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Kinetics of the Reaction between Phenylacetonitrile and 2-Chloro-5-nitro-1-(trifluoromethyl)benzene under Phase-Transfer Catalysis Conditions

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The substitution reaction of chloride by phenylacetonitrile anion in 2-chloro-5-nitro-1-(trifluoromethyl)benzene under phase-transfer catalysis has been studied. The kinetic profile of the reaction has been investigated as a function of variables such as (a) concentration of the reaction mixture components in the organic phase, (b) catalyst structure and concentration, (c) aqueous hydroxide ion concentration, and (d) temperature. The results were used to evaluate the second-order rate coefficients (k) of the substitution reaction in the organic phase. A mechanism to rationalize the kinetic results is proposed.

Introduction

An important problem for synthetic organic chemists is the nucleophilic substitution reactions in which anions react with nonpolar organic reactants. In these cases an environment should be created that ensures sufficient contact between the ions and the neutral organic reactant and, at the same time, provides a medium that maintains the nucleophilicity of the anion. Anions are, usually, strongly solvated in hydroxilic solvents and therefore poor nucleophiles, but on the other hand, they are not very soluble in nonpolar solvents when they are in the form of salts of common inorganic cations, like Na^+ or K^+. In this case, the use of a two-phase system, water–organic solvent, with some agent, the so-called phase-transfer catalyst, to transfer the anionic nucleophile to the organic phase has become quite popular.[1,2]

Phase-transfer catalysis (PTC) allows the synthesis of many compounds from poorly reactive starting materials. An increase in the yields or selectivity is usually obtained.

In normal PTC systems, the main principle of catalysis involves the continuous formation of a lipophilic ion pair between the anionic reactant and a lipophilic cation such as a tetraalkylammonium ion. The pair is further extracted from the water or the interface to the organic phase where it can effectively react with the water-insoluble second reactant.[2]

A great number of various organic reactions, such as etherification,[3] N-alkylation,[4] alkylation[5,6] and autooxidation of weak carbon acids,[7] isomerizations,[8] H/D-exchanges,[9] nucleophilic aromatic substitutions,[10,11] and many others,[1,12] are carried out under the above conditions. Moreover, due to the great industrial importance of the processes that involve interfacial transfer, considerable work is being done on the field for a better understanding of this kind of systems.[13]

The reaction of carbanions with haloaromatic compounds offers important synthetic possibilities by providing a way to introduce a carbon skeleton in an aromatic ring often accompanied by the introduction or change of functionality.

The PTC mechanism for the reactions of carbanions with a variety of electrophiles was proposed by Makosza *et al.*[12] A crucial point is the formation of the carbanion by proton abstraction from the CH acid dissolved in a nonpolar solvent by the concentrate aqueous NaOH at the phase boundary. The generated carbanions, as sodium derivatives, remain adsorbed at the surface of the aqueous phase. They can not migrate into the organic phase because of their low solubility or into the aqueous phase due to the strong salting-out effect. The catalyst, a lipophilic cation, exchanges anions at the interface, and the new "fully lipophilic" ion pair migrates into the organic phase where the reaction occurs. The free catalyst can, again, undergo the ion exchange at the interface.

The interfacial mechanism was proposed[6] for the reaction of phenylacetonitrile with bromoethane. In this case, the deprotonation and subsequent anion transfer from the interface to the bulk organic phase is the rate-limiting step.

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Although several aspects of the mechanism of PTC under neutral conditions have been elucidated,[14] the mechanistic picture for the PTC reactions performed in the presence of a strong base is still uncertain.

In this work we have studied the reaction of 2-chloro-5-nitro-1-(trifluoromethyl)benzene (CNTFB) with phenylacetonitrile anion (Nu^-) under PTC. The reaction was performed in toluene as the organic phase in the presence of a concentrated solution of aqueous NaOH and tetraalkylammonium (Q^+X^-) salts as the catalyst. Nucleophilic aromatic substitution (S_NAr) of chlorine was observed. Different aspects of the mechanism have been quantified.

