CROWN ETHER SALT CATALYSIS OF ESTER AMINOLYSIS IN AN APROTIC SOLVENT

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The $\text{RCO}_2^-$ catalyzed n-butylaminolysis of 4-nitrophenyl acetate in chlorobenzene has been studied. Logarithms of the catalytic rate constants can be linearly correlated with Taft polar substituent constants for the R groups. Product analysis as well as the lack of steric hindrance by bulky R substituents indicate that the carboxylates act as general base catalysts.

Carlom H3yqeH H-6yTHHaMHYH3 4-HHTpOdpeHHnaUeTaTa B xHop6eH3oJIe. YlorapHqbM KaTaHHTH- qeCKHX KOHCTaHT cKopOCTH JIHHel~HO 3aBHCHT OT IIOJ'I~IpHI,IX KOCTaHT 3aMeCTHTeJIe~ TaqbTa Ryl~I l"pyIIII R. AHa.IIH3 IIpoRyKTOB, a TaK~Ke OTCyTCTBHe cTepHqeCKHX IIpeIIJ:ITCTBHI~ O6~,e- MHCTblMH 3aMeCTHTeJ'~MH R yKa3b~BaeT Ha TO, tlTO Kap~OKCHYlaTI~I pea~py~oT KaK IlpH KaTa- YIH3e O~IJ.~MH OCHOBaHH~IMH.

Carboxylate catalyzed ester aminolyses in aprotic solvents are models for the action of carboxylates buried in hydrophobic areas of enzyme active sites and for the "active ester" method of amide bond formation /1, 2/.

To minimize synthetic and solubility problems emerging when using carboxylates as catalysts in aprotic solvents /3/ we have applied 18-Crown-6 (1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane) potassium carboxylate complexes to catalyze the n-butylaminolysis of 4-nitrophenyl acetate in chlorobenzene at 25 °C. The rates

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were followed spectrophotometrically by the method described earlier /4/. Besides, we have measured the electric conductivity of the complexes under the conditions of the kinetic experiments.

Catalyzed and uncatalyzed ester aminolyses take place according to a two-step mechanism involving the rate determining collapse of the intermediate /4/. In accord with recent findings /5/, I alone is an effective catalyst ($k_{cat} = 0.230 \text{ M}^{-2} \text{s}^{-1}$) of the n-butylaminolysis of 4-nitrophenyl acetate in chlorobenzene. Its carboxylate complexes $\text{I} \cdot \text{RCO}_2\text{K}$, however, exhibit enhanced catalytic abilities ($R = \text{CH}_3$, $k_{cat} = 5.32 \text{ M}^{-1} \text{s}^{-1}$).

Logarithms of the catalytic rate constants are in excellent correlation with the polar substituent constants /6/ of the R groups of the carboxylates (Fig. 1). The slight selectivity of the catalytic activity on the R substitution ($\rho^* = 0.18 \pm 0.01$; basicities of the carboxylates in water cover a range of more than five orders of magnitude /7/, yet, there is only an approximately 4-fold variation of the $k_{cat}$ values) might be attributed to a mechanism in which the rate is limited by the formation and not by the decomposition of the intermediate. This possibility is, however, ruled out by the fact that the observed rates are linear functions of the catalyst concentration /8/.

Fig. 1. log $k_{cat}$ vs. $\sigma^*$ of the R groups in $\text{I} \cdot \text{RCO}_2\text{K}$: 1. (CH$_3$)$_3$C, 2. (CH$_3$)$_2$CH, 3. CH$_3$CH$_2$, 4. CH$_3$, 5. C$_6$H$_5$CH$_2$, 6. ClCH$_2$, 7. CNCH$_2$, 8. Cl$_2$CH, 9. F$_3$C, 10. Cl$_3$C.