Nonlinear Brønsted and Hammett Correlations Associated with Reactions of 4-Chloro-7-nitrobenzofurazan with Anilines in Dimethyl Sulfoxide Solution

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ABSTRACT: The kinetics and mechanism of nucleophilic aromatic substitution reactions of 4-chloro-7-nitrobenzofurazan **1** with 4-X-substituted anilines **2a–g** (X = OH, OCH_3, CH_3, H, I, Cl, and CN) are investigated in a dimethyl sulfoxide (Me_2SO) solution at 25°C. The Hammett plot of log k_1 versus σ is nonlinear for all the anilines studied due to positive deviations of the electron-donating substituents. However, the corresponding Yukawa–Tsuno plot resulted in a good linear correlation with $\sigma + r(\sigma^+ - \sigma)$. The corresponding Brønsted-type plot is also nonlinear, i.e., the slope (β_{nuc}) changes from 1.60 to 0.56 as the basicity of anilines decreases. These results indicate a change in a mechanism from a polar S_NAr process for less basic nucleophiles (X = I, Cl, and CN) to a single electron transfer for more basic nucleophiles (X = OH, OCH_3, and CH_3). The satisfactory log k_1 versus E° correlation obtained for the reactions of **1** with anilines **2a–d** in the present system is consistent with the proposed mechanism. Interestingly, the $\beta_{\text{nuc}} = 1.60$ value measured for **1** in Me_2SO reflects one of the highest coefficients Brønsted ever observed for S_NAr reactions. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 152–160, 2013

INTRODUCTION

Nucleophilic substitutions of 4-chloro-7-nitrobenzofuranzan **1** with a series of 4-X-substituted anilines have been investigated in 70–30 (v/v) and 20–80 (v/v)

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H_2O-Me_2SO mixtures at 25°C. The single electron transfer (SET) mechanisms were proposed on the basis of the large Brønsted coefficients ($\beta_{\mathrm{nuc}} = 0.93$–$0.96$) [1].

The main interest in these reactions is that it constitutes a rare example in which the magnitudes of β_{nuc} values are substantially higher than that reported for polar S_NAr reactions [2–9].

As an extension of this work and to obtain further information on reactivity and on the electron-transfer mechanism in S_NAr reactions, exhaustive kinetic studies of the same reactions in dimethyl sulfoxide (Me_2SO) at 25°C with a wider range of 4-X-substitued anilines (X = OH, OCH_3, CH_3, H, I, Cl, and CN) have been investigated. The second-order rate constants have been obtained and analyzed in terms of aniline basicity and of the electronic effect of the substituents X borne by these aniline nucleophiles.

Surprisingly, we found that the structure–reactivity relationships displayed later in Figs. 2 and 4 show clear evidence of nonlinear behaviors. As will be seen, the nonlinear Brønsted (log k_1 vs. pK_a) and Hammett (log k_1 vs. σ) plots were interpreted as a change in mechanism from a polar S_NAr process for electron-withdrawing substituents to a SET for electron donating according to Scheme 1 and support the view that values of β_{nuc} close to or greater than 1 may be an indicator of electron transfer in nucleophilic aromatic substitution reactions.