The aromatic substrate was chosen because of our interest in the reactivity of trifluoromethyl aromatic derivatives. This type of compounds is of particular concern to the organic chemist due to the diverse and important applications of these compounds as polymers, blood substitutes, pharmaceuticals and pesticides,[15,16] and potential precursors to the synthesis of carboxylic acids.[17] In previous reports we presented the study of this kind of substrates, in reactions of the S_NAr with aliphatic amines, under homogeneous conditions.[18]

Experimental Section

General. UV–vis spectra were recorded on a Hewlett-Packard HP 8452 spectrophotometer. The GLC measurements were performed on a Varian Aerograph 2800 flame ionization instrument; a stainless steel column (5 ft × 0.125 in.) 1.5% OV-101 on Chromosorb G-HP, (100–120 mesh) was used. NMR spectra were acquired at a 200-MHz Brucker spectrometer.

Starting Materials. 2-Chloro-5-nitro-1-(trifluoromethyl)-benzene (CNTFB) and cetyltrimethylammonium bromide (CTAB) from Aldrich, phenylacetonitrile (HNu) from Merck, and 1-methylnaphthalene, tetrabutylammonium bromide (TBAB), and tetrabutylammonium chloride (TBAC) from Fluka were used without further purification.

Toluene and dichloromethane of HPLC quality (Sintorgan) were used as received.

Procedures. The kinetic experiments were carried out in a 20-mL three-necked flask equipped with a condenser and a mechanical stirrer. The reactor was immersed in a water bath where the temperature could be controlled within ±0.1 °C.

To start a kinetic run, known quantities of HNu, CNTFB, and the tetraalkylammonium salt (Q^+X^-), dissolved in 5 mL of toluene were introduced into the reactor at the desired temperature. Stirring rates were adjusted by a rotor revolution counter to 1000 ± 50 rpm.

At time zero a measured quantity of a thermostatized aqueous NaOH solution was added to the reactor. At given times, the stirring was stopped, the two phases were allowed to separate, and an organic phase aliquot (20 μL) was withdrawn from the reaction mixture. The extracted sample was immediately diluted with 5 mL of dichloromethane and quenched with 0.2 mL of hydrochloric acid (30% v/v).

The content of the organic phase was quantitatively analyzed either by GC, using 1-methylnaphthalene as an internal standard, or by UV–vis spectroscopy.

Thus, the kinetics of the reactions were performed following the GC disappearance of the substrate with respect to the internal standard or the increase in the absorbance maximum of the product (λ_{max} = 360 nm).

The pseudo-first-order rate constants (k_{obs}) were obtained by a nonlinear least-squares fit of the experimental concentration vs time values.

Calculation of Φ. In order to calculate Φ (eq 16), experiments were carried out as described before but with no CNTFB added. The amount of $[Q^+Nu^-]$ in the organic phase was spectrophotometrically determined by using the strong UV absorption band of the carbanion, Nu^-, at λ_{max} = 340 nm. A calibration curve was constructed using solutions of Q^+Nu^- of known concentrations. The Nu^- was quantitatively generated from the carbon acid through reaction with an excess of clean sodium metal under nitrogen, following a similar procedure as described[19] for the quantitative generation of sodium methoxide. TBAB was added to maintain the anions in solution.

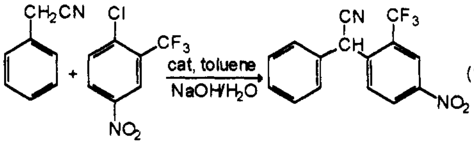
Preparative Synthesis of the Product. The CNTFB (8.0 mmol), phenylacetonitrile (17.6 mmol), and TBAB (0.34 mmol) were placed in a three-necked flask equipped with an efficient mechanic stirrer and a thermometer. After a short period of stirring, 4 mL of a 50% NaOH aqueous solution was added. The mixture was kept at 40 °C for 3 h. The crude mixture was extracted with dichloromethane and filtered on Florisil. Removal of the solvent and flash chromatography (silica gel, Merck, 60 mesh, eluent: petroleum ether–dichloromethane gradient) provided the compound, which was recrystallized from hexane–dichloromethane.

