

Leaving-group Effects upon the Methanolyse of Benzoyl Halides in Acetonitrile

By D. N. KEVILL* and W. F. K. WANG

(Department of Chemistry, Northern Illinois University, DeKalb, Illinois)

It was recently suggested¹ that the mixed second- and third-order kinetics observed for the methanolysis of *p*-nitrobenzoyl chloride in acetonitrile involves in both kinetic schemes a deprotonation at the methanolic oxygen of an addition complex, (I), of the acid chloride and methanol, to give a new intermediate which then loses chloride in preference to methoxide. Similar kinetic patterns (initial reaction rates in M sec.⁻¹) have now been observed for the reactions with 0.01 M to 1.28 M methanol in acetonitrile at 0.0° of benzoyl chloride:

$$10^5 d[\text{HCl}]/dt = (1.02 \pm 0.03)[\text{PhCOCl}][\text{MeOH}] + (4.25 \pm 0.06)[\text{PhCOCl}][\text{MeOH}]^2$$

and of benzoyl bromide:

$$10^5 d[\text{HBr}]/dt = (37.3 \pm 1.3)[\text{PhCOBr}][\text{MeOH}] + (60.8 \pm 2.4)[\text{PhCOBr}][\text{MeOH}]^2$$

One feature of the suggested mechanism¹ is the absence of carbon-halogen bond fission until after the rate-determining step. On the other hand, if the reaction involved a synchronous bimolecular displacement² by either methanol monomers or methanol dimers or a synchronous bimolecular displacement with or without electrophilic assistance from a second methanol molecule³ then appreciable carbon-to-halogen bond fission would be present within the transition states of the rate-determining steps.

In aprotic solvents, such as acetonitrile, the rates of reactions involving extensive carbon-to-leaving-group heterolysis within the transition state of the rate-determining step are very dependent upon the nature of the leaving group^{4,5} and

leaving group effects in aprotic solvents can be an important criterion of mechanism. For example, bimolecular dehydrohalogenations of 2-benzyl-2-halogeno-4,4-dimethyltetra-1-ones in acetonitrile at 25.0° differ in rate by 1500 for chloride ion promoted elimination and by 1160 for bromide ion promoted elimination depending upon whether the halogen substituent is bromine or chlorine.⁴ Similarly, the reaction of 2-octyl bromide with silver nitrate in acetonitrile at 44.6° proceeds 450 times more readily than the corresponding reaction of 2-octyl chloride.⁶ The S_N2 Finkelstein reactions of methyl chloride and methyl bromide with dissociated halide ion, in acetone at 25.0°, have relevant rate ratios of 425 for exchange with chloride, 382 for exchange with bromide, and 438 for exchange with iodide.⁷

The much lower ratios of 37 for the second-order rate coefficients and 14 for the third-order rate coefficients observed in the present study do not indicate appreciable carbon-to-halogen heterolysis within the transition states of the rate-determining steps and they are consistent with leaving group influences being secondary effects upon the rate of formation of (I) and upon the partitioning of (I) between release of methanol and deprotonation at the methanolic oxygen.⁸ Since the leaving group effect is greater for deprotonation by acetonitrile (second-order kinetics) than for deprotonation by the more basic methanol (third-order kinetics), at least a part of the effect must be upon the partitioning of (I).

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