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THE *TRANS* EFFECT IN SOME SUBSTITUTION REACTIONS OF PLATINUM(II) COMPLEXES

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During the past several years a number of my students have investigated the rates of the acid hydrolysis reactions of the complete series of ammonia–chloride complexes of platinum(II) for which the general equation (1) can be written for the reaction.

$$\mathrm{Pt^{II}\text{–}Cl + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Pt\text{–}OH_2 + Cl^-}\ . \tag{1}$$

The critical system in this series is the one involving the $[\mathrm{Pt(NH_3)Cl_3}]^-$ ion. In a study recently completed we have found that the two kinds of chloride react with different rates. The k_1 for one type of chloride approximately is ten times as great as that of the other. However, the aquo-complex, $[\mathrm{Pt(NH_3)Cl_2(H_2O)}]$, formed more rapidly, is actually thermodynamically the less stable so that at equilibrium the other isomer is the predominant species. In accordance with classical views on the *trans*-effect and stability we assign as the chloride *cis* to ammonia (called here the *cis*-chloride) that which is replaced most rapidly to yield the unstable isomer. Our rate constants for the entire series are in Table I.

TABLE I

RATE CONSTANTS FOR THE ACID HYDROLYSIS OF CHLORIDE LIGANDS IN THE CHLORO-AMMINE-COMPLEXES OF PLATINUM(II) AT 25 °C AND $\mu = 0.318$ *M*.

Complex		k_1 *(sec^{-1} · 10^5)*
$[\mathrm{PtCl_4}]^{2-}$		3.9
$[\mathrm{Pt(NH_3)Cl_3}]^-$	*cis-*	5.6
	trans-	0.62
cis-$[\mathrm{Pt(NH_3)_2Cl_2}]$		2.5
trans-$[\mathrm{Pt(NH_3)_2Cl_2}]$		9.8
$[\mathrm{Pt(NH_3)_3Cl}]^+$		2.6

For this series of rate constants it is necessary to formulate the kinetics quantitatively as separate *cis-* and *trans*-effects. Thus all six rate constants in Table I are given to within 20% by a simple formula,

$$k/n = 1.0 \cdot 10^{-5}\ \mathrm{sec}^{-1} \cdot (0.5)^m (2.4)^p \tag{2}$$

where n = the number of equivalent chlorides in the complex (a statistical factor)
m = the number of NH_3 *trans* to the replaced Cl^-, *i.e.* 0 or 1
p = the number of (NH_3) *cis* to the replaced chlorides, *i.e.* 0, 1 or 2.

The charge on the ion apparently has no primary effect on these rate constants. Presumably, a dissociative mechanism does not apply and the transition state likely consists of a trigonal bipyramid coordination figure in which the *trans*-ligand, the replaced chloride and the entering H_2O occupy equatorial positions. It appears that for the acid hydrolysis of the chloride–ammine systems the *cis*-neighbor has somewhat a greater influence on the kinetics than the *trans*-neighbor. Thus, in any theory concerning the kinetics directive effects by such groups, which are at best weakly *trans*-directive, more attention should be given to the *cis*-effect.

Undoubtedly a major factor with the strong *trans*-directors is, as Chatt *et al.*[1] and Orgel[2] have proposed, the withdrawal of electrons toward the *trans*-ligand into the π-type bonds, so the Pt-orbitals become more available for bonding to the fifth ligand in the transition state. Such excess negative charge on the electron withdrawing group will also serve to act repulsively with other ligands. The strongest of such interactions will be with ligands bonded at 90° to the π-electron withdrawing group. There are two such 90°-neighbors in the trigonal bypyramid transition state for the replacement of the *trans*-ligand but three such neighbors in the replacement of a *cis*-ligand in the transition state. Therefore, the electron withdrawal may deactivate the transition state in *cis*-substitution. Thus the ethylene in the $[Pt(C_2H_4)Cl]^-$ ion of Zeise's salt virtually labilizes the *trans*-chloride but reduces the rate of acid hydrolysis of the *cis*-chloride by a factor[3] of 0.15. A negative ion, such as chloride, is therefore especially effective in *cis*-deactivation in comparison to its rather weak *trans*-activation. Hence the ligand repulsions which are important in the equilibrium *trans*-effect can be considered to exert a strong influence on the kinetics also.

Finally, it seems appropriate to comment that the great utility of the *trans*-effect has focused attention upon differences in rates which are frequently rather modest. It is certainly an ambitious and formidable requirement for the models of bonding in the coordination complexes, which are admittedly crude, that they predict differences of the order of 0.5 kcal/mole in activation energies of the respective reactions.

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