Kinetics of Substitution of Alkyl- and Aryl-aquo-1,3-bis(biacetylmonoximeimino)propanatocobalt Monocations

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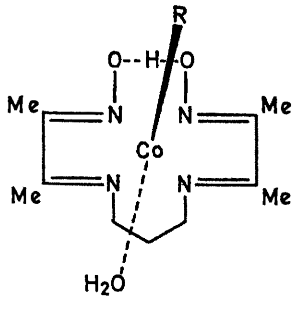
Summary The rates of various substitution reactions of alkyl- and aryl-aquo-1,3-bis(biacetylmonoximeimino)-propanatocobalt ions have been measured; the processes appear to be lim S_N1.

AN investigation has been made of the kinetics of substitution of complexes of the type $[RCo\{(DOH)(DO)pn\}H_2O]^+$, (I).[1] The replacement of the aquo-group by imidazole, benzimidazole, and triphenylphosphine in acetone containing 1% water by volume was followed spectrophotometrically at 25·0 ± 0·2° using a stop-flow apparatus.



(I)

A reversible lim S_N1 process such as equation (1) follows the kinetic pattern:[2]

$$k_{\mathrm{obs}} = \frac{k_1[\mathrm{Y}^-] + k_2k_4/k_3}{k_2/k_3 + [\mathrm{Y}^-]}$$

$$\mathrm{M\,H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{M} + \mathrm{H_2O} \quad \text{where } k_2 = k_2'[\mathrm{H_2O}] \qquad (1)$$

$$\mathrm{M} + \mathrm{Y} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{MY}$$

Graphs of $1/k_{\mathrm{obs}}$ against $1/[\mathrm{Y}]$ for the reaction studied are linear, and give the data shown in the Table. No evidence was found for any k_4 terms. Upper limits for k_4 are 0·002, 0·01, and 0·01 times the values of k_1 for the reactions of imidazole, of benzimidazole, and of triphenylphosphine, respectively. Support for these limits comes from studies of equilibria between reactants and products.

TABLE

Rate data for process (1)

	Y = Imidazole		Benzimidazole		Triphenylphosphine	
	k_1	k_2/k_3	k_1	k_2/k_3	k_1	k_2/k_3
Ph	3·6 ± 0·3	0·10 ± 0·01	6·9 ± 1·7	0·15 ± 0·04	4·9 ± 0·0	0·013 ± 0·000
Me	24·8 ± 5·6	0·18 ± 0·04	40·9 ± 7·5	0·18 ± 0·04		
$\mathrm{PhCH_2}$	226 ± 28	0·15 ± 0·02				
Et	251 ± 23	0·13 ± 0·01				
$\mathrm{Pr^n}$	602 ± 139	0·35 ± 0·08				

Units: k_1 in sec.$^{-1}$, k_2/k_3 in moles litre^{-1}; data fitted by least-mean-squares technique (at least 13 points per graph); errors are standard deviations.

The following points emerge from the results in the Table:

(i) The absence of any appreciable dependence on the incoming ligand in the k_1 term (as well as the linearity of the plots of $1/k_{\mathrm{obs}}$ against $1/[\mathrm{Y}]$) indicates that a lim S_N1 process does in fact occur. (Small variations in k_1 terms with change of incoming ligand are often observed in lim S_N1 processes in non-aqueous solvents[3]).

(ii) A large *trans*-labilizing effect occurs, at least if oxidation states are assigned, $\mathrm{R^{-I}Co^{III}}$, in the manner frequently used for d^8 platinum complexes[4]: $\mathrm{Co^{III}\{(DOH)(DO)pn\}Br_2}$, which contains no cobalt–carbon link, aquates slowly enough to be followed by traditional techniques, as opposed to stopped-flow. [In contrast to the *trans*-position, the *cis*-positions are inert: the rate of replacement of the {(DOH)(DO)pn} group in (I) is very slow].

(iii) The kinetic *trans*-effect shown by k_1 rises in the sequence: R = Ph < Me < Et < $\mathrm{Pr^n}$, which might be attributed to increasing donor character, as a similar sequence is observed in organic S_N1 processes.[5] However in organic systems the benzyl group is even more labilizing than the n-propyl in contrast to what is found here.[5] [When R is isopropyl, the overall reaction in equation (1) is very fast].

(iv) The ratios k_2/k_3 (which are approximately equal to 0·556 k_2'/k_3) reflect a greater affinity of the R Co{(DOH)(DO)pn} group for imidazole and benzimidazole as compared with water, as might be expected solely on a basis of σ-interactions. However the very high affinity of PhCo(DOH)(DO)pn towards triphenylphosphine suggests that π-effects are important.

The data can be compared with those obtained for other macrocyclic cobalt complexes. Our values of k_1k_3/k_2, that is of k_{obs} in the first-order range in Y^-, lie between 35 and 13,000 M^{-1} sec.$^{-1}$. Cobalt(III) haematoporphyrin exchanges water for cyanide and thiocyanate ions by a lim S_N1 process, the values of k_1k_3/k_2 lying in the range observed here.[6] Aquocobalamin exchanges water for these anions and for azide and imidazole by either an S_N1 or S_N2 mechanism with second-order rate constants[7] between 27 and 7100 M^{-1} sec.$^{-1}$. However, in these cases the groups *trans* to the outgoing ligands are water and benzimidazole, respectively, neither of which is strongly *trans*-directing like the alkyl and aryl groups used here.

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