The neutral form of the product shows a UV–vis absorption band in dichloromethane at λ_{max} = 360 nm (log ϵ = 3.85) while its anionic form absorbs at λ_{max} = 560 nm.

The NMR spectra of the neutral product were as follows: ^1H NMR (200 MHz, DMSO-d_6, TMS) (ppm) = 6.15 (s, 1H, CH), 7.45 (m, 5H, C_6H_5), 8.00 (d, $1H_{arom}$, J = 8.9Hz), 8.50 (d, $1H_{arom}$, J = 2.9 Hz), 8.59 (dd, $1H_{arom}$, J = 8.9, 2.9 Hz); ^{13}CNMR (50.32 MHz, DMSO-d_6, TMS) δ (ppm) = 37.85 (C_{aliph}), 122.17 (–CF_3), 122.30 (–CN), 133.30 (–CNO_2), unassigned peaks in the range 127.64–129.40.

Results and Discussion

Kinetic Experiments. The reaction of CNTFB with phenylacetonitrile under PTC conditions afforded upon treatment with acid, phenyl[2-(trifluoromethyl)-4-nitrophenyl]acetonitrile (eq 1) in quantitative yield (>97%) as shown by TLC, GC, and UV–vis analyses of the reaction mixtures at infinite time.



(1)

In a typical procedure, CNTFB (2.30 mmol) was reacted with phenylacetonitrile (5.25 mmol) and TBAB (0.15 mmol, 9.4% w/w with respect to CNTFB) in 5 mL of toluene and 4 mL of NaOH (50% w/w), at different temperatures. In every case the reaction follows a good first-order kinetic. Representative results are shown in Table I. As can be observed, the kinetic data obtained by GC and UV–vis analyses are quite comparable (runs 1–5). It should be also noticed that there is no difference in the values of observed pseudo-first-order rate constant, k_{obs}, if the reaction is performed under room light or in the dark (runs 7 and 9) indicating that the reaction is not photosensitive. Moreover, when the reaction was followed by UV–vis as shown in Figure 1, an isosbestic point at 298 nm was observed, thus evidencing the cleanness of the reaction. Furthermore, the optical densities at infinite

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Table I. Typical Kinetic Data for the Reaction of CNTFB with Phenylacetonitrile under PTC Conditions[a]

no.	[HNu] (M)	T (°C)	Q	[NaOH] (% w/w)	$10^4 k_{obs}$[b] (s^{-1})	$10^4 k_{obs}$[c] (s^{-1})
1	0.25	40.0 ± 0.1	TBAB	50	0.64	0.63
2	0.82	40.0 ± 0.1	TBAB	50	1.63	1.57
3	1.24	40.0 ± 0.1	TBAB	50	2.46	2.52
4	1.65	40.0 ± 0.1	TBAB	50	3.48	3.56
5	2.45	40.0 ± 0.1	TBAB	50	4.78	4.84
6	1.05	26.0 ± 0.1	TBAB	50	1.50	
7	1.05	40.0 ± 0.1	TBAB	50	2.19[d]	
8	1.05	58.0 ± 0.1	TBAB	50	3.88	
9	1.05	40.0 ± 0.1	TBAB	50	2.17	
10	1.05	40.0 ± 0.1	TBAC	50	2.17	
11	1.05	40.0 ± 0.1	CTMAB	50	1.61	
12	1.05	40.0 ± 0.1	TBAB	47	0.36	
13	2.39	40.0 ± 0.1	TBAB	47	0.91	
14	1.05	40.0 ± 0.1	TBAB	68	11.39	

[a] 2.38 mmol of CNTFB in 5 mL of toluene and 4 mL of NaOH in water. [b] Kinetics followed by UV–vis spectroscopy. [c] Kinetics followed by GC. [d] Reaction performed in darkness.

