

certainly less than 1.0 per cent and probably less than 0.5 per cent. This is insignificant for all purposes of radiocarbon dating.

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Steric and Electronic Effects in Electron Transfer Reactions

THERE is at present no satisfactory theory to account for the rates of electron transfer from one metal ion to another via a bridging group. Two attempts have been made, both based on the assumption that the probability of electron transfer during the lifetime of the activated complex is small. The first relationship took the form¹:

$$k_{bi} \cong k_f(C_1 P_{rs} \tau)^2$$

where k_{bi} is the observed overall rate constant for the reaction, k_f is the rate constant for the formation of the activated complex, C_1 is a constant, and P_{rs} the mobile bond order² between the atoms r and s associated with the metal ions. τ is the mean lifetime of the activated complex. This conjugation theory of electron transfer was extended by including the effect of charged reactants on the rate of formation and the mean lifetime of the activated complex³, giving at zero ionic strength the relationship:

$$\ln K_0 = C_0 + \ln p_{rs}^2 - \frac{3Z_A Z_B \epsilon^2}{DkT r_{AB}}$$

where Z_A and Z_B are the charges on the ions A and B , C_0 is a constant, D is the dielectric constant of the medium, k is the Boltzmann constant, T is the temperature, and r_{AB} the distance between the metal centres. A comparison has been made³ with results obtained experimentally in the chromium(II) reduction of various pentamminecobalt(III) complexes. Agreement is better with the second theory than with the first, but not good. The suggestion was made that improvement of the M.O. calculations and the electrostatic treatment might produce substantial numerical agreement. Neither theory takes into account the steric effects of substituent groups (that is, groups present as part of the ligand but not participating directly in the electron transfer path). Such groups are important: the rate constants for the reduction of $(\text{NH}_3)_5\text{CoO}_2\text{C}-R^{2+}$ fall off from 0.32 $\text{M}^{-1} \text{sec}^{-1}$ to 0.04 $\text{M}^{-1} \text{sec}^{-1}$ as R changes from CH_3 to *cyclo* C_6H_{11} , even though the path length for the electron transfer remains unchanged⁴.

Fig. 1 shows a plot of some rate constants as a function of Taft's σ^* parameter⁵. In all cases, the electron transfer path is $\text{metal}_A-\text{O}-\text{C}-\text{O}-\text{metal}_B$. Since the van der Waals radius of a $-\text{CH}_3$ group is almost identical⁶ with that of a $-\text{Br}$, the steric effects in the two ligands should be the same, so that ρ^* in the Taft equation:

$$\log k - \log k_{ref.} = \rho^* \sigma^* + E_s$$

(E_s is the steric factor) can be evaluated for the electron transfer process. The experimental value is -0.04 ,

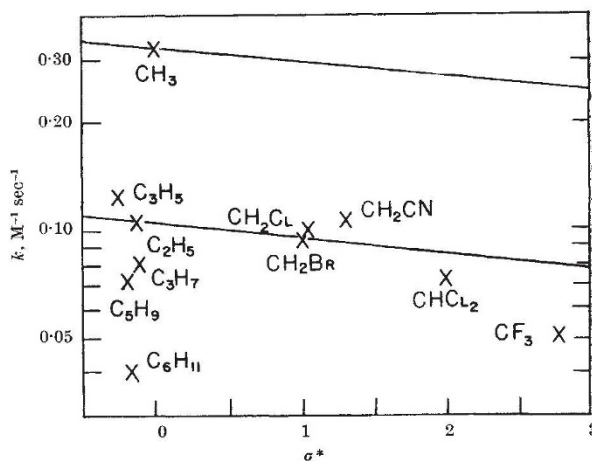


Fig. 1. Rate constants, k , for the chromium(II) reduction of carboxylatopentamminecobalt(III) complexes $(\text{NH}_3)_5\text{CoO}_2\text{C}-R^{2+}$ plotted against σ^* values of R .

similar to the values obtained for the acid hydrolysis of carboxylic esters. If a line with this slope is drawn through the value for the reference compound (acetatopentamminecobalt(III), $R = -\text{CH}_3$), the E_s values for the other substituents can be obtained. The values are shown in Table 1. With the exception of that for the dichloromethylene, the E_s values follow the same trend previously found in ester hydrolyses⁷, indicating that any electron transfer theory proposed for bridging reactions must take into account not only the mobile bond order of the bridge and the distance between the metal centres, but also the steric effects of the ligands.

Table 1. STERIC SUBSTITUENT CONSTANTS, E_s

Substituent	E_s	Rate constant reference
CH_3-	0.0	
C_2H_5-	-0.49	
C_3H_7-	-0.61	8
ClCH_2-	-0.47	9
BrCH_2-	-0.49	
$\text{Cl}_2\text{CH}-$	-0.56	9
CNCH_2-	-0.43	9
$\text{F}_3\text{C}-$	-0.70	10
<i>Cyclo</i> C_6H_5-	-0.43	4
<i>Cyclo</i> C_6H_7-	-0.65	4
<i>Cyclo</i> $\text{C}_6\text{H}_{11}-$	-0.90	4

If the bond order is calculated without consideration of the electronic substituent effects, the empirical relationship at 25° and ionic strength equal to 1 is:

$$\log k_{bi} = 7.28 + \log p_{rs}^2 + \rho^* \sigma^* - \frac{3Z_A Z_B \epsilon^2}{DkT r_{AB}} + E_s$$

Similar considerations seem to apply in the electron transfer through *ortho* substituted benzoates, where the experimental data are much more limited.

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