as much of our raw data for the earlier work[3] as could be located but cannot find the source of the discrepancy. A plausible surmise is that we applied the pH to pD correction by *subtracting* 0.41 units from the electrode readings made in D_2O rather than *adding*. This would render the recorded $[D^+]$ values about 6.6 times ($10^{0.82}$) larger than they should have been, so that the observed acid-catalyzed rate constants in D_2O would appear to be 1/6.6 as great as they really were. Thus, the k_c^H/k_c^D ratio in the earlier study should have been reported at approximately 2.5/6.6 = 0.38, in reasonable agreement with our new finding.

Turning now to the "high acid" runs, it is clear that plots of k vs. [acid] are no longer linear (see Figure 1). This kind of kinetics in an acid-catalyzed reaction can be explained by means of mechanism A above whenever K_1 is *not* negligible, since then $k = k_1K_1[H^+]/(1 + K_1[H^+])$, and with saturation preprotonation, k maximizes at the value of k_1. However, this explanation is untenable here, since the values of K_1^H and K_1^D required to fit the present data are of the order of magnitude of unity, much larger than is reasonable for these systems.[4,16]

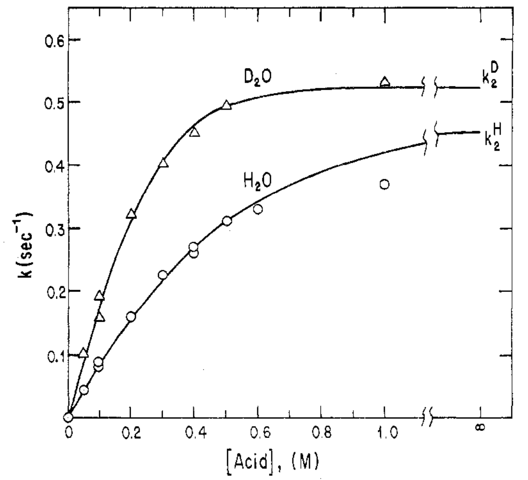

Figure 1. Experimental pseudo-first-order rate constants for the acid-catayzed decarboxylation of $Co(en)_2CO_3^+$ ion: ○, in H_2O solvent; △, in D_2O solvent. Curves were calculated by procedure described in text and illustrated in Figure 2.

Furthermore, at these higher acidities, the ring-opening rate constant $k_1K_1[H^+]$ overtakes and may even exceed the value of the decarboxylation rate constant k_2, since the latter is known[17] to be of the order of magnitude of 1 s^{-1}.

Accepting the above reasoning, we have interpreted the "high acid" rate data in the following manner. Reactions A2 and A3 become a pseudo-first-order unidirectional successive reaction system of the type

$$X \xrightarrow{k'} Y \xrightarrow{k''} Z$$

governed by the rate constants $k' = k_1K_1[H^+]$ and $k'' = k_2$. Since our rate data were all made by means of absorbance change measurements, the rate law is of the form[18a]

$$D_t - D_\infty = a' \exp(-k't) + a'' \exp(-k''t)$$

where a' and a'' are known functions[18b] of the initial concentration of reactant X, the molar absorbances ϵ_x, ϵ_y, and ϵ_z, and the two rate constants. As shown in the Appendix, if one knows the values of ϵ_x, ϵ_y, and ϵ_z and one of the two rate constants, one can evaluate a "best fit" value for the second rate constant from the observed $(D_\infty - D_t)$ data. In the present case, at 512 nm the molar absorbances are[19] ϵ_x = 131 M^{-1} cm^{-1}, ϵ_y = 112 M^{-1} cm^{-1}, and ϵ_z = 70 M^{-1} cm^{-1}. Also $k_c = k_1K_1$, which is known from the "low aciditiy" experiments (where k_2 is relatively very rapid). The figures resulting from this analysis are k_2^H = 0.45 s^{-1} and k_2^D = 0.52 s^{-1}. The values of k at the various "high acidities" can now be calculated (see Appendix) and are displayed as the solid curves of Figure 1. The experimental fit satisfactorily supports the analysis, and shows the decarboxylation rate to be ~0.5 s^{-1} for either the H_2O or D_2O systems, in reasonable agreement with the earlier rough estimates.[17] That there should be little or no solvent isotope effect in this type of reaction is not unexpected. The constant k_2 refers only to CO_2 elimination (reaction A3), where deuteration of the reactant aquobicarbonato species can have only a small isotope effect, since O–C bond fission is probably the dominant transition-state process. To provide a further test of this concept, we measured the rate constant of decarboxylation of the monodentate carbonato complex ion, $Co(NH_3)_5CO_3^+$, by stopped-flow technique at 25 °C in 1 M acid, at which acidity k_{obsd} is equivalent to k_2 of this discussion.[10b] The values obtained were 1.10 s^{-1} in H_2O and 1.06 s^{-1} in D_2O (average of six determinations), showing that the k_2^H/k_2^D ratio is essentially unity for this reactant.[20]

