acids (in comparison with those derived from the 2- and 3-systems) also stabilize radical-ions which intervene in reduction of the respective $(NH_3)_5Co(III)$ complexes.[27]

Stabilization of a radical-ion intermediate, facilitating electron transfer by adjacent attack, comes to light here, largely because other effects which have been invoked to account for acceleration of electron-transfer reactions in carboxylatocobalt(III) complexes (i.e., remote attack, chelation, and increased negative charge on the bridging group) are ruled out in the reduction of the methylated and protonated 4-pyridine-carboxylato complexes.

The lesson to be learned is that specific rate of reduction is a reliable guide neither to the site of attack nor the direction of electron flow. In particular, the "fast" reduction of such complexes as the o-benzoyl-benzoato (Table III) and the pyruvato[16] derivatives could conceivably be rationalized by considering stabilization of a radical-ion intermediate in attack on the carboxylato group (e.g., XIII), rather than by assuming transient chelation and electron transfer through the carbonyl group. However, the difficulty

(27) N-Ethyl-4-carbethoxypyridinyl, a stable free radical closely related to our N-substituted 4-carboxypyridine complexes, has been isolated recently (E. M. Kosower and E. J. Poziomek, J. Am. Chem. Soc., 85, 2035 (1963)).

XIII
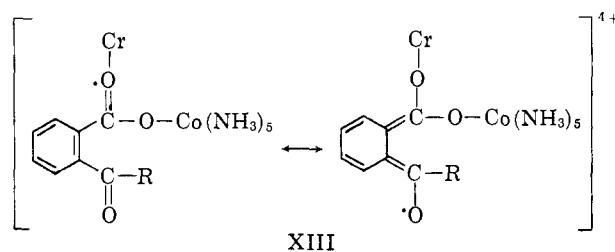
in reducing the carbonylbenzoato acids in our series, in contrast to the ease in reducing many of the pyridine-carboxylic acids, leads us to favor the radical-ion intermediate in rapid reductions of pyridinecarboxylato complexes but not in reductions of the carbonyl complexes. With the carbonyl complexes, a low-lying vacant orbital, while not low enough to accept an electron from Cr^{2+}, may nevertheless be involved in the resonance transfer of an electron from the reducing agent to the Co(III) center.

Tracer Experiments on Alkaline Hydrolysis of Some Oxalate Ammonia Cobalt(III) Complexes

BY CARLOS ANDRADE AND HENRY TAUBE

When $Co(NH_3)_5C_2O_4^+$ releases $C_2O_4^{2-}$ in alkaline solution at 25°, C–O bond breaking takes place in <1% of the hydrolytic events, but some solvent oxygen is incorporated into the $C_2O_4^{2-}$ by exchange. At 100°. the total incorporation of solvent oxygen is greatly decreased and the $C_2O_4^{2-}$ formed has very nearly the isotopic composition of the original oxalate. When $Co(en)_2C_2O_4^+$ hydrolyzes, one C–O bond is broken for the release of each oxalate, and extensive oxygen exchange accompanies the hydrolytic reaction. The observations made with $Co(en)_2C_2O_4^+$ are interpreted on the basis that the first act of the hydrolysis, leading to opening of the chelate, takes place by C–O scission and the second by Co–O scission.

In the course of work we are doing on oxygen exchange between oxalatoamminecobalt(III) complexes and solvent in acid solution, we found it interesting—and necessary—to do oxygen tracer experiments on the hydrolysis of these complex ions. These tracer studies are concerned with issues somewhat different from those of the exchange experiments; for this reason as well as the additional one that some of the effects are quite striking, the results of the tracer experiments appear to merit separate publication. Our results would appear to have a bearing on studies which have been done on the reactions of carboxylate chelate complexes in alkaline solution.[1] They are also of interest in comparison with results which we have obtained for the methyl esters of oxalic acid and which will be described in a forthcoming publication.

Experimental

Preparation of Complex Salts.—$[Co(NH_3)_5C_2O_4H](ClO_4)_2$ was prepared[2] by the reaction of $[Co(NH_3)_5OH_2](ClO_4)_3$ with $H_2C_2O_4$

in water. Analysis showed 20.20% oxalate (calcd., 20.37%) and 46.17% ClO_4^- (calcd., 46.04%). $[Co(en)_2C_2O_4]ClO_4$ (not necessarily anhydrous) was prepared from the chloride[3] by double decomposition. The perchlorate salt was not analyzed, but a report of analysis of $[Co(en)_2C_2O_4]Cl \cdot 3H_2O$ showed 16.48% Co (calcd., 16.52%).).

