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SOLVOLYSIS OF BENZOYL CYANIDES IN METHANOL-ACETONITRILE AND METHANOL-ACETONE MIXTURES.

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Abstract: Rate constants for solvolysis of benzoyl cyanides in methanol-acetonitrile and methanol-acetone mixtures were determined. Effects of substituent and solvent indicated that the reaction preceeds via an associative S_N2 mechanism.

Benzoyl cyanide is known to behave like an acyl halide rather than a keto nitrile.[1] To one's surprise however there has been hitherto very little work done on this aspect of benzoyl cyanide; while nucleophilic substitution of benzoyl halide is widely studied,[2] the report on the reaction of benzoyl cyanide is scarce or pratically non-existent to our knowledge. As a part of our works on nucleophilic substitution at a carbonyl carbon,[3] we have recently undertaken the study on nucleophilic substitution of benzoyl cyanide with special regards to assessing the relative leaving ability of cyanide group. In this work we report on the methanolysis of benzoyl cyanides in MeOH-MeCN and MeOH-$(Me)_2CO$ solvents, (1).

$$YC_6H_4COCN \quad + \quad CH_3OH \longrightarrow YC_6H_4COOCH_3 \quad + \quad HCN \qquad (1)$$

Substrates, YC_6H_4COCN where Y = p-CH_3, H and p-Cl, were prepared and purified by a well known method.[4] Identification of the prepared substrates and products analysis were performed using m.p.,[5] b.p.,[6] i.r.,[7] u.v., g.l.c. and titration of CN^- [8] and found to be in satisfactory agreement with literature values[9] or with expected values.

When a substrate was introduced into methanol, substrate peak at $\lambda = 263$ nm[10] diminished whereas product (methylbenzoate) peaks at $\lambda = 228$, 270 and 278 nm[11] grew progressively. Kinetic runs to determine pseudo-first order rate constants k were carried out using two independent methods to check the consistency; (i) by repetitive scanning of growth of the uv peak at $\lambda = 228$ nm and (ii) by conductivity measurements of the reaction mixture. Comparison of the two rate constants thus determined were found to agree within ±5 % with four determinations at two different solvent compositions (100 % and 70 % MeOH) and at two different temperatures (15 and 20°C). All subsquent determination of k values were done with conductometry.

Results are presented graphically in Fig. 1. Rate increases in general with the increase of

MeOH content, but distinct maximum behavior at ∿90 % MeOH is exhibited. This type of rate maximum has been shown to be a result of cooperative effect of polarity/polarizability (π^*) and hydrogen bond donor acidity (α) of the solvent mixtures;[12,13] this implies the importance of bond breaking as well as bond formation in the transition state since the effect of π^* is predominantly on bond formation while that of α is on bond breaking.[12]

