Substituent Effects on the Hydrolysis of *p*-Substituted Benzonitriles in Sulfuric Acid Solutions at (25.0 ± 0.1) °C

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The rate constants of the hydrolysis of *p*-substituted benzonitriles with sulfuric acid solutions (18.2 M to 10 M) have been determined spectrophotometrically at (25.1 ± 0.1) °C. It was found that the catalytic activity of sulfuric acid was strongly inhibited by water. The logarithms of the observed rate constants were correlated with different substituent inductive (localized) and resonance (delocalized) constants. The results of the correlation studies indicated that the rate-determining step of the hydrolysis of benzonitriles in 18.2 M sulfuric acid was the addition of a nucleophile, and the hydrolysis was clearly enhanced by the electron-withdrawing inductive effect, while the rate-determining step of the hydrolysis of *p*-substituted benzonitriles in 10.0 M sulfuric acid was most probably the protonation of benzonitriles, and the rate constants increased by both electron-donating resonance and inductive effects. A mixture of the two mechanisms most probably occurred in 15.3 to 17.0 M sulfuric acid. HSO_4^- rather thanwater most probably acted as nucleophile in the hydrolysis of benzonitriles especially at high concentrations of sulfuric acid solutions.

Key words: Sulfuric Acid; Benzonitriles; Hydrolysis; Rate Constants; Inductive Effect; Resonance Effect.

1. Introduction

It is known that the reaction of nitriles with sulfuric acid leads to the formation of amides [1 – 3]. Krieble and Noll [4] studied the hydrolysis of hydrogen cyanide and aliphatic nitriles in hydrochloric and sulfuric acids. They found that the hydrolysis of amides is several times faster than of nitriles in dilute acid solutions, whereas the relation is reversed in concentrated acid solutions, and concluded that sulfuric acid is a more poor catalyst than hydrochloric acid in the hydrolysis of nitriles.

Liler and Kasanovic [1] investigated the hydrolysis of benzonitrile in 100% sulfuric acid conductometrically at 25 °C and two mechanisms were proposed:

$$PhCN + 2H_2SO_4 \rightleftharpoons PhCONH_2 + H_2S_2O_7, \quad (1)$$

$$PhCN^+H + HSO_4^- + H_2SO_4 \rightleftharpoons PhCON^+H_3 + HS_2O_7^-. \quad (2)$$

Hydrolysis of benzonitrile [2] was studied over a wide range of temperatures (25 °C to 110.6 °C) and the data were analyzed on the basis of their acidity. Water was proposed to act as a nucleophile in the rate-determining step of the hydrolysis of benzonitrile.

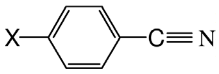


Fig. 1. Chemical structure of the benzonitriles studied. X = H, CH_3, OH, OCH_3, F, Cl, Br, I, CF_3, $N(CH_3)_3$.

The reactions of nitriles [3] were also investigated in 100% sulfuric acid by gas-liquid chromatography. The *N*-acylamidines and amides were formed, but the formation rate of amides increased by addition of potassium hydrogen sulfate or aromatic compounds. The formation of *N*-acylamidines was attributed directly to the presence of active sulfur trioxide.

The spectra of some *p*-substituted benzamides [5] in 18.2 M sulfuric acid at 25 °C showed the same or higher λ_{max} values (0 – 4 nm) than that of the corresponding benzonitriles and sulfuric acid when they were left in a UV cell for 24 h.

The most recent works on the hydrolysis of nitriles focused on the metal ion [6] and enzymatic [7, 8] hydrolysis.

The purpose of the present work is to study the substituent effects on the hydrolysis of benzonitriles in order to obtain more information about variations of the inductive and resonance effects and to suggest plau-

Table 1. Wavelengths (λ_1) of the hydrolyzed products of *p*-substituted benzonitriles chosen to monitor the absorbance variations with time and isosbestic points (λ_2) for the spectral curves.