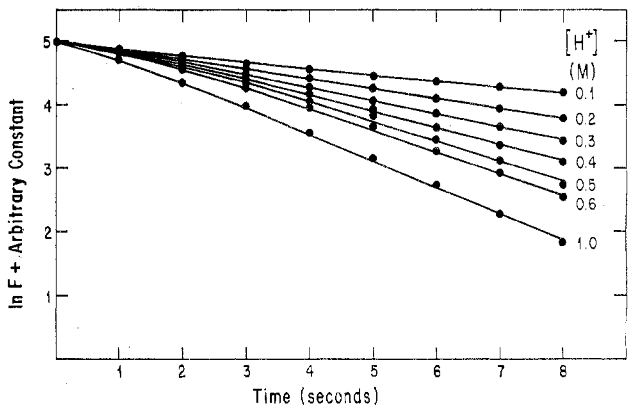

Figure 2. Procedure for evaluating rate constants at high-acid concentration in H_2O solvent.

As an additional experimental confirmation of our solvent isotope effect results for $CoN_4CO_3^+$ complex ions, we carried out a limited study of the species $Co(bpy)_2CO_3^+$. The aquation rate of this ion is known to be extremely slow,[9] though not quite so slow as the rate[2] for $Co(py)_4CO_3^+$. The experimental data at various temperatures in 1 M $HClO_4$ were as follows (I = 1.0 M):

	20 °C	30 °C	40 °C
$10^4k_c^H$ (s^{-1})	1.31	4.65	17.7 (9.1)[a]
$10^4k_c^D$ (s^{-1})	3.97	10.2	45.6
k_c^H/k_c^D	0.33	0.46	0.39

[a] Extrapolated from the data Francis and Jordan[9] obtained at various acidities between 52 and 69 °C (I = 1.0 M (NaCl)).

While there is considerable variability in the k_c^H/k_c^D ratio, its average value of 0.39 is in good agreement with the data for $Co(en)_2CO_3^+$ (k_c^H/k_c^D = 0.43, as discussed above), though somewhat at variance with the 0.55 value for $Co(py)_4CO_3^+$. However, the latter had of necessity to be derived[2] from experiments performed in 5.0 M $HClO_4$ in the temperature range 40–60 °C, so a somewhat modified isotope effect is probably to be expected.

To sum up, we now conclude that the overall rate constant for acid-catalyzed dechelation of bidentate carbonato complex ions is the product of a very small preprotonation equilibrium constant (K_1) and a ring-opening rate constant (k_1). In all of our papers concerning this type of reaction[21] prior to ref 2, the assumption has been made that direct proton transfer occurs in the rate-determining step (mechanism B above), an assumption now shown to be erroneous since it was based on the incorrect solvent isotope data already discussed. However, the published figures previously assigned to k_1 may now be correctly assigned to the product k_1K_1, with the proviso that the corresponding activation parameters $\Delta H^\ddagger_1$ and $\Delta S^\ddagger_1$ include a contribution (probably small) from the ΔH_1 and ΔS_1 corresponding to K_1. The wide variation in k_c (about 7 orders of magnitude between $Co(py)_4CO_3^+$ and α-$CO(EDDA)CO_3^+$, for example[23]) has been ascribed to differences in the strength of the Co–O bond resulting from differences in the electron-donating capabilities of the nonreacting ligands,[9,24] as well as to possible steric and solvation factors.[23] However, since $k_c = k_1K_1$, an alternative possibility exists by means of which the large variation is explainable. This is to assume that k_1 (the ring-opening rate constant) is essentially constant throughout the series but that K_1 varies widely as the basicity of the carbonyl group varies. In a sense, this is but another way of correlating the decarboxylation rate with the electron-donating capabilities of the nonreacting ligands,[25] since the more negative the carbonato ligand becomes, the greater will be K_1. This assumption requires that K_1 vary by up to 7 orders of magnitude, a very unlikely possibility for protonation of the carbonyl grouping,[4] which is rather remote from the metal ion center. It therefore seems more likely that, though K_1 may provide some of the variability in k_c, most of