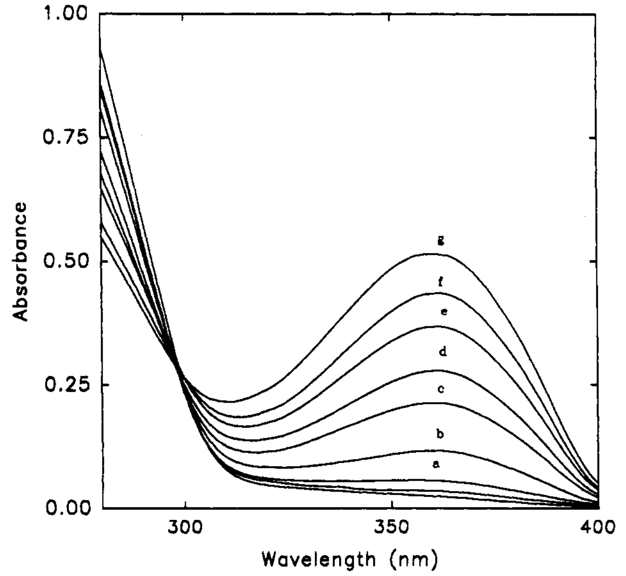

Figure 1. UV–vis characteristic spectra for the reaction of CNTFB with phenylacetonitrile. Conditions: run 9 in Table I for (a) 9, (b) 15, (c) 25, (d) 42, (e) 52, (f) 68, and (g) 88 min.

time were identical to those solutions prepared with standard phenyl[2-(trifluoromethyl)-4-nitrophenyl]acetonitrile on the basis of complete consumption of CNTFB. Thus, no evidence of a possible reaction[11] of this nucleophile with the nitro group of the aromatic substrate has been found.

An Arrhenius plot of the data at different temperatures (runs 6, 8, and 9 in Table I) allowed the calculation of the activation parameters, $\Delta H^{\ddagger} = 21 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -245 \pm 3$ J mol^{-1} K^{-1}. These values are consistent with the complexity of proposed mechanisms when carbanions are the nucleophiles.[3b,20]

In order to gain some insight on the mechanism of this reaction the influence of several variables were investigated as follows.

Concentration of Phenylacetonitrile. The kinetics of the reaction was studied at different phenylacetonitrile concentrations, keeping the other experimental conditions fixed. The experimental results are shown in Figure 2. As can be observed, the plot of the k_{obs} vs [HNu] shows a downward curvature.

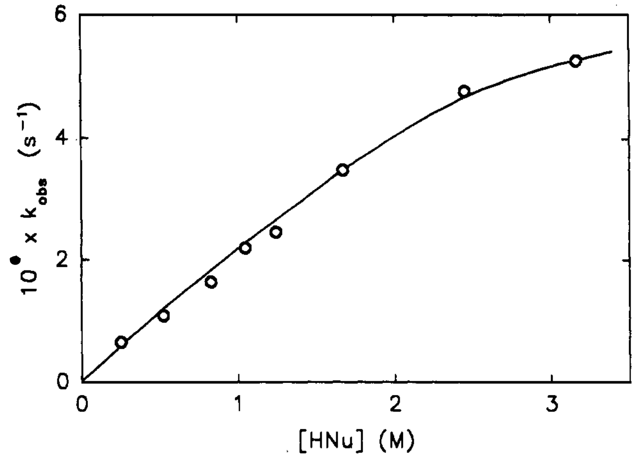

Figure 2. Dependence of k_{obs} upon the phenylacetonitrile concentration, [HNu]. Catalyst: TBAB. Temperature: 40 °C.