Substituent	λ_1, nm	λ_2, nm	Substituent	λ_1, nm	λ_2, nm
H	250	235	CH_3	265	245
OH	276	254	OCH_3	288	259
F	260	236	Cl	262	246
Br	271	264	I	296	266
CF_3	241	229	$N(CH_3)_2$	240	226

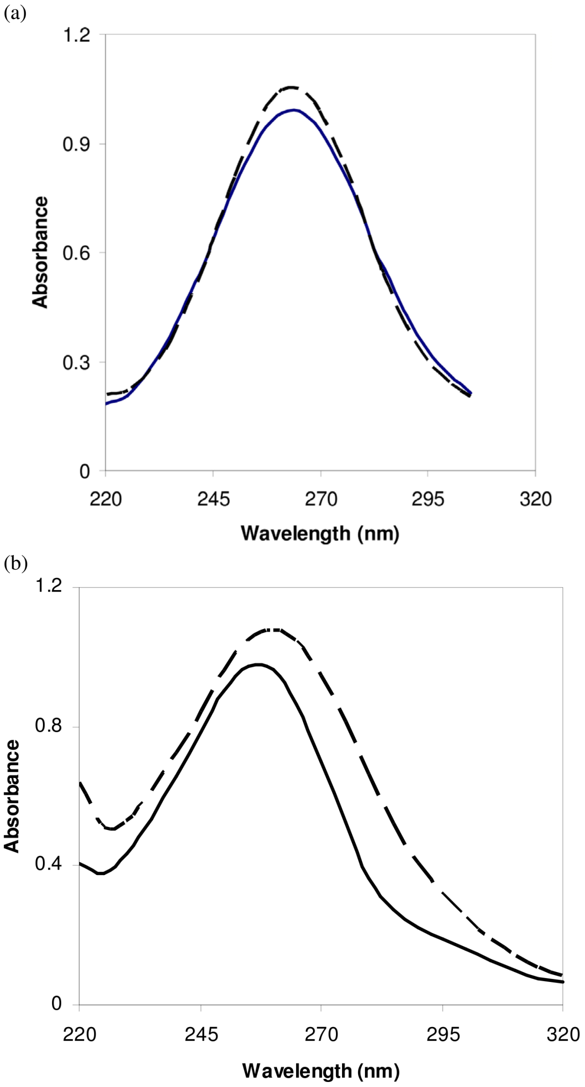


Fig. 2. (a) UV spectra for the hydrolysis of *p*-nitrobenzonitrile in 18.2 M sulfuric acid; solid line, at zero time; dashed line, after 6 h. (b) UV spectra of *p*-nitrobenzonitrile (solid line) and *p*-nitrobenzamide (dashed line) in ethanol.

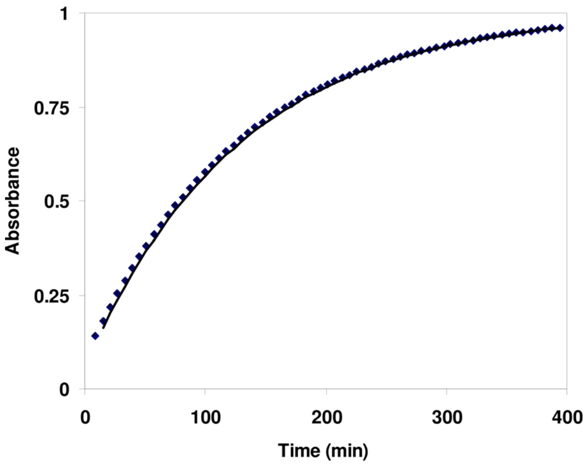


Fig. 3. The change of absorbance with time for the hydrolysis of benzonitrile in 18.2 M sulfuric acid. The solid line represents $A_t = (A_\infty - A_0)e^{-kt} + A_\infty$.

sible mechanisms congruent with experimental observations. Thus, the hydrolysis of several benzonitriles (Fig. 1) was carried out in sulfuric acid solutions at (25.0 ± 0.1) °C.