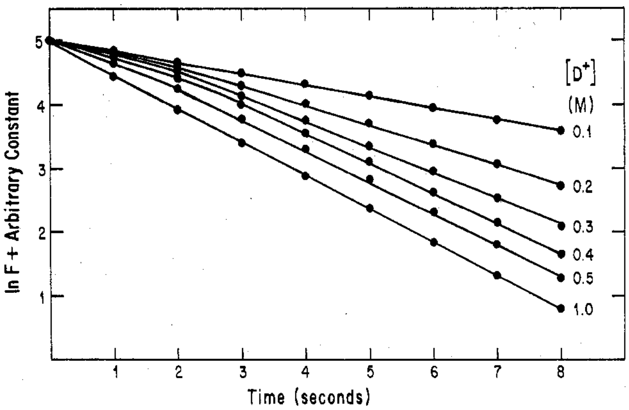

Figure 3. Same as Figure 2 but in D_2O solvent.

it must result from variations in k_1, identified as the Co–O bond-fission step of reaction A2,[14] and in keeping with the proposal discussed above[9] concerning the electronic effects of the nonparticipating ligands.

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Appendix

Consider a first-order reaction system

$$X \xrightarrow{k'} Y \xrightarrow{k''} Z$$

the progress of which is followed by the change in the absorbance function $(D_t - D_\infty)$ with time. It is readily shown[18] that

$$(D_t - D_\infty) = a'e^{-k't} + a''e^{-k''t} \tag{I}$$

where

$$a' = [X]_0 \left\{ \frac{k'(\epsilon_x - \epsilon_y) - k''(\epsilon_x - \epsilon_z)}{k' - k''} \right\} \tag{II}$$

and

$$a'' = [X]_0 \left\{ \frac{k'(\epsilon_y - \epsilon_z)}{k' - k''} \right\} \tag{III}$$

In these, $[X]_0$ is the initial concentration of reactant X and ϵ_x, ϵ_y, and ϵ_z are the molar absorptivities of the three successive species. Given ϵ values of 131, 112, and 70, respectively,[19] one can define a function F such that

$$F = (D_t - D_\infty) \left\{ \frac{k' - k''}{[X]_0} \right\} = (19k' - 61k'')e^{-k't} + 42k'e^{-k''t} \tag{IV}$$

It turns out that for F to be a positive function $k' = k_1K_1[H^+]$ and $k'' = k_2$ when $(19k' - 61k'') > 42k'$, while $k' = k_2$ and $k'' = k_1K_1[H^+]$ when $42k' > (19k' - 61k'')$.

It is noted that at any instant, the apparent observed rate constant k is given by $-d \ln F/dt$, but this value is not necessarily constant over a period of time. However, in our stopped-flow experiments, the plots of $\ln (D_t - D_\infty)$ appeared to be linear (except for the initial 1 s eliminated by the electronic delay procedure), in spite of the biphasic nature of eq IV. On substituting the known k_1K_1 values in eq IV and utilizing estimates of k_2 obtained from the limiting values of k at high acidity (approximately 0.5 s^{-1}–see Figure 1), curves may be plotted as illustrated in Figures 2 and 3 for various experimental $[H^+]$ and $[D^+]$ values. Such $\ln F$ vs. t curves are almost exactly linear for $t > 1$ s, in spite of the form of eq IV. The least-squares slopes of these long linear portions yield the apparent observed rate constants, k. By selecting "best fit" values of k_2 of 0.45 s^{-1} in H_2O and 0.52 s^{-1} in D_2O, it is possible to obtain calculated values of k which, with one exception in the H_2O system, closely duplicate the experimental data, as shown by the solid curves of Figure 1.

Registry No. $Co(en)_2CO_3^+$, 17835-73-3; $Co(bpy)_2CO_3^+$, 35594-87-7; $Co(NH_3)_5CO_3^+$, 15844-68-5.

