are an integral part of the X-ray diagram obtained from pseudorutile.

G. TEUFER

Engineering Department,

A. K. TEMPLE*

Development Department,
E. I. du Pont de Nemours and Co.,
Wilmington, Delaware.

* Present address: Mobil Chemical International, Ltd., 150 East 42nd Street, New York.

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Mechanism of the Acid Hydrolysis of Pentammine Cobalt Complex Ions

UNEQUIVOCAL evidence in support of a particular mechanism for the acid hydrolysis reaction (1) has not, as yet, been obtained.

$$[Co(NH_3)_5X^{2+}] + H_2O \rightleftharpoons [Co(NH_3)_5H_2O^{3+}] + X^- \quad (1)$$

$$(X = F^-, Cl^-, Br^-, I^-, NO_3^-, H_2PO_4^-)$$
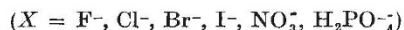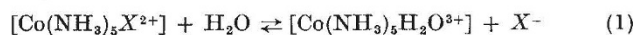
Several recent communications[1-4] serve to emphasize that the problem is still an open issue. In any kinetic investigation a knowledge of the species present is of prime importance, particularly, in a reaction of type (1), where ion-pairs are likely to occur; the acceleration of reaction (1) by added anions has been observed[5,6]. In a recent detailed investigation for $(X = Cl^-)$, Laurie and Monk[7] attributed these accelerations to ion-pairs being more reactive than the free complex ion; the thermo-dynamic dissociation constants derived from the rate data for the proposed ion-pairs were in good agreement with values from investigations of the electromotive force[8]. The results are collected in Table 1. It is the purpose of this communication to show the importance of these results with regard to two misconceptions and to the mechanism of reaction (1).

According to Basolo and Pearson[9], increased reaction rates in the presence of added anions cannot be attributed solely to more reactive ion-pairs. Their conclusion is made invalid by the above results and by the findings of Davies[10] on other similar reactions. Moreover, Basolo[11] takes the increase in hydrolysis rate with decrease in positive charge on the complex to be indicative of an S_N1 reaction; for example, for similar low-spin d^6 complexes the decrease in reactivity follows the order Fe(II) > Co(III) > Pt(IV), but in such a sequence differences in ligand field strength will also be operative. For the species $[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_5Cl]L^+$, and $[Co(NH_3)_5Cl]M^0$, where $L-$ and M^{2-} are ion-pairing anions, ligand field strength differences are negligible and the observed[7] increase in hydrolysis rate along the series may be attributed solely to the lowering of the positive charge. These rate increases (Table 1) are, however, small (the activation energy changes by only 0·1 kcal on lowering the charge from +2 to 0) and can be interpreted in terms of an S_N2 mechanism in which the lowering of the positive charge promotes the removal of the chloride ligand (ion–ion interaction) but discourages attack by the nucleophilic water molecule (ion–dipole interaction). The former effect, being the greater, would predominate, giving the observed increases and at the same time preserving the well-established

Table 1*

Ligand	Nitrate	Glycollate	Sulphate	Malonate	Phthalate
k_2/k_1	1·1	1·15	2·05	2·13†	2·95
K	0·09	0·03₅	0·0032	0·0050	0·0030

* Data taken from ref. 7.
† Incorrectly given as 2·08 in ref. 7. k_2/k_1 is the ratio of the reaction rate constant of the ion-pair to that of the free complex ion, at 35°. K is the thermodynamic dissociation constant at 35° C.

"bond breaking more important than bond making" order.

Langford's analysis[3] of the free-energy data suggests that for an S_N1 mechanism to occur the entering nucleophile must be previously present in the second co-ordination sphere of the Co(III) ion. If this is so, then the non-entry of the ion-pairing anion into the first co-ordination sphere must rule out an S_N1 process. By similar reasoning an S_N2-trans mechanism can be discounted.

The data presented comply with an S_N2-cis-type mechanism, in which the transition state involves an extended Co—X bond and an adjacent weak bond between the cobalt-atom and a water molecule present in the second co-ordination sphere, the reaction being completed by the breaking of the Co—X bond and the simultaneous entering of the water molecule. The inclusion of the extended Co—X bond is in accordance with Vlcek's deductions[12] from polarography measurements and means that expansion of the inner co-ordination sphere is not necessary. For minimum potential energy the ion-pairing anion must be "trans" to the departing ligand and hence would not be expected to enter the inner-co-ordination sphere on the basis of this mechanism. The proposed mechanism also fits in well with other observations on deuteration[13] and steric hindrance[14] effects and the findings that complexes of the type cis-$[Co(en)_2XCl^+]$, $X = NCS^-$, N_3^-, and NO_2^-, hydrolyse without stereochemical change[15].

Finally, it is to be noted that the mechanism proposed above is very similar to the "solvent-assisted dissociation" process favoured by others (for example, see ref. 2). Indeed, the difference may be one of semantics only.

STUART H. LAURIE

C.S.I.R.O. Division of Protein Chemistry,
Wool Research Laboratories,
Parkville, Melbourne, Victoria.

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Enzymatic Etching of Single Crystals of Naphthalene

IT was previously observed[1] that when crystals of naphthalene, which had been grown from the vapour phase, were immersed in an aqueous suspension of soil pseudomonads for about 10 min at room temperatures, a small number (about 10^2 cm^{-2}) of well-defined, pyramidal pits were produced on the principal habit faces {00l}. This result was tentatively interpreted to mean that preferential attack of the naphthalene by the pseudo-monads occurred at the regions of emergence of dislocations, a view which was consonant with: (i) the conclusions of Kochendorfer[2], who indicated that dislocations lying in {010} planes, having a Burgers vector in the [001] direction, might be possible in naphthalene; (ii) the results of Koslovskii[3], who observed growth spirals on the {00l} faces of certain naphthalene crystals; (iii) the more recent work of Sears[4], who also proffered evidence for dislocations emergent at {00l} faces. The result agreed