The hydrolysis of *p*-nitro-, *p*-acetyl- and *p*-formylbenzonitriles has not been included due to the fact that λ_{max} and the absorbance of these compounds are nearly the same as those of the products in sulfuric acid solutions (Fig. 2).

2. Experimental

2.1. Chemicals

Benzonitriles were purchased from Aldrich Chemical Company except for *p*-iodobenzonitrile which was bought from Kodak Company. Benzonitriles were 98 – 99% pure and were used without further purification. Sulfuric acid (98%) was obtained from BDH; its concentration was determined by titrating a sample against standard sodium hydroxide solution and found to be 18.2 M. Other solutions of sulfuric acid were prepared by diluting the 18.2 M sulfuric acid. Water used in this study was deionized and freshly redistilled from $KMnO_4$/NaOH.

2.2. Kinetic Measurements

Changes in the absorbance versus time (Fig. 3) were followed by monitoring absorbance variations of the product at the wavelength of minimum absorption of the corresponding *p*-substituted benzonitrile at (25.0 ± 0.1) °C. These wavelengths for different *p*-substituted benzonitriles in 18.2 M sulfuric acid are

Table 2. Observed rate constants (k_{obs}, 10^6 s^{-1}) for the hydrolysis of *p*-substituted benzonitriles by sulfuric acid at (25.0 ± 0.1) ℃.

Substituent	10.0 M	12.0 M	13.0 M	14.0 M	15.3 M	16.6 M	17.0 M	17.6 M	18.2 M
H	0.53 ± 0.01	2.82 ± 0.02	6.72 ± 0.02	11.59 ± 0.03	37.43 ± 0.04	68.55 ± 0.03	85.86 ± 0.05	107.20 ± 0.07	128.17 ± 0.08
CH_3	0.76 ± 0.02	3.68 ± 0.01	8.82 ± 0.02	14.35 ± 0.04	43.34 ± 0.03	76.90 ± 0.03	92.01 ± 0.04	110.26 ± 0.08	122.14 ± 0.09
OH	1.09 ± 0.01	5.38 ± 0.02	11.85 ± 0.03	18.17 ± 0.04	56.15 ± 0.02	100.51 ± 0.07	120.12 ± 0.07	151.99 ± 0.06	168.57 ± 0.04
OCH_3	1.06 ± 0.01	5.06 ± 0.01	10.99 ± 0.03	17.82 ± 0.05	55.68 ± 0.04	99.54 ± 0.03	121.71 ± 0.05	151.95 ± 0.06	168.32 ± 0.09
F	0.59 ± 0.01	3.01 ± 0.01	8.03 ± 0.01	13.07 ± 0.02	44.85 ± 0.03	84.52 ± 0.06	108.29 ± 0.04	146.13 ± 0.08	184.39 ± 0.06
Cl	0.50 ± 0.02	2.43 ± 0.02	7.20 ± 0.04	12.19 ± 0.03	42.19 ± 0.04	86.31 ± 0.03	110.00 ± 0.06	146.65 ± 0.08	189.45 ± 0.06
Br	0.48 ± 0.01	2.43 ± 0.03	6.71 ± 0.04	11.85 ± 0.02	42.98 ± 0.03	83.25 ± 0.04	108.82 ± 0.06	146.66 ± 0.06	190.42 ± 0.07
I	0.49 ± 0.01	2.38 ± 0.01	6.57 ± 0.02	11.65 ± 0.04	41.12 ± 0.05	78.38 ± 0.04	106.80 ± 0.04	142.92 ± 0.08	186.83 ± 0.09
CF_3	0.33 ± 0.02	1.70 ± 0.02	5.02 ± 0.03	9.87 ± 0.03	32.93 ± 0.03	70.65 ± 0.07	106.80 ± 0.05	130.64 ± 0.06	178.40 ± 0.08
$N(CH_3)_2$						74.66 ± 0.04	114.41 ± 0.07	159.80 ± 0.07	210.03 ± 0.05