Procedure.—For all experiments, salts of normal isotopic composition were used, added to aqueous alkaline solutions enriched in O^{18}. With the oxalato complexes as reactants, reaction is so slow that the product complex undergoes serious deterioration (as in the case of the pentaammine complex), or it undergoes exchange (as in the case of the bisethylenediamine complex) during the course of the reaction, and isotopic analysis of only the product oxalate is feasible. The solutions after the reaction were filtered to remove solid material, then acidified to a faint acid reaction, and a solution of $AgNO_3$ was added to precipitate $Ag_2C_2O_4$. The $Ag_2C_2O_4$ was collected by filtration, washed with water of normal isotopic composition and then with CH_3OH, and dried at 40° for 12 hr. and then in a vacuum desiccator for 12 hr. The CO_2 released by heating the solid to complete decomposition was collected and analyzed by mass spectrometer (Atlas Model M86). The isotopic composition of the solvent was determined by the Anbar–Guttmann[4] method.

(1) D. H. Busch, D. W. Cooke, K. Swaminathan, and Y. A. Im, "Advances in the Chemistry of Coordination Compounds," Macmillan Company, New York, N. Y., 1961; D. H. Busch, K. Swaminathan, and D. W. Cooke, Inorg. Chem., 1, 260 (1962).

(2) P. Saffir and H. Taube, J. Am. Chem. Soc., 82, 13 (1960).
(3) A. Werner and A. Wilmos, Z. anorg. Chem., 21, 145 (1899).
(4) M. Anbar and S. Guttmann, Intern. J. Appl. Radiation Isotopes, 5, 233 (1959).

Results

The results obtained with $Co(NH_3)_5C_2O_4^+$ and $Co(en)_2C_2O_4^+$ are shown in Tables I and II, respectively. The symbol E represents the enrichment ratio of the species under consideration, that is, the ratio O^{18}/O^{16}

TABLE I

TRACER RESULTS[a] ON THE HYDROLYSIS OF $Co(NH_3)_5C_2O_4^+$

No.	(NaOH), M	Time of reaction, min.	Hydrolysis, %	Temp., °C.	E of solvent	E of oxalate	n
1	1.4	10	...	25	7.86	1.020	0.01[b]
2	1.4	5	...	100	4.32	1.023	.03[b]
3	1×10^{-4}	7600	...	25	7.60	1.009	.006[b]
4	3.21	7600	...	25	9.25	1.200	.096[b]
5	3.85	30,000	...	25	5.13	1.742	.71[b]
6	1×10^{-4}	63	...	71	6.52	1.021	.01[b]
7	0.25	12	4.7	25	4.30	1.024	.02
8	0.25	22	8.5	25	4.30	1.067	.07
9	0.25	2900	>96	25	4.99	1.34	.33
10	1.4	900	100	25	3.07	1.29	.55
11	1.4	2	100	100	4.04	1.067	.07
12	6×10^{-3}	20	100	100	4.97	1.021	.00

[a] E for complex = 1.000; concentration of complex, $\sim$0.02 M; concentration of $Na_2C_2O_4$, $\sim$0.04 M. [b] Blank experiments taking $Na_2C_2O_4$ of normal isotopic composition through the exchange procedure. The other values of n in the table are corrected for the slight pick-up of solvent oxygen indicated by the blank experiments. Experiments 4 and 5 show that exchange of $C_2O_4^{2-}$ with H_2O in OH^- does occur, but the reaction is very slow.

TABLE II

TRACER EXPERIMENTS[a] ON THE HYDROLYSIS OF $Co(en)_2C_2O_4^+$

No.	Temp., °C.	(NaOH)$_0$, M	Time,[b] min.	E of solvent	E of oxalate	n
1	90	1.97	10	7.16	3.64	1.72
2	90	1.97	10	7.16	3.58	1.68
3	71	0.00273	60	7.50	2.70	1.05
4	71	0.333	7	6.75	5.26	2.96
5	71	1.51	2	7.34	5.27	2.70
6	25	4.96	7200	7.09	5.52	<2.96

[a] E for complex = 1.000; complex 0.025 M. [b] In all experiments except the third, the reaction time is sufficiently long to ensure that hydrolysis is more than 98% complete; in expt. 3, the complete consumption of the alkali corresponds to hydrolysis of 8.9% of the complex, but making use of the measurements of rate reported in ref. 6 we calculate that 7.6% of the complex was hydrolyzed.

in the species compared to the ratio for CO_2 prepared from oxalate of normal isotopic composition; n represents the number of oxygen atoms derived from the solvent for each $C_2O_4^{2-}$ formed as product.