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(15) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **91**, 3207 (1969).
(16) It should further be noted that in our study[15] of the aquation of the complex ion $Co(NH_3)_4CO_3^+$ the very low basicity of this species was qualitatively evident from experiments in which the pH was monitored as an indication of the reaction rate.
(17) Rough estimates of the value of k_2 at 25 °C are available for the related $Co(tren)CO_3^+$ ion (T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **93**, 91 (1971); $k_2 \sim 1$ s^{-1}; tren ≡ β,β',β''-triaminotriethylamine) and for the $Co(en)_2CO_3^+$ ion itself (V. W. Cope, S. Chen, and M. Z. Hoffman, *ibid.*, **95**, 3116 (1973); $k_2 \sim 0.9$ s^{-1}), both under somewhat lower ionic strength conditions than in the present work.
(18) R. G. Wilkins, "The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974: (a) p 22, (b) p 23.
(19) Careful determinations of the ϵ values at 512 nm, the monitoring wavelength for the stopped-flow runs, were made of the significant complexes by Mr. W. K. Wan of our laboratory. The ϵ_x (for $Co(en)_2CO_3^+$) value was obtained from a purified stock sample of this complex and ϵ_z (for *cis*-$Co(en)_2(H_2O)_2^{3+}$) from another sample of $Co(en)_2CO_3^+$ immediately after acidification and evolution of the CO_2. The complex *cis*-$Co(en)_2(OH)CO_3$ was prepared by partial base hydrolysis of a third sample of $Co(en)_2CO_3^+$ and ion-exchange purification of the hydroxycarbonato product (W. K. Wan and G. M. Harris, to be submitted for publication). While the value of ϵ_y should refer to *cis*-$Co(en)_2(OH_2)CO_3H^{2+}$, the instability of the latter necessitates the use of the figure we obtain for the hydroxocarbonato product. Some error is introduced by this assumption, but trial computations show that considerable variation of the value of ϵ_y has little effect on the calculated magnitude of k_2.
(20) A recent study confirms our finding that the k_2^H/k_2^D ratio is close to unity (Y. Pocker and D. W. Bjorkquist, *J. Am. Chem. Soc.*, **99**, 6537 (1977)).
(21) (a) See T. P. Dasgupta, *Inorg. Chim. Acta*, **20**, 33 (1976), Table II, for a complete listing of tetramine complexes. (b) Acid-catalyzed decarboxylation rate data for the anionic complexes $Co(NTA)CO_3^{2-}$ (NTA ≡ nitrilotriacetic acid) and the two geometrical isomers of Co-

$(EDDA)CO_3^-$ (EDDA ≡ ethylenediaminediacetic acid) are also available.[22,23]

(22) T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **13**, 1275 (1974).

(23) R. van Eldik, T. P. Dasgupta, and G. M. Harris, *Inorg. Chem.*, **14**, 2573 (1975)).

(24) A rough correlation is possible in terms of either the average p*K* of the amine ligand(s) or the p*K* of the product diaquo complex obtained by decarboxylation.[9]

(25) This possibility was suggested tentatively but not supported experimentally in the study by Francis and Jordan.[9]

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Complexes of the Platinum Metals. 14.[1] Nitrato Derivatives of Ruthenium, Osmium, Rhodium, and Iridium

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Nitrato complexes of the platinum group metals have been prepared by treating selected hydridic or zero oxidation state precursors with nitric acid, neat or in organic media. Products obtained in this manner include $[M(NO_3)_2(CO)(PPh_3)_2]$, $[M(NO_3)_2(CO)_2(PPh_3)_2]$ (M = Ru or Os), $[M'(NO_3)_3(PPh_3)_2]$, and $[M'(NO_3)_2(NO)(PPh_3)_2]$ (M′ = Rh or Ir). The species $[M(NO_3)_2(CO)(PPh_3)_2]$ undergo carbonylation to yield the dicarbonyls $[M(NO_3)_2(CO)_2(PPh_3)_2]$ and alcoholysis followed by β-elimination to form the hydrides $[MH(NO_3)(CO)(PPh_3)_2]$. The latter products are readily carbonylated to afford the species $[MH(NO_3)(CO)_2(PPh_3)_2]$. The new complexes have been characterized and their stereochemistry has been assigned by reference to spectroscopic data. The complex "$Rh(NO_3)(NO)_2(OPPh_3)_2$" has been reformulated as $[Rh(NO_3)_2(NO)(PPh_3)_2]$. However, one product obtained on treating $[RuH_2(CO)(PPh_3)_3]$ with nitric acid has been tentatively identified as a triphenylphosphine oxide derivative $[Ru(NO_3)_3(NO)(OPPh_3)(PPh_3)]$. The ability of $[Ru(NO_3)_2(CO)(PPh_3)_2]$ to catalyze the dehydrogenation of primary and secondary alcohols is noted.