EXPERIMENTAL

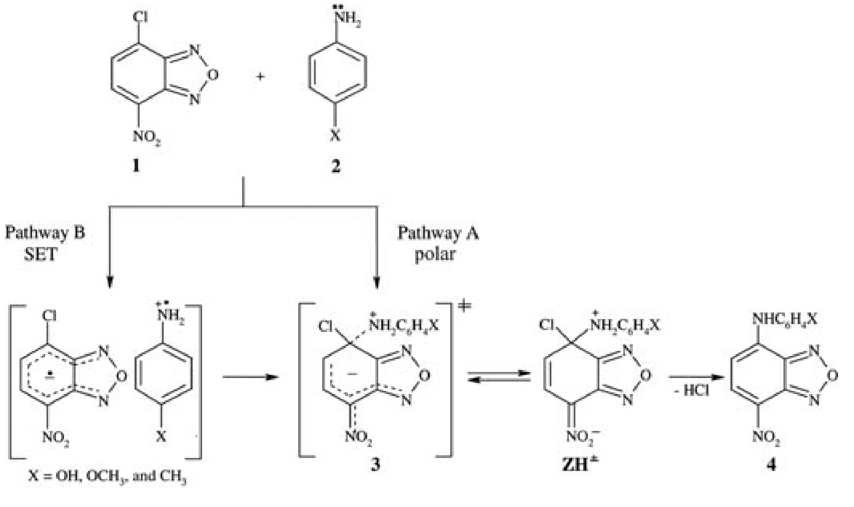
4-Chloro-7-nitrobenzofurazan **1** (Fluka BioChemica) was used as received. Anilines **2a–g** (Aldrich) were recrystallized or redistilled before use whenever necessary. Me_2SO was distilled over calcium hydride at a reduced pressure and was stored under nitrogen.

The kinetic study was performed using a Shimadzu UV–vis model 1650 PC spectrophotometer. All the reactions were carried out under pseudo–first-order conditions in the presence of excess aniline. Generally, the aniline concentration was varied over the range 1×10^{-3} to 8×10^{-1} mol dm^{-3}, whereas the 4-chloro-7-nitrobenzofurazan concentration was 3×10^{-5} mol dm^{-3}.

RESULTS AND DISCUSSION

Kinetic Studies

The S_NAr reactions of a number of 4-X-substituted anilines **2a–g** by 4-chloro-7-nitrobenzofurazan **1** have been kinetically studied in dimethyl sulfoxide at 25°C. In all experiments, only one relaxation time corresponding to the quantitative formation of the substitution products **4a–g** (482 nm < λ_{max} < 498 nm) was observed. A typical experimental is illustrated in Fig. 1, which shows the set of UV–vis absorption spectra, describing the progressive conversion of the



Scheme 1 A detailed possible mechanistic interpretation for the reaction of 4-X-substituted anilines **2a–g** with 4-chloro-7-nitrobenzofurazan **1** in Me_2SO at 25°C.