Discussion

The results obtained with $Co(NH_3)_5C_2O_4^+$ (cf. Table I) show that the $C_2O_4^{2-}$ released on hydrolysis derives some of its oxygen from the solvent. In expt. 7, the extent of hydrolysis is small, so that the effects of exchange are minimized. We note that in this case the value of n is very small, and we must conclude that incorporation of solvent oxygen by C–O bond breaking is small. At most, 1% of the hydrolytic events involve C–O bond cleavage. On complete hydrolysis of

the complex, the maximum effect of the exchange is experienced (cf. expt. 9 and 10; exchange increases somewhat as the concentration of alkali increases (expt. 10 compared with 9, and 11 compared with 12) and decreases as the temperature rises (expt. 11 compared with 10). The latter observation indicates that substitution of the Co(III) center has a higher activation energy than substitution at the carboxyl group.

Work on the kinetics of hydrolysis of $Co(NH_3)_5C_2O_4^+$ is in progress.[5] It is worth mentioning that in the range of (OH^-) covered by our studies, the rate is not simply first order in (OH^-) but that a term second order in (OH^-) also appears.

The average isotopic composition of the oxalate released on complete hydrolysis is related to the exchange and hydrolysis specific rates k_e and k_h by the following equation.

$$A_\infty = \int_0^\infty k_h A_s \, e^{-k_h t}(1 - e^{-k_e t} \, dt) \qquad (a)$$

so that

$$A_\infty/A_s = k_e/(k_e + k_h) \qquad (b)$$

In these equations A_∞ represents the exchange enrichment of the oxalate on complete hydrolysis, and A_s represents the maximum enrichment that would be achieved by complete exchange with the solvent of the exchangeable oxygens in question. If we assume that complete exchange would result in a value of $n = 2$ (i.e., both and only the oxygens of the carboxyl directly bound to Co(III) exchange), and noting that n is measured as 0.33 in expt. 9, then k_h/k_e for the conditions of the experiment is calculated as 5.1. However, as shown by expt. 12, hydrolysis by C–O bond breaking occurs at most in $1/100$ of the events and therefore, if an intermediate
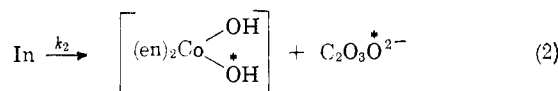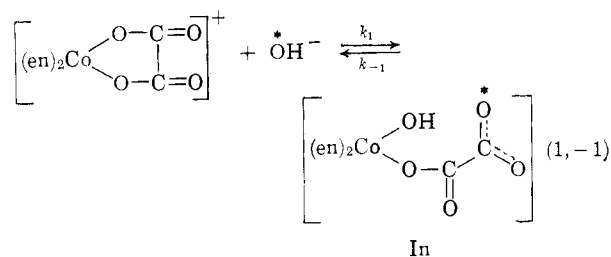
$$\begin{matrix} & H \\ & O \\ & | \\ Co-O-&\overset{|}{\underset{|}{C}}O^- \\ & R \end{matrix}$$
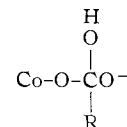
is assumed, C–O bond cleavage leading to hydrolysis is less than $1/20$ as rapid as C–O bond cleavage leading to exchange.

Some of the values of n recorded in Table II are so large that the conclusion that oxygen exchange accompanies hydrolysis of the chelated form of the oxalate complex is unavoidable. Experiment 3 in comparison with expt. 4 and 5 demonstrates that the incorporation of oxygen is not solely by exchange. The extent of exchange measured by 2.7 atoms out of 4 on complete hydrolysis (cf. expt. 4) would result in only 0.1 and 0.2 atom of solvent oxygen being introduced on 8% hydrolysis, and if it is measured by 1.7 atoms out of 3 (that is, attributing the incorporation of 1.0 atom to C–O bond breaking) the exchange of ca. 0.1 atom by exchange on 8% hydrolysis would be expected. Thus we conclude that release of $C_2O_4^{2-}$ from $Co(en)_2C_2O_4^+$ entails breaking one and only one C–O bond.