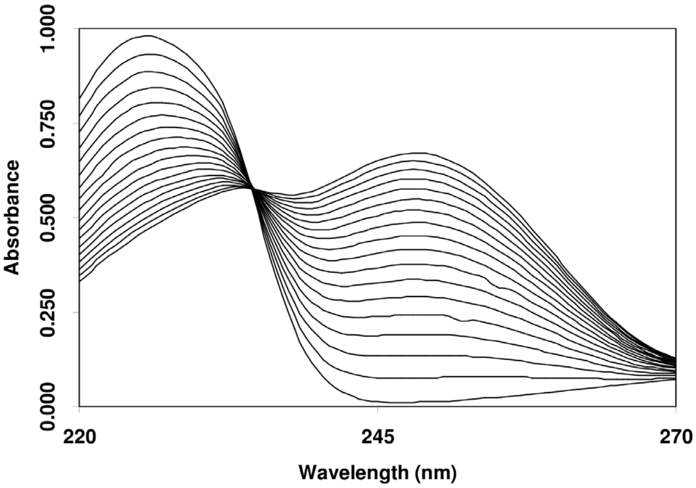


Fig. 4. UV spectra for the hydrolysis of benzonitrile in 18.2 M sulfuric acid (collected every 15 min).

shown in Table 1. The chosen wavelengths were not fixed in all solutions of sulfuric acid, for example, they decreased by 4 to 6 nm in 10 M sulfuric acid. Good isosbestic points for the spectral curves (Fig. 4) of all benzonitriles were observed (Table 1). The absorbance spectra were collected by using a Varian/Cary 2390 spectrophotometer connected with a data station (Varian DS-15) and a thermostat (Julabo F3). In each experiment, 3 mL of sulfuric acid solution were placed in a thermostated quartz cell. Then a 5 μL aliquot of stock solution ($5.0 \cdot 10^{-2}$ M) of the appropriate *p*-substituted benzonitrile, which was dissolved in HPLC methanol, was injected into the quartz cell. After rapid mixing, the absorbance of the solution was measured at appropriate intervals. The output of the absorbance versus time was stored automatically using a kinetic storage program (Varian 85-180081-00). The pseudo-first-order rate constants (observed rate constants) were calculated using a kinetic calculation program (Varian 180080-00) and found to be first-order with correlation coefficients higher than 0.999.

3. Results and Discussion

The observed rate constants (k_{obs}) for the hydrolysis of *p*-substituted benzonitriles have been determined in sulfuric acid solutions (18.2 M to 10.0 M) at (25 ± 0.1) ℃ (Table 2). Hydrolysis in sulfuric acid with concentrations smaller than 10 M are too slow to follow at (25.0 ± 0.1) ℃. All the spectra of the hydrolysis of *p*-substituted benzonitriles showed good isosbestic points indicating that only one product was formed during the hydrolysis of *p*-substituted benzonitriles. The hydrolysis of *p-N,N*-dimethylaminobenzonitrile has been studied only in 18.2 M to 16.6 M sulfuric acid solutions. Atomic and electronic energies of *p*-substituted benzonitriles and their protonated forms were calculated; *p-N,N*-dimethylaminobenzonitrile was found to be protonated at $(CH_3)_2N$ [9]. In addition, the substituent constants for $(CH_3)_2N^+H$ have not been reported.

The following conclusions were made by studying Table 2. First, the observed rate constants of *p*-

Table 3. Slopes, intercepts, correlation coefficients (R) and standard error (SE) of estimate of the plots of $\log k_{\mathrm{obs}}$ versus $\log\,[\mathrm{H_2SO_4}]$.