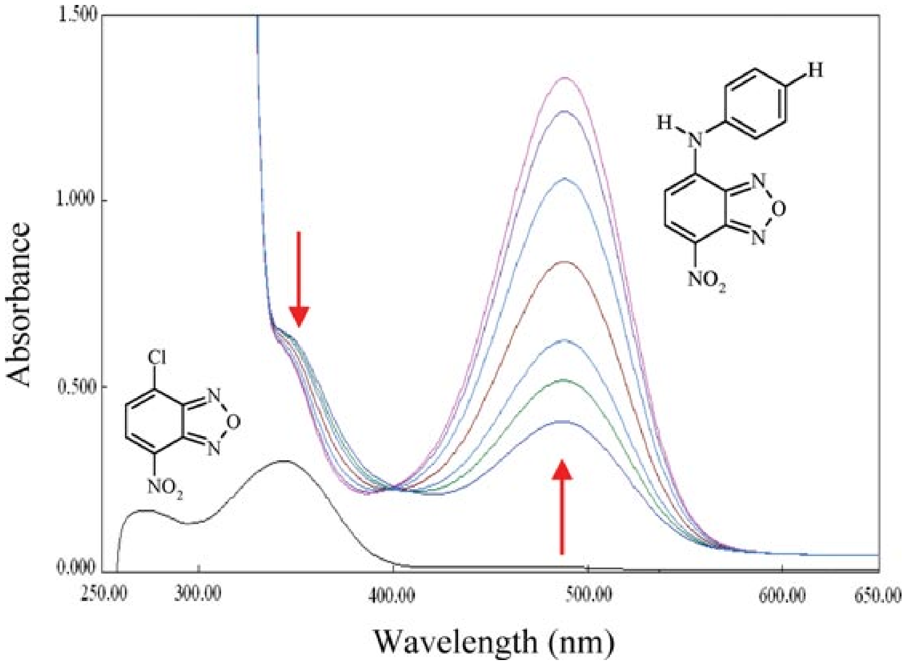


Figure 1 Reactions of 4-chloro-7-nitrobenzofurazan **1** (3×10^{-5} mol dm^{-3}) and aniline **2d** (10^{-2} mol dm^{-3}) by absorption spectroscopy in Me_2SO at 25°C. Scan interval = 25 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1 to the product **4d**. The process was found to be very clean, confirmed by the presence of an isobestic point at $\lambda = 400$ nm. Pseudo–first-order rate constants (k_{obsd}) were determined from the equation $\ln\,(A_\infty - A_t) = -k_{\text{obsd}}t + \ln(A_\infty - A_o)$. The correlation coefficient for the linear regression was usually higher than 0.9970 (see Table I). The plots of k_{obsd} versus the aniline concentration were linear ($R^2 > 0.9954$) passing through the origin, indicating that general base catalysis by the second aniline molecule is absent and confirming the first order of the reactions of **1** with **2a–g**. Moreover, the plots of log (k_{obsd}) versus log [**2a–g**]$_0$ were linear ($R^2 > 0.9968$) having slopes close to unity, indicating a first-order dependence of the reaction rate on [**2a–g**]$_0$ (see Fig. S1 in the Supporting Information).

All the reactions studied in this work followed the simple kinetic law given by Eq (1), where k_1 is the second-order rate constant for the aniline addition to the 4-chloro-7-nitrobenzofurazan **1**.

$$k_{\text{obsd}} = k_1\,[\mathbf{2a-g}]_0 \qquad (1)$$

The $k_1$values were determined from the slope of these linear plots. Generally six different aniline concentrations were used to determine k_1 values. The rate constants measured were reproducible to within ±5%. Kinetic data are summarized in Table I.

Brønsted Behavior and Mechanistic Interpretation

When the logarithm of the second-order rate constants, k_1, measured in dimethyl sulfoxide for the reactions of 4-chloro-7-nitrobenzofurazan **1** with 4-X-substituted anilines **2a–g** were plotted against the pK_a values of the conjugate acids of the anilines **2a–g** in the dimethyl sulfoxide solution [10,11] (see Table II), a plot, showing two straight lines exhibiting two different slopes, is obtained with a break observed for the unsubstituted aniline **2d** (Fig. 2).

As can be seen, the Brønsted-type plot for the reactions of 4-chloro-7-nitrobenzofurazan **1** is described by two linear relationships: The first line observed for electron-acceptor X-substituents ($\beta_{\text{nuc}} = 0.56$, p$K_\text{a} <$ 3.82) is defined by the following equation:

$$\log k_1 = -4.07 + 0.56\,\text{p}K_\text{a} \quad \left(R^2 = 0.9961\right) \qquad (2)$$

and the second straight line, for the electron-donating X-substituents ($\beta_{\text{nuc}} = 1.60$, p$K_a > 3.82$), is defined by

$$\log k_1 = -8.04 + 1.60\,\text{p}K_\text{a} \quad (R_2 = 0.9982) \qquad (3)$$

A careful examination of the literature showed that Brønsted plots highlighting two straight lines with two different slopes are rarely reported in S_NAr reactions.

Table I k_{obsd} and k_1 Values for the Reactions of 4-Chloro-7-nitrobenzofurazan **1** with 4-X-Substituted Anilines **2a–g** in Me_2SO at 25°C

