

## The Solvolysis of *trans*-Di-(*p*-toluato)bis(ethylenediamine)cobalt(III) Perchlorate in Acetic Acid: a non-S<sub>N</sub>1CB Base Solvolysis

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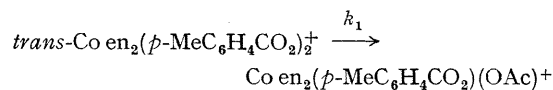
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**Summary** The S<sub>N</sub>1CB (conjugate base) mechanism of base hydrolysis does not apply to the solvolysis of *trans*-[Co en<sub>2</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in acetic acid.

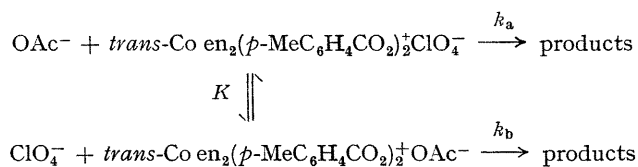
In an earlier report, it was shown that the isomerization rate of *cis*-[Co en<sub>2</sub>(OAc)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in acetic acid is retarded by the addition of sodium acetate.<sup>1</sup> The retardation was ascribed to the formation of an acetate ion pair that is significantly less reactive than the perchlorate ion pair initially present.

The effect of sodium acetate on the solvolysis of *trans*-[Co en<sub>2</sub>(*p*-toluato)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in acetic acid has now been studied at 84.5°. The product of the solvolysis is an equilibrium mixture of the Co en<sub>2</sub>(OAc)<sub>2</sub><sup>+</sup> isomers. The reaction was followed spectrophotometrically by observing the decrease in absorbance at 29.10 kK, an isosbestic point of the Co en<sub>2</sub>(OAc)<sub>2</sub><sup>+</sup> equilibrium mixture.<sup>1</sup> The complex concentration was kept at 10<sup>-2</sup> M. During the solvolysis, an isosbestic point was observed at 19.4 kK, demonstrating that the only observable species are the initial reactant and product equilibrium mixture. The first-order rate constant, *k*<sub>obs</sub>, was measured as a function of NaOAc concentration

from the slope of ln(*A* - *A*<sub>∞</sub>)-time plots and is ascribed to the first step of the solvolysis (*cf.* ref. 2):



The dependence of *k*<sub>obs</sub> on NaOAc concentration is shown in the Figure, a large retardation being observed primarily when [NaOAc] < [complex]. The limiting rate is essentially realized at [NaOAc] = [complex]. These results may be interpreted similarly to the diacetato isomerization, as an ion pair-ion pair equilibrium:<sup>1</sup>



With the treatment and assumptions previously employed,<sup>1</sup> the constants may be evaluated as: *k*<sub>a</sub> = 2.6 × 10<sup>-4</sup> sec.<sup>-1</sup>,

$k_b = 0.36 \times 10^{-4} \text{ sec.}^{-1}$ , and  $K \text{ ca. } 2.5 \times 10^3$ . The lower reactivity of the acetate ion pair further indicates that acetate substitution derives from the solvent rather than any added acetate ion and is consistent with the "solvent-assisted dissociation" mechanism previously suggested for the diacetate isomerization.<sup>1b</sup> The lower rate is caused by the delocalization of negative charge in the solvent sphere of the acetate ion pair.<sup>1</sup>

The above solvolysis reaction is formally analogous to base hydrolysis in water, with acetate replacing hydroxide as the lyate ion. It is well known that cationic cobalt(III)

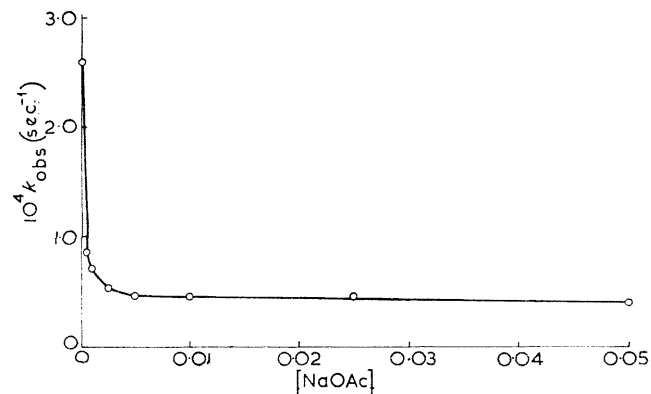


FIGURE. The solvolysis rate constant for  $\text{trans-}[\text{Co en}_2(p\text{-MeC}_6\text{H}_4\text{CO}_2)_2]\text{ClO}_4$  ( $10^{-2} \text{ M}$ ) in acetic acid at  $84.5^\circ$  as a function of  $\text{NaOAc}$  concentration.

ammines undergo hydrolysis by hydroxide at greatly enhanced rates as compared to the corresponding aquations.<sup>3</sup> The commonly accepted mechanism for the enhanced reactivity due to  $\text{OH}^-$  is the  $\text{S}_{\text{N}}1\text{CB}$  (conjugate base) mechanism<sup>3,4</sup> but other reasonable mechanisms have been suggested by Chan<sup>5</sup> (ion pairing) and Gillard<sup>6</sup> (redox equilibria).

There have been no studies of solvolyses of cobalt(III) ammines by lyate ions of solvents other than water. Enhanced rates of substitution by basic anions in methanol for the  $\text{Co en}_2\text{Cl}_2^+$  isomers have been attributed to methoxide ion formation;<sup>7</sup> however, these are much slower than aqueous base hydrolyses whereas the conjugate base mechanism would predict larger rates due to the lower dielectric constant of methanol.<sup>8</sup> The retardation of the rate of solvolysis of  $\text{trans-}[\text{Co en}_2(p\text{-MeC}_6\text{H}_4\text{CO}_2)_2]\text{ClO}_4$  in acetic acid, a water-like solvent of even lower dielectric constant ( $\epsilon = 6$ ), by addition of the lyate ion demonstrates that in this case the conjugate base mechanism does not apply, although a study of the same and related complexes in water gave the expected enhancements.<sup>2</sup> It is probable, therefore, that acetate is insufficiently basic to produce the conjugate base, and that the conjugate base mechanism may be unique to the more basic hydroxide ion (it has been shown that a  $\mu$ -amido-bridge may be introduced into  $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{4+}$  by concentrated aqueous alkali<sup>9</sup>). Solvolyses by base in solvents of low dielectric constant may be more appropriately treated through ion pairing phenomena.

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<sup>3</sup> F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd edn., John Wiley, New York, 1967, pp. 177—193.

<sup>4</sup> F. J. Garrick, *Nature*, 1937, **139**, 507.

<sup>5</sup> S. C. Chan, *J. Chem. Soc. (A)*, 1966, 1124.

<sup>6</sup> R. D. Gillard, *J. Chem. Soc. (A)*, 1967, 917.

<sup>7</sup> R. G. Pearson, P. M. Henry, and F. Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379 and 5382.

<sup>8</sup> Ref. 3, p. 210.

<sup>9</sup> M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, 1968, **90**, 615.