Substituent	Slope	Intercept	*R*	*SE*
H	9.4	−15.7	0.998	0.26
CH_3	8.8	−14.9	0.997	0.31
OH	8.7	−14.6	0.997	0.27
OCH_3	8.8	−14.8	0.998	0.27
F	9.8	−16.1	0.998	0.25
Cl	10.2	−16.6	0.998	0.27
Br	10.3	−16.7	0.998	0.27
I	10.2	−16.6	0.998	0.26
CF_3	10.9	−17.4	0.998	0.26

substituted benzonitriles decreased by decreasing the concentrations of sulfuric acid solutions. Second, the reactivity of *p*-tolunitrile in 18.2 M sulfuric acid was the smallest and of *p-N,N*-dimethylaminobenzonitrile it was the highest. This observation is in agreement with the hydrolysis of benzonitriles in 100% sulfuric acid at 40 °C, where the reactivity was found to decrease in the order: *p*-nitrobenzonitrile > *p*-chlorobenzonitrile > *p*-tolunitrile. Third, changing the substituents of benzonitriles had small effects on the rate constants, especially in solutions of sulfuric acid high concentrations. Finally, the hydrolysis rate of *p*-cyanophenol was the fastest while of *p*-triflouromethylbenzonitrile it was the slowest in 10 M sulfuric acid.

The above observations indicate that electron-withdrawing groups speed up the hydrolysis of benzonitriles in 18.2 M sulfuric acid, while they slow down the hydrolysis in 10.0 M solution. Therefore, the mechanism of the hydrolysis of *p*-substituted benzonitriles in 18.2 M sulfuric acid is different from that in 10.0 M sulfuric acid.

The relation between $\log k_{\mathrm{obs}}$ and $\log\,[\mathrm{H_2SO_4}]$ is expected to be nonlinear due to the following reasons. First, the hydrated sulfuric acid has different ratios of water molecules to sulfuric acid molecules depending on the sulfuric acid concentration. Second, two mechanisms for the hydrolysis of benzonitriles are expected. Third, the ratio of the activity coefficients in the rate law should not equal in all sulfuric acid solutions. However, the plots of $\log k_{\mathrm{obs}}$ versus $\log\,[\mathrm{H_2SO_4}]$ were found to be linear. The calculated numbers of molecules of sulfuric acid that are involved in the hydrolysis of *p*-substituted benzonitriles were found to be 9 to 11 (Table 3). This might be due to the bonding of sulfuric acid to the transition state through H-bonding. Hyland and O'Connor [2] suggested that the intermediate resulting from the reaction of benzonitrile and sulfuric acid is solvated by water molecules, but it seems that as the acid concentration increasing the water molecules of solvation would be gradually replaced by molecules of sulfuric acid.

In *para* derivatives of benzene the inductive and resonance effects can be expressed as the sum of two components [10, 11]. Therefore, the logarithms of the observed rate constants (k_{obs}) of *p*-substituted benzonitriles were correlated by using different inductive (localized) and resonance (delocalized) substituent constants. The correlations between $\log k_{\mathrm{obs}}$ against σ^{o} [11–13] and $\sigma_{\mathrm{p}}{}^{+}$ [12–14]; σ^{i} [15, 16] and $\sigma_{\mathrm{p}}{}^{+}$; σ_{I} and $\sigma_{\mathrm{R}}{}^{+}$; σ_{I} and $\sigma_{\mathrm{R}}{}^{(\mathrm{BA})}$ [17–21]; F and R^{+} [14]; F and R [14, 20, 21] were done. The best correlation coefficients (R) and standard error of estimates (SE) were obtained by applying F and R^{+} according to:

$$\log k_{\mathrm{obs}} = \log k_{\mathrm{H}} + \rho_F F + \rho_R + R^{+}. \tag{3}$$

The k_{obs} and k_{H} are the observed rate constants of *p*-substituted benzonitrile and the calculated rate constants of benzonitrile, respectively. $\log k_{\mathrm{H}}$ was obtained by solving (3). The maximum percentage differences between k_{obs} of benzonitrile and k_{H} did not exceed 5%. The values of $\log k_{\mathrm{H}}$, ρ_F and $\rho_R{}^{+}$ are shown in Table 4.