X	[*p*-X-Aniline] (mol dm^{-3})	k_{obsd}(s^{-1})	k_1(mol^{-1} dm^3 s^{-1})	Correlation coefficient
OH	1×10^{-3}	1.39×10^{-3}	1.57	0.9954
	2×10^{-3}	3.19×10^{-3}		
	4×10^{-3}	7.16×10^{-3}		
	6×10^{-3}	1.01×10^{-2}		
	8×10^{-3}	1.32×10^{-2}		
	1×10^{-2}	1.53×10^{-2}		
OCH_3	5×10^{-3}	1.94×10^{-3}	4.40×10^{-1}	0.9986
	8×10^{-3}	3.17×10^{-3}		
	1×10^{-2}	4.45×10^{-3}		
	2×10^{-2}	8.31×10^{-3}		
	3×10^{-2}	1.37×10^{-2}		
	5×10^{-2}	2.16×10^{-2}		
CH_3	5×10^{-3}	4.13×10^{-4}	7.22×10^{-2}	0.9998
	8×10^{-3}	6.48×10^{-4}		
	1×10^{-2}	8.10×10^{-4}		
	2×10^{-2}	1.54×10^{-3}		
	4×10^{-2}	2.89×10^{-3}		
	6×10^{-2}	4.44×10^{-3}		
H	1×10^{-2}	1.12×10^{-4}	1.27×10^{-2}	0.9995
	2×10^{-2}	2.20×10^{-4}		
	4×10^{-2}	4.47×10^{-4}		
	6×10^{-2}	6.80×10^{-4}		
	8×10^{-2}	9.26×10^{-4}		
	2×10^{-1}	2.50×10^{-3}		
I	1×10^{-2}	3.58×10^{-5}	3.61×10^{-3}	0.9973
	2×10^{-2}	6.87×10^{-5}		
	4×10^{-2}	1.40×10^{-4}		
	5×10^{-2}	1.86×10^{-4}		
	6×10^{-2}	2.33×10^{-4}		
	8×10^{-2}	3.21×10^{-4}		
Cl	5×10^{-2}	2.32×10^{-4}	3.59×10^{-3}	0.9972
	1×10^{-1}	4.64×10^{-4}		
	2×10^{-1}	8.19×10^{-4}		
	4×10^{-1}	1.70×10^{-3}		
	5×10^{-1}	2.01×10^{-3}		
	6×10^{-1}	2.30×10^{-3}		
CN	1×10^{-2}	3.50×10^{-6}	4.16×10^{-4}	0.9967
	2×10^{-2}	8.20×10^{-6}		
	4×10^{-2}	1.50×10^{-5}		
	6×10^{-2}	2.63×10^{-5}		
	8×10^{-2}	3.15×10^{-5}		
	1×10^{-1}	4.20×10^{-5}		

Table II pK_a for Anilinium Ions in Dimethyl Sulfoxide Solution and Oxidation Potentials, E°, Values of the 4-X-Substituted Anilines **2a–g**

Aniline (X)	**2a** (OH)	**2b** (OCH_3)	**2c** (CH_3)	**2d** (H)	**2e** (I)	**2f** (Cl)	**2g** (CN)
pK_a	5.15[a]	4.75[a]	4.34[b]	3.82[b]	3.02[a]	2.79[b]	1.22[a]
$E°$ (V)[c]	0.76	0.79	0.92	1.02	1.02	1.01	–

[a] Values were determined by extrapolation using a relationship between pK_a and Hammett σgaluesg (similar pK_a vs. σ correlations are well documented in other systems [11] p.

[b] pK_a values of anilines are taken from [10].

[c] In aqueous solution, from [29].