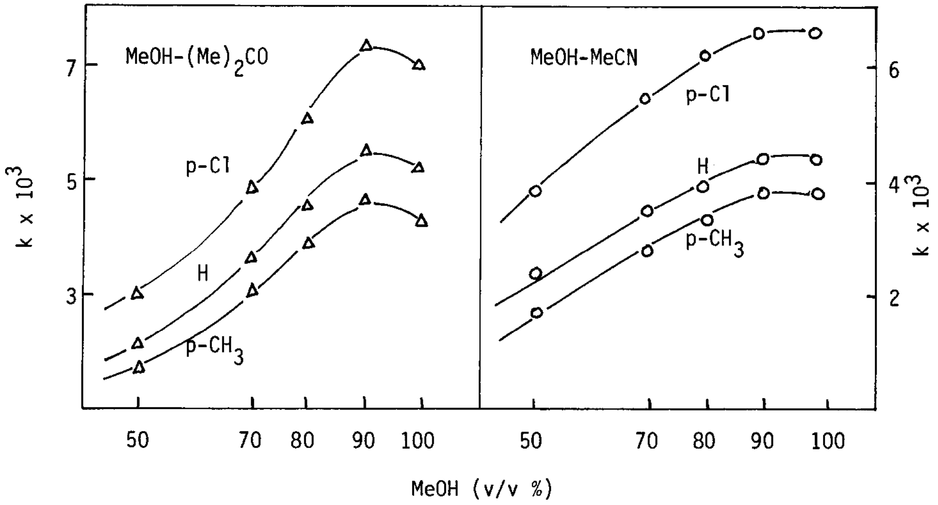

Figure 1. Plots of pseudo-first order rate constants vs. volume % of methanol for the reaction of para-substituted benzoyl cyanides in methanol-acetonitrile (25°C) and methanol-acetone (25.3°C) mixtures.

Table 1. Hammett ρ Values for the Solvolysis of para-Substituted Benzoyl Cyanides in Methanol-Acetonitrile and Methanol-Acetone Mixtures at 35°C.

MeOH (v/v %)	MeOH-MeCN		MeOH-(Me)$_2$CO	
	ρ	r	ρ	r
100	0.46	0.984	0.46	0.984
90	0.49	0.982	0.43	0.988
80	0.49	0.972	0.49	0.985
70	0.54	0.994	0.61	0.989
50	0.60	0.999	0.92	0.999

r:Correlation coefficients.

Hammett ρ values are summarized in Table 1. Inspection of this table reveals that the ρ is positive and increases with the increase of MeCN content, i.e., with the increase of π^* value. This is an indication that bond formation is favored by the more polar solvent.

If we assign virtually separate ρ values for the two processes, $\rho_{form} > 0$ and $\rho_{break} < 0$, the net effect is the prevailing contribution of bond formation; thus bond formation is ahead of

$$\rho = \rho_{form} + \rho_{break} > 0 \qquad (2)$$

bond breaking and bond formation is favored by the larger π^* value, i.e., by the more polar solvent. This is confirmed with a greater ℓ(0.60) compared to m(0.43) value[15] of the extended Grunwald-Winstein parameters.[16] Comparision of these with the corresponding values for benzoyl chloride solvolysis ($\ell = 0.46$ and $m = 0.31$)[17] shows that both bond formation and breaking at the transition state are somewhat greater in the benzoyl cyanide solvolysis, indicating slightly better leaving ability of CN^- as compared with Cl^-.

Fitting of rate data in MeOH-MeCN solvents[12] to the solvatochromic correlation (3) of Taft,[13]

$$XYZ = XYZ_o + a\alpha + s\pi^* \qquad (3)$$

gave following parameters at 25°C: p-CH_3, $a = 4.04$, $s = 2.82$; H, $a = 4.14$, $s = 3.14$; p-Cl, $a = 3.87$, $s = 3.48$. Thus susceptibility of k (XYZ in eq.(3)) to π^*, i.e., "s" is increased by an electron-withdrawing substituent whereas the susceptibility parameter "a" changes little. As a result the ratio a/s is decreased by the change of substituent from p-CH_3 to p-Cl. This can be interpreted as an increase of bond formation relative to bond breaking as the substituent is changed from p-CH_3 to p-Cl;[14] the greater the bond formation, the greater the charge separation and hence the more the transition state is stabilized by polar solvent (greater π^* medium).

We therefore conclude that methanolysis of benzoyl cyanide proceeds via an associative S_N2 mechanism.

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5. The m.p. of para-substituted benzoyl cyanides (literature values[9] are given in parenthesis)

were: p-CH$_3$, 47∿49°C (47∿49°C); H, 30∿31°C (30∿32°C); p-Cl, 37∿39°C (37∿39°C).

6. The b.p. of para-substituted benzoyl cyanides were: p-CH$_3$, 71∿74°C /0.1 mm; H, 95∿97°C /0.1 mm (105°C / 0.1 mm);[9] p-Cl, 103∿106°C / 0.1 mm.
7. Two i.r bands at 1670 cm^{-1} (-C=O) and at 2110 cm^{-1} (-C≡N) were identified.[9]
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