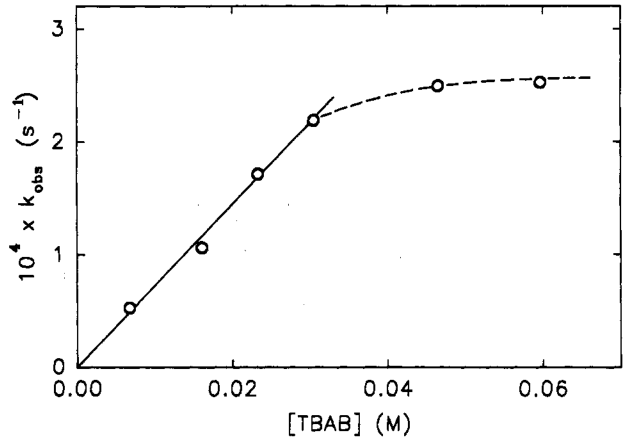

Figure 3. Dependence of k_{obs} with the catalyst concentration, [TBAB]. Conditions: 2.30 mmol of CNTFB, 5.24 mmol of phenylacetonitrile in 5 mL of toluene, and 4 mL of NaOH 50% w/w. Temperature: 40 °C.

Concentration of the Catalyst. When the kinetics of the reaction was studied by varying the concentrations of the catalyst, TBAB, the experimental results shown in Figure 3 were obtained.

Two different behaviors become apparent: (i) At low initial concentrations of catalyst, [Q°], a linear dependence on k_{obs} was found with a slope of $(7.13 \pm 0.44) \times 10^{-3}$ M^{-1} s^{-1}. Such linear tendency is characteristic when the HNu deprotonation occurs at the interface and the rate-limiting step is the nucleophilic substitution.[6] An indication that deprotonation occurs at the interface can also be obtained when neat HNu is poured, drop by drop, over the reaction mixture kept without stirring. Thus, the characteristic deep blue color of the product anionic form appears first at the phase boundary.

The intercept of the plot in Figure 3 is negligible, and it would correspond to an undetectable rate of the uncatalyzed reaction. An experiment performed without both catalyst addition and stirring showed that the blue product develops very slowly at the phase boundary where it finally remains. This experiment shows that the reaction at the interface, although much slower, also occurs.

(ii) Over a certain concentration of catalyst, ca. 10% (Figure 3), the reaction rate changes very little. This is probably because, under the given stirring and temperature

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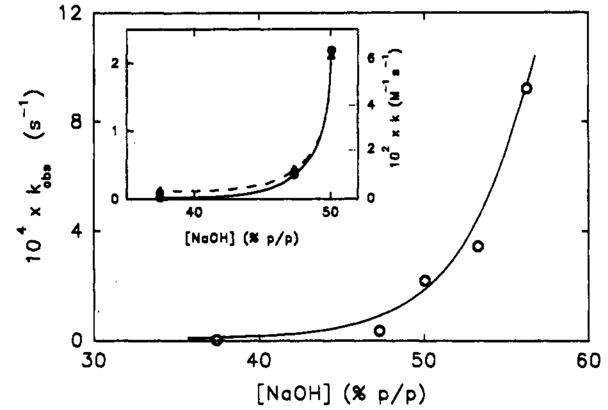

Figure 4. Dependence of k_{obs} on the NaOH concentration. Conditions: 2.30 mmol of CNTFB, 5.24 mmol of phenylacetonitrile, and 0.15 mmol of TBAB in 5 mL of toluene. Temperature: 40 °C. Inset shows the dependence of k_{obs} (O) and k (△) on NaOH concentration.

conditions, the mass transfer of the active species into the organic phase reaches a limiting value due to interface saturation. At this point, the addition of more catalyst will not help the reaction to proceed faster.

Nature of the Catalyst. Although most of the experiments in this work were performed using TBAB as the catalyst, kinetic runs were also carried out using tetrabutylammonium chloride (TBAC) and cetyltrimethylammonium bromide (CTMAB).