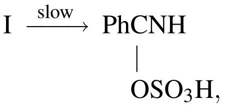
All these calculations indicate that the values of the reaction constants ($\rho_{\mathrm{P}}{}^{+}$ $\rho_R{}^{+}$ $\rho_R{}^{(\mathrm{BA})}$, $\rho_R{}^{+}$ and ρ_R) were negative, but these values were small in solutions of concentrated sulfuric acid. The values of reaction constants (ρ^{o}, ρ^{i}, σ_{I}, ρ_F, ρ_F) were negative in dilute sulfuric acid solutions and positive in concentrated sulfuric acid. The correlation coefficients and standard error of estimates in 15.3 M to 17.0 M sulfuric acid were not as good as those in lower or higher concentrations of sulfuric acid solutions. Two mechanisms for the hydrolysis of the *p*-substituted benzonitriles were predicted from these calculations and findings (Tables 2, 4). The first mechanism was in 18.2 M sulfuric acid, where the inductive (electron-withdrawing) effect is the only important factor. The second one was in 10.0 M sulfuric acid where the inductive and resonance (electron-donating) effects became important. The mixture of these two mechanisms was predicted in 15.3 to 17.0 M sulfuric acid.

The first mechanism for the hydrolysis of benzonitriles in 18.2 M sulfuric acid is suggested to explain the previous findings:

$$\mathrm{PhCN} + \mathrm{H_2SO_4} \rightleftharpoons \underset{\mathrm{I}}{\mathrm{PhCN^{+}HHSO_4{}^{-}}}, \tag{4}$$

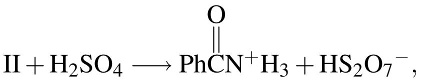
$[H_2SO_4]$, M	$\log k_H$	ρ_F	ρ_{R^+}	R	SE, 10^2
10.0	-6.25 ± 0.04	-0.39 ± 0.02	-0.35 ± 0.02	0.996	1.3
12.0	-5.55 ± 0.03	-0.38 ± 0.01	-0.33 ± 0.01	0.998	1.0
13.0	-5.16 ± 0.05	-0.2 ± 0.03	-0.25 ± 0.01	0.99	1.4
14.0	-4.92 ± 0.04	-0.14 ± 0.02	-0.19 ± 0.02	0.992	0.9
15.3	-4.42 ± 0.05	-0.02 ± 0.04	-0.16 ± 0.03	0.988	1.0
16.6	-4.16 ± 0.08	0.08 ± 0.01	-0.11 ± 0.02	0.977	1.0
17.0	-4.05 ± 0.10	0.18 ± 0.03	-0.06 ± 0.02	0.943	1.4
17.7	-3.97 ± 0.04	0.27 ± 0.4	0.06 ± 0.01	0.99	0.7
18.2	-3.9 ± 0.04	0.41 ± 0.03	0.00 ± 0.01	0.991	0.8

Table 4. Correlation between $\log k_{obs}$ of *p*-substituted benzonitriles with F and R^+ [14].



$$\mathrm{I} \xrightarrow{\text{slow}} \underset{\mathrm{OSO_3H},}{\mathrm{PhCNH}} \tag{5}$$

