Acid-catalysed Oxygen-18 Exchange Studies with Oxalatobis-(2,2′-bipyridine)cobalt(III) and Oxalatobis-(2,2′-bipyridine)chromium(III) Cations in Water

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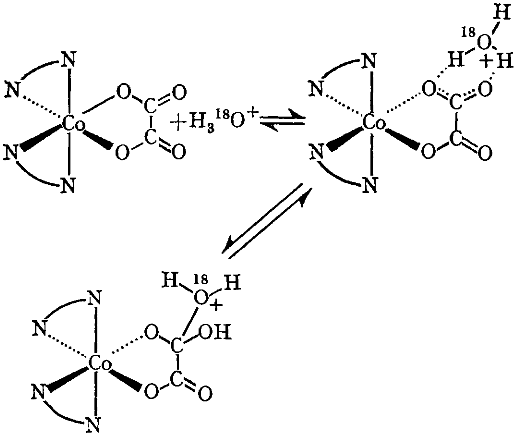
RECENTLY, the rates of oxygen exchange between oxalato-metal complexes and oxygen of solvent water have been much studied.[1,2] Comparative studies of the influence of the metal ion on these reactions have been confined to the tris(oxalato)-complexes of cobalt(III) and chromium(III). We report here the marked difference in exchange behaviour found for the two heterochelate complexes [Co ox $(bipy)_2$]Cl and [Cr ox $(bipy)_2$]Cl (ox = oxalate ion, bipy = 2,2′-bipyridine). For the cobalt complex under acid conditions only two of the four oxalate oxygens are readily exchanged with solvent oxygen, while for the chromium analogue all four oxalate oxygens undergo exchange.

With [Co ox (bipy)$_2$]Cl the rate of exchange is directly proportional to the acid concentration, at least up to 2N. The rate constant, *k*, calculated by multiplying the slope of the ln $(a_\infty - a_t)$ *versus* time plot by the number of kinetically indistinguishable oxygen atoms in the complex (two in this case) in 1·0 N-HCl at 33° is $8{\cdot}96 \times 10^{-5}$ sec.$^{-1}$. (a_∞, a_t represent the atom fractions of oxygen-18 in the complex at times '∞' and '*t*' respectively). After longer reaction times (1·0 N-HCl, 33°) the exchange of the remaining two oxygen atoms in the oxalate ligand is detected. For this slow exchange, $k = 3{\cdot}6 \times 10^{-7}$ sec.$^{-1}$. In 2N-HCl, at 33°, there is virtually no second-stage exchange so that here the rate-controlling step is not acid-catalysed, but is in fact being retarded.

In contrast to the cobalt(III) complex, studies on the corresponding chromium(III) complex under precisely similar conditions have shown all four oxalate oxygens to be kinetically equivalent and to be exchanged at a much faster rate than is observed with the cobalt(III) complex. The results obtained are: $k = 5{\cdot}92 \times 10^{-4}$ sec.$^{-1}$ (1N-HCl, 33°); $E_a = 18{\cdot}3$ kcal./mol.$^{-1}$; $\log_{10}A$ (sec.$^{-1}$) = 9·84.

The mechanism by which exchange of carbonyl oxygen occurs between water and the complex is probably the same for the chromium and the cobalt compounds under the experimental conditions used. This mechanism is essentially that proposed by Roberts and Urey[3] for acid-catalysed exchange of oxygen in the carbonyl group, and has been suggested subsequently in the exchange studies of Andrade[4] which are closely related to this present work. It was also shown for the complex [Co ox (en)$_2$]$^+$ (en = ethylenediamine) that two oxygens were readily exchanged with water under acid conditions and that these rates were similar to those for acid-catalysed carbonyl oxygen exchange in dimethyl oxalate.[4] This similarity extends to the present study on [Co ox (bipy)$_2$]$^+$ for which the rate constant for the faster oxygen exchange reaction is of the same order of magnitude as that found for [Co ox (en)$_2$]$^+$. Likewise, the second, slower, exchange rate constant found for [Co ox-(bipy)$_2$]$^+$ may be compared with the value $1{\cdot}72 \times 10^{-8}$ sec.$^{-1}$ in 0·7 M-HCl at 25° estimated for the slower exchange in [Co ox (en)$_2$]$^+$. The mechanism already suggested to account for the two rates of oxygen exchange found in [Co ox (en)$_2$]$^+$ may be extended to the bipyridine analogue. Thus the second slower exchange is a consequence of the slower interchange of the carbonyl and carboxyl oxygens by rotation about the C–C bond. We have found no evidence for aquation during the exchange reaction and further, optically active [Co ox (bipy)$_2$]$^+$ does not racemise in acid solution.[5] These observations tend to support an interchange mechansim as suggested by Andrade. A mechanism based on the attack of water on cobalt might be expected to lead to some hydrolysis products while slow dissociation of oxalate to the half-bonded stage could provide a path for racemisation.



If the interchange mechanism alone accounts for the exchange of oxygen bound to the metal, then the difference between the cobalt(III) and chromium(III) complexes studied here implies a more rapid interchange for the latter than for the former. For [Cr ox (bipy)$_2$]$^+$ the interchange is faster than or equal to the rate of carbonyl oxygen exchange while for the [Co ox (bipy)$_2$]$^+$ the second, slower, exchange rate is a measure of the interchange process. Alternatively, the kinetic equivalence of all four oxygens in the chromium(III) case may be explained by the mechanism of Bunton, *et al.*,[1] involving an initial protonation followed by dissociation to the half-bonded oxalate stage for which the two oxygen atoms attached to carbon become equivalent. A half-bonded mechanism for chromium receives some support from the fact that [Cr ox (bipy)$_2$]$^+$ is found to racemise in acid solution.[6]

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[4] C. Andrade, Ph.D. Thesis, University of Chicago, 1964.
[5] J. A. Broomhead and M. Dwyer, unpublished work.
[6] J. A. Broomhead and N. Kane-Maguire, unpublished work.