In these experiments, CNTFB (2.300 mmol), phenylacetonitrile (5.250 mmol), and catalyst (0.153 mmol) in 5 mL of toluene were stirred at 1000 rpm with 4 mL of the NaOH (50% w/w). The temperature was kept at 40 ± 0.1 °C. The values obtained for k_{obs} are depicted in Table I.

As was expected, no differences were found when bromide was replaced by chloride. However, the values for k_{obs} decreased when CTMAB was used.

It is known[2] that the larger the "lipophilic chain" in the alkylammonium salts the more effective the phase-transfer catalysts are, although the symmetry of the ion is also an important factor. For catalysts with only one long chain, such as CTMAB, it has been proposed[21] that they may form inverse micelles in this kind of system. The mechanism of catalysis in this case remains unclear, although it has been suggested[21] that under these circumstances extra water can be delivered into the organic phase, giving a weaker, "more hydrated" nucleophile and, therefore, a slower reaction. This explanation may account for our results with this catalyst.

Concentration of the Base. The effect of changing the NaOH concentration on the observed reaction rate constant is shown in Figure 4. Above [NaOH] ca. 45% an increase in base concentration produces a fast increase in k_{obs}. On the other hand, below this value, the k_{obs} is small and almost insensitive to the amount of water.

At high base concentration, dehydration of the organic phase by the hydroxide ions and an increase in the rate of the deprotonation–extraction steps might occur. Both effects agree with the explanation of the increase in the observed rate coefficient with the base concentration.

It should also be noted that at [NaOH] higher than 65% (run 14 in Table I) the rate of reaction seems to decrease again, probably due the lack of enough water to propitiate the mass transport of ions.[22]

Mechanism

For the S_NAr reaction between a given aromatic substrate (ArX) with an "in situ" generated nucleophile, by deprotonation of a weak acid precursor (HNu) with a strong base, and according to the hitherto presented kinetic data, the following mechanistic steps can be written

$$\mathrm{HNu_{int} + OH^-_{int} \overset{K}{\rightleftharpoons} Nu^-_{int} + H_2O_{int}} \quad (2)$$

$$\mathrm{Q^+X^-_{org} + Nu^-_{int} \overset{K_s}{\rightleftharpoons} Q^+Nu^-_{org} + X^-_{int}} \quad (3)$$

$$\mathrm{ArX_{org} + Q^+Nu^-_{org} \xrightarrow{k} ArNu_{org} + Q^+X^-_{org}} \quad (4)$$

$$\mathrm{ArX_{org} + Nu^-_{int} \xrightarrow{k^o} ArNu_{org} + X^-_{int}} \quad (5)$$

where the subscripts int and org indicate the interface and the organic phase, respectively. k and k^o are the second-order rate coefficients for the reaction of ArX with $Q^+ Nu^-_{org}$ and Nu^-_{int}, respectively.

K is the HNu acidity constant defined as

$$K = \frac{[\mathrm{Nu^-}]_{int}[\mathrm{H_2O}]_{int}}{[\mathrm{HNu}]_{int}[\mathrm{OH^-}]_{int}} \quad (6)$$

K represents the acid–base equilibrium at the phase boundary that produces the carbanion as Na^+ derivative. Usually, this carbanion cannot migrate either into the organic phase because Na^+ cannot move with carbanions or into the aqueous phase due to the strong salting out effect.[12]

K_s is the selectivity constant[2] for the extraction of Nu^- with respect to that of X^-, defined as

$$K_s = \frac{[\mathrm{Q^+Nu^-}]_{org}[\mathrm{X^-}]_{int}}{[\mathrm{Q^+X^-}]_{org}[\mathrm{Nu^-}]_{int}} \quad (7)$$