The results of Table II taken alone do not lead to a decision as to whether bond breaking takes place on opening the chelate or in the second step of the reaction. However, the results of Table I show that for the mono-

(5) R. B. Jordan.

dentate oxalate there is virtually no C–O bond breaking at 25 or 100°. This suggests that C–O bond breaking occurs on opening the chelate and not in the second stage when the configuration resembles that of Co-(NH₃)₅C₂O₄⁺. On this basis, the explanation of the exchange effects can take the forms shown in reactions 1, −1, and 2. The equations as written represent the

$$\left[(en)_2Co\begin{smallmatrix}O-C=O\\ \\O-C=O\end{smallmatrix}\right]^+ + \overset{*}{O}H^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[(en)_2Co\begin{smallmatrix}OH\\ \\O-C\end{smallmatrix}\right] \quad (1,-1)$$

In

$$In \xrightarrow{k_2} \left[(en)_2Co\begin{smallmatrix}OH\\ \\OH\end{smallmatrix}\right] + C_2O_3\overset{*}{O}^{2-} \quad (2)$$

isotopic course of the reaction during the initial stages, when the effects of the reversal of reaction 1 are not yet felt. Reaction −1 competing with 2 accounts for the exchange. If this mechanism is correct, reaction 2 must have a higher activation energy than −1 to account for the decrease in extent of exchange at high temperature. This requirement is consistent with the conclusion reached for Co(NH₃)₅C₂O₄⁺ that substitution at Co has a higher activation energy than substitution at C. For the mechanism we suggest for oxygen exchange to be consistent with the observation[6] that the rates of hydrolysis, oxalate exchange, and loss of optical activity are equal, we need only require that the intermediate In does not undergo racemization or oxalate exchange before it decomposes by reaction 2, a requirement that does not seem unreasonable.

Using eq. b and taking the data for expt. 4 of Table II as showing that complete hydrolysis leads to exchange of 1.96 atoms out of a possible of 3, k_1/k_c is calculated as 0.53. The ratio k_1/k_c does appear to be weakly dependent on (OH⁻); thus k_1/k_c from expt. 5 ((NaOH) = 1.5 M) is 0.77. This trend is borne out also by comparing the result of expt. 6 with those for expt. 1, 2, and 5. From the trend of n with temperature shown by expt. 1, 2, and 5, n for expt. 6 is expected to be close

(6) S. Sheel, D. T. Meloon, and G. M. Harris, Inorg. Chem., 1, 170 (1962).

to 4, but the actual value is only slightly in excess of that observed in expt. 5, and the defect from the expected value is probably caused by the change in (OH⁻). It is quite possible that the changes in chemistry with change in (OH⁻) revealed by the tracer work are reflected in the kinetics of the reaction—that is, terms higher than first order in (OH⁻) may enter the rate law. The highest concentration of OH⁻ used in the work described in ref. 6 was approximately 0.024 M, which is considerably below the highest concentration of OH⁻ in our experiments.

It should be noted that the course of events in alkaline hydrolysis of chelated oxalate is quite different from that observed in the acid hydrolysis of the complex ion Co(NH₃)₄CO₃⁺.[7] In the latter system, opening the chelate apparently takes place by Co–O bond breaking; the second step is not directly analogous to that which takes place with the oxalato complex, as it involves release of CO₂, rather than of CO₃²⁻, and this occurs with C–O bond breaking. A detailed and fruitful comparison of the two reactions is difficult because the compositions of the activated complexes are different, but a few remarks on each may be in order. For the oxalato complex the path involving the amido intermediate (and Co–O bond breaking) competes with direct attack by OH⁻ at C, leading to C–O bond breaking. It is expected that chelation would diminish the rate of Co–O bond breaking in the amido intermediate, and it is therefore not entirely unexpected that attack at the C–O position becomes successfully competitive with it, particularly since, as exchange measurements in acid solution show, attack by a base such as H₂O at the carbonyl adjacent to Co(III) takes place with considerable facility.[8] The difference between CO₃²⁻ and C₂O₄²⁻ in the first step presumably arises because of the greater strain in the four-membered compared to the five-membered ring. This suggests that Co–O bond breaking will be observed when (NH₃)₄CoCO₃⁺ hydrolyzes in alkaline solution; this point is at present under investigation in these laboratories.

(7) F. A. Posey and H. Taube, J. Am. Chem. Soc., 75, 4099 (1953).
(8) C. Andrade and H. Taube, to be published.