REACTION BETWEEN 4-NITROBENZOYL CHLORIDE AND 1-ETHYL-4-METHOXYCARBONYLPYRIDINYL RADICAL

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Abstract

Rates of reaction between benzoyl chloride and its 4-nitro derivative with 1-ethyl-4-methoxycarbonylpyridinyl radical in acetonitrile and 1,2-dimethoxyethane were measured. The reduction potential for 4-nitrobenzoyl chloride was also measured.

1-Ethyl-4-methoxycarbonylpyridinyl radical (py·) reacts with alkyl halides[1] and benzyl halides[2,3] by atom abstraction[1,2] and/or an electron transfer route.[3] All these halides have C–X (X = halogen) as sigma bond. In order to study the effect on the reaction rate of an C–X bond involving π bonds, benzoyl chloride and its 4-nitro derivative were selected. The solvent sensitivity of the reaction rates of py· with both, the substituted and the unsubstituted benzoyl chloride, and the reduction potential of 4-nitro derivative were determined.

Benzoyl chloride reacts with the pyridinyl radical, py·, with the rate constants $1 \cdot 65 \times 10^{-3}$ l. mol^{-1} s^{-1} and 2×10^{-4} l. mol^{-1} s^{-1} in acetonitrile (Z = 71·3) and 1,2-dimethoxyethane (Z = 59·1) respectively. These rate constants were calculated according to the (general) scheme given in equations (1) and (2):[1-3]

$$A+B \xrightarrow{\text{slow}} C+D \tag{1}$$

$$C+B \xrightarrow{\text{fast}} \text{products} \tag{2}$$
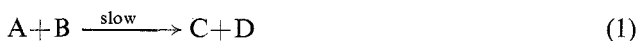
where B = py·; A = halide.

In Table 1, the kinetic results and other pertinent data are collected for benzoyl chloride and 4-nitrobenzoyl chloride (4-NBOCl) and these are compared with those of benzyl chloride and 4-nitrobenzyl chloride (4-NBCl).

The solvent sensitivity criterion for the two types of reactions (electron transfer and atom abstraction) have been established in the case of benzyl halide and 4-nitrobenzyl halides.[2,3] From the solvent sensitivity of the rate constants, given in Table 1, it is quite clear that the unsubstituted benzoyl chloride reacts with the radical through atom transfer while the 4-nitrobenzoyl chloride reacts with the radical through electron transfer.

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[1] Kosower, E. M., and Schwager, I., *J. Am. chem. Soc.*, 1964, **86**, 5528.

[2] Mohammad, M., and Kosower, E. M., *J. Am. chem. Soc.*, 1971, **93**, 2709.

[3] Mohammad, M., and Kosower, E. M., *J. Am. chem. Soc.*, 1971, **93**, 2713.

From the reduction potentials of the 4-nitrobenzoyl chloride (see Table 1) and 1-ethyl-4-methoxycarbonylpyridinum cation ($E_{1/2} = -1 \cdot 10$ against Ag/AgClO$_4$)[3] an equilibrium constant of about 30 l. mol^{-1} is obtained. Also, it is assumed that the rate constant for the decomposition of 4-nitrobenzoyl anion radical is greater than

TABLE 1

KINETIC AND ELECTROCHEMICAL DATA

Rate constants measured at 25°. Reduction potential measured against Ag/AgClO$_4$ (0·01M in acetonitrile with 0·1M tetra-n-butylammonium perchlorate)

Chloride	Rate constants (l. mol^{-1} s^{-1})		Reduction potential	Anion stability
	Acetonitrile[a]	1,2-Dimethoxyethane[a]		
Benzoyl	$1 \cdot 65 \times 10^{-3}$	$2 \cdot 0 \times 10^{-4}$	—	—
4-Nitrobenzoyl	6×10^3	30	$-1 \cdot 01$	unstable[b]
Benzyl[3]	$3 \cdot 31 \times 10^{-4}$	$5 \cdot 3 \times 10^{-6}$	—	—
4-Nitrobenzyl[3]	$2 \cdot 4 \times 10^4$	$8 \cdot 3$	$-1 \cdot 16$	unstable[c]

[a] In earlier work: for acetonitrile Z = 71·3; for 1,2-dimethoxyethane Z = 59·1. [b] No oxidation wave was found in cyclic voltammetry up to a scan rate of 20 V/s. [c] Rate constants in ref. 4.

10 s^{-1} but less than 10^3 s^{-1} (which is not unreasonable, since the C–Cl bond in benzoyl chloride is even stronger than in benzyl chloride; the anion 4-NBOCl$^-$ may have about the same stability as 4-NBCl$^-$).[4] These data are consistant with the mechanism I of Mohammad and Kosower[3] with k_2 (the rate of dissociation of py$^+$, NBOX$^-$, ion pair) about 10^2 s^{-1}.

Experimental

Preparation of the free radical and purification of solvents have been described earlier.[1-3] Benzoyl chloride and 4-nitrobenzoyl chloride were purified according to Perrin.[5] Benzoyl chloride was further purified by fractionation under high vacuum and the 4-nitro derivative by vacuum sublimation.

Kinetic and electrochemical measurements were carried out as described earlier.[2-4]

Acknowledgments

4 Mohammad, M., Hajdu, J., and Kosower, E. M., *J. Am. chem. Soc.*, 1971, **93**, 1792.

5 Perrin, D. D., Armarego, W. L. F., and Perrin, D. R., "Purification of Laboratory Chemicals," (Pergamon Press: Oxford 1966.)