Other equilibria may be proposed as depicted in eqs 8 and 9. However, when possible, they are considered to be

$$\mathrm{Q^+X^-_{org} + OH^-_{int} \rightleftharpoons Q^+OH^-_{org} + X^-_{int}} \quad (8)$$

$$\mathrm{Q^+OH^-_{org} + HNu_{org} \rightleftharpoons Q^+Nu^-_{org} + H_2O_{org}} \quad (9)$$

quite shifted to the left because the very hydrophilic OH^- ions are difficult to extract in competition with the more lipophilic halide ions (X^-) and Nu^-.[2,12] Moreover, it has been shown that the hydroxide ion transfer to the organic phase only occurs when both very weak acids and the hydrophilic catalyst counterion HSO_4^- are involved.[8,9a,b] Thus, under the present experimental conditions the $[Q^+OH^-]_{org}$ may be negligible and the equilibria eight and nine will not be further considered.

The kinetic rate (r) for the substitution product formation should then be the contribution of two reactions,

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one that occurs in the organic phase bulk (eq 4) and another at the interface (eq 5).

$$r = -\mathrm{d}[\mathrm{ArX}]/\mathrm{d}t = (k[\mathrm{Q^+Nu^-}]_{\mathrm{org}} + k^\circ[\mathrm{Nu^-}]_{\mathrm{int}})[\mathrm{ArX}] \tag{10}$$

Actually, the reaction at the phase boundary (eq 5) seems to be much slower than the one assisted by the catalyst and can be ignored in eq 10. Besides, when the nucleophile precursor and the base are in great excess over the catalyst, it can be assumed that $[\mathrm{Q^+\ Nu^-}]_{\mathrm{org}}$ remains constant throughout the reaction and eq 10 can be written as follows

$$r = k_{\mathrm{obs}}[\mathrm{ArX}] \tag{11}$$

where k_{obs} is the observed first-order rate coefficient, given by eq 12

$$k_{\mathrm{obs}} = k[\mathrm{Q^+Nu^-}]_{\mathrm{org}} \tag{12}$$

Equation 13 can be obtained by application of the steady-state hypothesis to this mechanism and taking into account that $[\mathrm{Q^\circ}] = [\mathrm{Q^+X^-}]_{\mathrm{org}} + [\mathrm{Q^+Nu^-}]_{\mathrm{org}}$

$$k_{\mathrm{obs}} = \frac{kKK_{\mathrm{s}}[\mathrm{Q^\circ}][\mathrm{HNu}]_{\mathrm{int}}[\mathrm{OH^-}]_{\mathrm{int}}}{[\mathrm{X^-}]_{\mathrm{int}}[\mathrm{H_2O}]_{\mathrm{int}} + KK_{\mathrm{s}}[\mathrm{HNu}]_{\mathrm{int}}[\mathrm{OH^-}]_{\mathrm{int}}} \tag{13}$$

For the sake of simplicity, and in order to be compared with the experimental data, eq 13 can be written in the form of eq 14

$$k_{\mathrm{obs}} = \frac{k[\mathrm{Q^\circ}][\mathrm{HNu}]_{\mathrm{int}}}{\Phi^{-1} + [\mathrm{HNu}]_{\mathrm{int}}} \tag{14}$$

where $\Phi = KK_{\mathrm{s}}[\mathrm{OH^-}]_{\mathrm{int}}/[\mathrm{X^-}]_{\mathrm{int}}[\mathrm{H_2O}]_{\mathrm{int}}$

If it is assumed that $[\mathrm{HNu}]_{\mathrm{int}}$ is equal to the HNu concentration in the organic phase bulk, eq 14 predicts the behavior found in Figure 2. Actually, eq 14 fits the experimental data quite well (Figure 2, solid line) and allows us to calculate the values of $k[Q^\circ] = 1.92 \times 10^{-3}\ \mathrm{s^{-1}}$ and $\Phi = 0.125\ \mathrm{M^{-1}}$.

