Acid-catalysed Oxygen-18 Exchange Studies with Chromium(III) and Cobalt(III) Oxalato-complexes in Aqueous Solutions

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CONTRARY to previous findings[1] that all oxygens in the complex $[Co(C_2O_4)_3]^{3-}$ exchange with water, we find, under closely similar experimental conditions, that only six oxygens exchange. This behaviour is similar to that reported previously for certain mono-oxalato cobalt(III) complexes.[2,3]

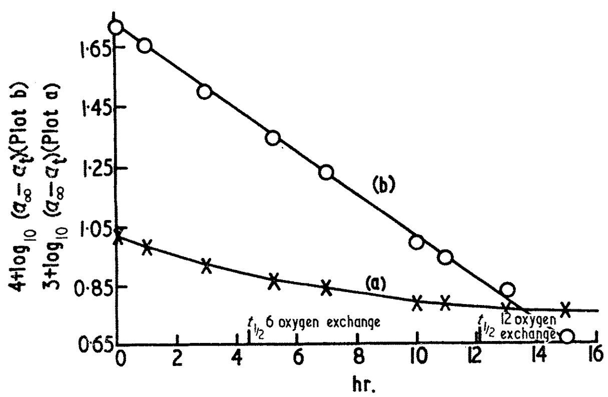

FIGURE. *The plot of log* (a_∞—a_t) *against time for the acid-catalysed exchange of oxygen between* $[Co(C_2O_4)_3]^{3-}$ *and water.* [Complex] = 0·063M; [HCl] = 1 mol l.$^{-1}$; *Temperature* 25°. *Plot* (a) *calculated for exchange of all twelve oxygens. Plot* (b) *calculated for exchange of only six oxygens.*

In the Figure, plots of $\log_{10} (a_\infty - a_t)$ against time are given for the two possible cases, showing (a) all 12 oxygens exchanging, and (b) only 6 oxygens exchanging. Plot (b) is linear for 3 half-lives while plot (a) begins to curve well before one half-life period.

Previous workers based their deductions that all twelve oxygens are kinetically equivalent on the observation that the $^{18}O/^{16}O$ ratios for the CO_2 released on thermal decomposition of the complex was the same as that for the cobalt oxide residue. However, this deduction is probably not valid. It has been shown in these laboratories that isotopic scrambling occurs on thermal decomposition.

The complex $[Co(C_2O_4)bipy_2]Cl$ has been labelled at the carbonyl positions for the complex $[Cr(C_2O_4)bipy_2]Cl$ at all the positions using, for both, water containing 1·28 atom % oxygen-18. In each case, after thermal decomposition, the $^{18}O/^{16}O$ ratios for the products, the carbon dioxide, the carbon monoxide, and the metallic residue were determined and found to be identical but different for each complex, the actual value for the products from the chromium complex corresponding to labelling at all four positions and from the cobalt to labelling at two positions in the oxalato-group.

Although the oxygen isotopes become distributed in the products of thermal decomposition, the oxygen in the carbon dioxide produced from $[Co(C_2O_4)bipy_2]Cl$ does not have a normal statistical distribution for the 44, 46, 48 species. In further studies, the complexes $[Co(C_2O_4)bipy_2]Cl$ and $[Cr(C_2O_4)bipy_2]Cl$ have been labelled in the positions mentioned above using 22 atom % oxygen-18 water. After thermal decomposition of the complexes (400°), the 46/44 ratios of the carbon dioxide produced, were determined. Portions of the carbon dioxide from each complex were circulated over a white-hot platinum filament, other portions (unheated) being used for reference measurements. The carbon dioxide from the chromium complex showed no change in 46/44 ratio after heating, that from the cobalt complex, however, decreased by about 3%, corresponding to the establishment of the equilibrium,

$$2C^{16}O^{18}O \rightleftarrows C^{16}O_2 + C^{18}O_2.$$

The oxygen exchange rate constants (1N-HCl, 25°) for various cobalt and chromium oxalato-complexes are shown in the Table. The rate constants are calculated by multiplying the slope of the $-\ln(a_\infty - a_t)$ against time plot by the number of kinetically indistinguishable oxygen atoms in the complex.

For the chromium complexes, $a_\infty = a_W$, the atom fraction of oxygen-18 in the solvent water; for the cobalt complexes $a_\infty = (a_W + a_O)/2$ where a_O is the atom fraction of oxygen-18 in the complex initially. The data presented by Bunton *et al.*[1] do not allow a rate constant to be re-calculated for comparison with our result for $[Co(C_2O_4)_3]^{3-}$. The Table shows that the chromium oxalato-complexes exchange oxygen with water more rapidly than the analogous cobalt complexes but the relative rates are approximately the same for the two series.

More detailed studies of oxygen exchange for these complexes already indicate that a re-interpretation of their significance in the study of racemisation mechanisms will be necessary.

First-order rate constants for the acid-catalysed exchange of oxygen between various oxalato-complexes and water, (1 N-HCl, 25°).

[a]Complex ion	Number of oxygens exchanging	$10^4 \times$ Rate constant (sec.$^{-1}$)	Relative rate
$[Co(C_2O_4)_3]^{3-}$	6	2·64	1
$[Co(C_2O_4)_2en]^-$	4	1·71	0·65
[b]$[Co(C_2O_4)en_2]^+$	2	0·48$_5$	0·18
$[Co(C_2O_4)bipy_2]^+$	2	0·42	0·17
[c]$[Cr(C_2O_4)_3]^{3-}$	12	12·75	1
[d]$[Cr(C_2O_4)_2phen]^-$	8	9·04	0·71
[d]$[Cr(C_2O_4)_2bipy]^-$	8	9·20	0·72$_5$
[d]$[Cr(C_2O_4)en_2]^+$	4	2·76	0·21
[d]$[Cr(C_2O_4)phen_2]^+$	4	2·69	0·21
[d]$[Cr(C_2O_4)bipy_2]^+$	4	2·71	0·21

[a] en = ethylenediamine; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline.
[b] Result obtained by J. Mann and T. Wuth.
[c] Result from ref. 2.
[d] Results obtained by Mr. N. Kane-Maguire.

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