Introduction

Oxygen donor ligands, with the notable exception of β-diketonate[2] and carboxylate[3] anions, do not feature extensively in the low oxidation state chemistry of the platinum metals and rarely cohabit with ligands of strong π-acceptor character within the same coordination sphere.[4] Nitrate ligands in particular are generally associated with high oxidation state systems involving aqueous or liquid nitrogen oxide solutions and are rarely encountered in low oxidation state complexes containing phosphines, carbon monoxide, or related π-acceptor ligands.[5]

The nitrate anion shows particularly weak Lewis base properties; it is a poor σ donor and has little if any π-acceptor capacity. In addition the high polarity of $M-ONO_2$ bonds, caused by the strong inductive effect of the nitrate anion, facilitates nucleophilic attack on nitrato complexes. For these reasons the nitrate anion is widely regarded as a highly labile ligand of relatively poor coordinating power, particularly toward platinum group metals.[5,6]

However, a few stable complexes of the platinum group metals containing nitrate anions and strong π-acceptor ligands within the same coordination sphere have been reported. Methods of synthesis employed include metathesis using silver nitrate, addition of nitrogen oxides to dioxygen complexes, oxidation of bound nitrosyl or nitrito ligands, and the treatment of hydridic or low oxidation state complexes with nitric acid.[6] The last-mentioned process has been employed in the present work to synthesize a range of new nitrato complexes containing triphenylphosphine ligands.[7]

Our interest in nitrato complexes arises from our earlier work on the closely related perfluorocarboxylato derivatives[8] and reflects the importance of labile oxygen donor ligands in the chemistry of homogeneous platinum metal catalysts.

Experimental Section

Platinum metal salts were supplied by Johnson Matthey Ltd. and were converted into triphenylphosphine complexes by standard literature procedures.[9] Unless otherwise indicated reactions were performed under nitrogen and products were worked up in air. Yields are based on platinum metal content. Analytical results, obtained by the microanalytical laboratory, University College London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared and NMR data, collected using a Perkin-Elmer 457 grating spectrophotometer and a Bruker HFX90 NMR spectrometer, respectively, are recorded in Table II. Mass spectra were obtained using an AEI MS30 mass spectrometer. *Hazard warning*! Ethanol is liable to violent oxidation by concentrated nitric acid; it is therefore important to note that in the present work only dilute (≤6 M) nitric acid was employed in ethanolic media.

Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II). Method a. Finely powdered carbonyldihydridotris(triphenylphosphine)ruthenium (0.5 g) was added, portionwise, to vigorously stirred 16 M nitric acid (40 mL) at 273 K and the mixture allowed to stand for 5 min. The resultant yellow viscous oil was separated by decantation, washed successively with water and cold methanol, and then crystallized from dichloromethane–methanol. The required product was filtered off, washed successively with methanol and petroleum ether, and then dried in vacuo as yellow crystals (0.23 g, 54%).

Method b. A suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.40 g) in 3 M nitric acid (15 mL) was boiled under reflux for 1 h. The resulting yellow suspension was filtered off and recrystallized from dichloromethane–methanol and then was washed successively with methanol and petroleum ether and dried in vacuo to yield yellow crystals (0.19 g, 56%).

Similarly prepared by method a from carbonyldihydridotris(triphenylphosphine)osmium was **carbonylbis(nitrato)bis(triphenylphosphine)osmium(II)** as yellow crystals (59%).

Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II). A suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.20 g) in 1-propanol (15 mL) and triethylamine (0.5 mL) was boiled under reflux for 15 min. After the mixture was cooled, the precipitated product was filtered off, washed with ethanol and petroleum ether, and then dried in vacuo as white crystals (0.18 g, 98%).

Similarly prepared from carbonylbis(nitrato)bis(triphenylphosphine)osmium was **carbonylhydridonitratobis(triphenylphosphine)osmium(II)** as white crystals (98%).

Similarly prepared from carbonylbis(nitrato)bis(triphenylphosphine)ruthenium in deuteriomethanol with a reaction time of 1.5 h was **carbonyldeuteridonitratobis(triphenylphosphine)ruthenium(II)** (70%).

Dicarbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II). Method a. A suspension of tricarbonylbis(triphenylphosphine)ruthenium (0.50 g) in 6 M nitric acid (15 mL) and ethanol (15 mL) was boiled under reflux for 15 min. The precipitated product was

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