Estimation of the Intrinsic Second-Order Rate Coefficient. The intrinsic second-order rate coefficient, k (eq 4), for the $\mathrm{S_NAr}$ reaction in the organic phase can be obtained from two different kinds of data. From the nonlinear least-squares fit of the data in Figure 2 by means of eq 14, a value of $k = 6.29 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ for [NaOH] = 50% is calculated.

An alternative way involves the evaluation of k from the slope of the k_{obs} vs $[Q^\circ]$ plot according to eq 14. This procedure requires Φ at the working conditions to be known. In order to do that, experiments were performed under the same kinetic conditions but in the absence of the aromatic substrate, i.e., where only steps 2 and 3 of the mechanism can occur. Under this circumstance eq 15 can be written as

$$KK_{\mathrm{s}} = \frac{[\mathrm{Q^+Nu^-}]_{\mathrm{org}}[\mathrm{X^-}]_{\mathrm{int}}[\mathrm{H_2O}]_{\mathrm{int}}}{([\mathrm{Q^\circ}] - [\mathrm{Q^+Nu^-}]_{\mathrm{org}})[\mathrm{HNu}]_{\mathrm{int}}[\mathrm{OH^-}]_{\mathrm{int}}} \tag{15}$$

To get the value of Φ eq 15 should be rewritten as eq 16.

$$\Phi = \frac{KK_{\mathrm{s}}[\mathrm{OH^-}]_{\mathrm{int}}}{[\mathrm{X^-}]_{\mathrm{int}}[\mathrm{H_2O}]_{\mathrm{int}}} = \frac{[\mathrm{Q^+Nu^-}]_{\mathrm{org}}}{([\mathrm{Q^\circ}] - [\mathrm{Q^+Nu^-}]_{\mathrm{org}})[\mathrm{HNu}]_{\mathrm{int}}} \tag{16}$$

The concentration of $\mathrm{Q^+Nu^-}$ in the organic phase was spectrophotometrically determined while the $[\mathrm{HNu}]_{\mathrm{int}}$ was assumed to be the same as $[\mathrm{HNu}]_{\mathrm{org}}$. The Φ values obtained were 0.124, 0.093, and 0.020 $\mathrm{M^{-1}}$ for 50.0, 47.3, and 37.5% of NaOH, respectively. Thus, by the introduction of the proper value of Φ in the slope of the linear part of the k_{obs} vs $[Q^\circ]$ plot (Figure 3, eq 14) a value of $k = 6.17 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ for [NaOH] = 50% was obtained. As can be seen, good estimates for k within experimental error were obtained by two independent methods.

By an analogous procedure the k values were evaluated for other [NaOH]. The results were 1.31×10^{-2} and $0.35 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ for 47.3 and 37.5% of NaOH, respectively.

As can be seen in Figure 4 (inset), the intrinsic k follows the same trend of k_{obs}. This means that the main responsiblity for the observed changes in k_{obs} would lie in the variations of the carbanion nucleophilicity. It is known[22,23] that the higher water content in the organic phase, the higher degree of nucleophile hydration and, therefore, the lower its activity. This explains why the nucleophilicity of the ion pair in the organic phase, and consequently, the magnitude of k, sharply decreases with the level of hydration until saturation is attained.

Conclusions

The reaction between phenylacetonitrile and CNTFB in toluene in the presence of aqueous concentrated NaOH and a PT catalyst is a very clean reaction. The kinetic studies show that the formation of the carbanionic nucleophile occurs at the phase boundary. The latter is then introduced in the organic phase by the catalyst as an ionic pair. Under the conditions used a catalyst concentration of about 10% w/w of the substrate is sufficient to reach the highest rate. The catalytic power of the alkylammoniun salt used seems independent of the counterion but diminishes when it has a long lipophilic chain, like CTMAB.

The system is very sensitive to the base concentration, which mainly changes the degree of nucleophile hydration in the organic phase and consequently strongly affects the rate of reaction.

As a final remark, it can be stated that the reported data allowed us to draw a complete kinetic formulation of the reaction mechanism clarifying a rather foggy aspect in the literature.

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