II



$$\mathrm{II} + H_2SO_4 \longrightarrow \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{N^+H_3} + HS_2O_7^-, \tag{6}$$

$$HS_2O_7^- + H_3O^+ \longrightarrow 2\,H_2SO_4. \tag{7}$$

100% H_2SO_4 comprises a dynamic equilibrium involving at least seven well-defined species. The contents of self-dissociation products in sulfuric acid at 25 °C are (values are given in mmol per kg solvent): HSO_4^- (15.0), $H_3SO_4^+$ (11.3), H_3O^+ (8.0), $HS_2O_7^-$ (4.4), $H_2S_2O_7$ (3.6), H_2O (0.1) [22]. The results of calculations show that the vapour pressure of sulfur trioxide becomes noticeable only at acid contents higher than 98% [23]. Therefore, the concentrations of the SO_3, $HS_2O_7^-$ and $H_2S_2O_7$ become negligible at 98% (18.2 M) H_2SO_4, while the concentrations of HSO_4^-, H_3O^+ and H_2O increase [22]:

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-, \; K_{H_2O} = \sim 1. \tag{8}$$

In the first step of this mechanism sulfuric acid reacts as a undissociated molecule with benzonitriles to form ion-pairs (I) or complex compounds. A complex with the formula $HCN \cdot H_2SO_4$ was previously isolated [2]. The concentration of the undissociated sulfuric acid becomes negligible below 14 M, whereas the concentration of 15.25 M corresponds to the 1 : 1 hydrate [22]. The addition of the nucleophile HSO_4^- is the rate-determining step. Similarly structure II was proposed for the reaction of hydrochloric acid with some nitriles [24, 25]. Previous work has shown that benzonitrile is a very weak base and is less than half protonated in 99.8% sulfuric acid [1]. The calculated value of pK_{AH}^+ for protonated benzonitrile was found to be -10.45 [2]. From the signs and magnitudes of the reaction constants that were obtained in this work the transition state structure III (Fig. 5) is suggested for the formation of II.

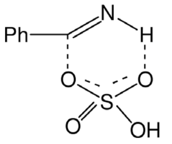


Fig. 5. Transition state structure III.

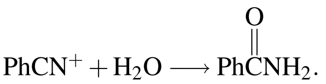
In the last step of the mechanism, $HS_2O_7^-$ reacts with H_3O^+ [22], because its concentration increases according to the dissociation of sulfuric acid with water (8):

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-, \; K_{id} = 5.1 \cdot 10^{-5}. \tag{9}$$

The second mechanism for the reaction of *p*-substituted benzonitriles with 10 M sulfuric acid is proposed to explain the signs and magnitudes of the reaction constants:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-, \tag{10}$$

$$PhCN + H_3O^+ \rightleftharpoons PhCN^+H + H_2O, \tag{11}$$



$$PhCN^+ + H_2O \longrightarrow \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH_2}. \tag{12}$$

The protonation of *p*-substituted benzonitriles and the addition of nucleophiles to protonated benzonitriles are slow. If the protonation of benzonitriles is the rate-determining step, the sings of the reaction constants are expected to be negative, but if nucleophilic addition is the rate-determining step then the sings of the reaction constants are positive. All calculated values of the reaction constants in 10 M sulfuric acid were negative. There are two possibilities to explain the signs of the reaction constants. First, protonation of benzonitrile is the rate-determining step, and therefore the signs of the reaction constants are negative. The nucleophile is most probably HSO_4^- but not water, at least at sulfuric acid concentrations higher than 10 M, since water activities [23, 26] of 10 M, 11 M, 13 M, 14 M, and 15.3 M are 0.10, 0.06, 0.03, 0.01, and 0.006, respectively. Second, if protonation of benzonitriles and nucleophilc addition are both slow, then the effect of the substituent on the stability of the protonated benzonitrile relative to benzonitrile itself is compensated by the opposite influence on the extent of nucleophilic attack on this conjugated benzonitrile. Therefore, the reaction constants can be expressed by the following equations:

$$\rho_{\mathrm{I}} = \rho_{(11))\mathrm{I}} + \rho_{(12)\mathrm{I}}, \tag{13}$$

$$\rho_R = \rho_{(11)R} + \rho_{(12)R}, \tag{14}$$

where the numbers are those of equations (11) and (12).

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