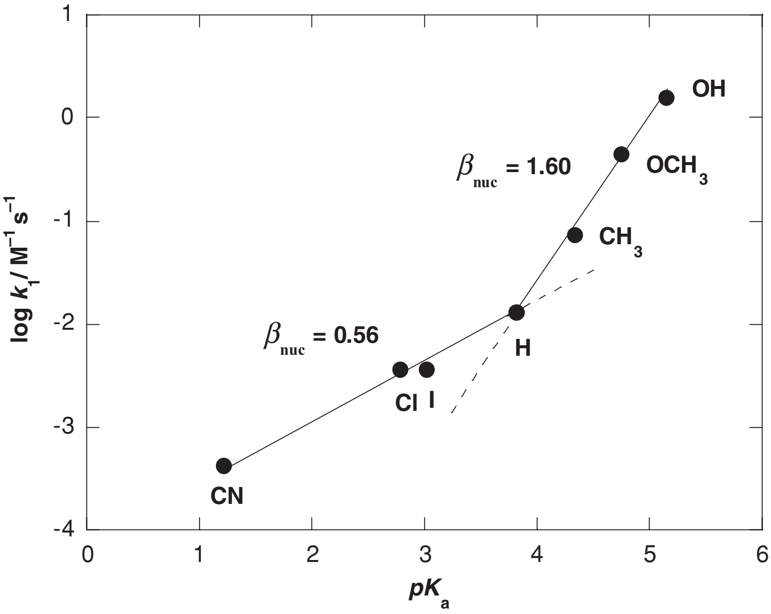


Figure 2 Brønsted-type plot for the reactions of 4-chloro-7-nitrobenzofurazan **1** with 4-X-substituted anilines **2a–g** in Me_2SO at 25°C.

However, nonlinear Brønsted-type plots have been reported for many nucleophilic substitution reactions [12–18]. Koh and coworkers, for example, have observed a curved Brönsted-type plot with β_{nuc} decreasing from 0.71 ± 0.03 to 0.21 ± 0.06 as the pyridine basicity increases for the reaction of methyl chloroformate with X-pyridines in acetonitrile, at 25°C [13b]. Um and coworkers investigated the reactions of O-4-nitrophenyl X-substituted thionobenzoates with substituted X-pyridines in 20 mol% Me_2SO at 25°C. Curved Brønsted plots are obtained with a change in slope from a large value ($\beta_x = 1.38 - 1.41$) to a small value ($\beta_x = 0.36 - 0.39$) at $pK_a = 9.30$, corresponding to the unsubstituted pyridine [15a].

The coefficient of Brønsted β_{nuc} (0.56), obtained for this series of anilines **2e–g**, is very close to those obtained by several authors in dimethyl sulfoxide [3,19–21]. Based on the fact that the magnitude of β_{nuc} values has been suggested to represent the degree of electron transfer at the rate-determining transition state [3,19–24], the measured β_{nuc} value of 0.56 (e.g., for reactions with electron-withdrawing substituents) suggests that at the transition state the degree of carbon–nitrogen bond formation is approximately half complete in the transition state and falling in the typical domain of polar nucleophilic aromatic substitutions mechanism (pathway A, Scheme 1) in which the formation of the zwitterionic σ-adduct ($ZH^{\pm}$) is the rate-determining step with fast decomposition of this intermediate into the substituted product **4**.

However, the β_{nuc} value of 1.60 (for reactions with electron-donating substituents) is greater than unity, definitively larger than value observed in the range of polar S_NAr reactions (from 0.50 to 0.70) [2–8]. It has to be noted that β_{nuc} values close to or greater than 1 have been observed for nucleophilic aromatic substitutions reactions, for example, $\beta_{nuc} = 1.43$ and 1.30 for a reaction of 3-methyl-1-(4-nitrobenzofurazanyl)-imidazolium ions with a series of 4-X-substituted anilines (X = NH_2, OCH_3, CH_3, and H) in H_2O-Me_2SO mixtures containing 30% and 80% Me_2SO, respectively [1]. $\beta_{nuc} = 0.95$ for the reaction of 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine with phenolate ions in aqueous solution has also been reported [25].

Terrier and coworkers have recently discussed the origin of the abnormally high β_{nuc} values and suggested that these values are the reflection of a possible contribution of a SET process [1]. On the other hand, it is well known that σ-complexation and S_NAr processes, involving strongly electron-deficient aromatic or heteroaromatic substrates, may proceed via the electron-transfer mechanism [3, 26–28].

Accordingly, the larger β_{nuc} value (1.60) obtained in the present work for electron-donor X-substituents (X = 4-OH, 4-OCH_3, and 4-CH_3) suggests a SET mechanism (pathway B, Scheme 1) in which the formation of the substitution products **4a–c** will then proceed through initial (fast) electron transfer from the aniline donor **2a–c** to the 4-chloro-7-nitrobenzofurazan **1**

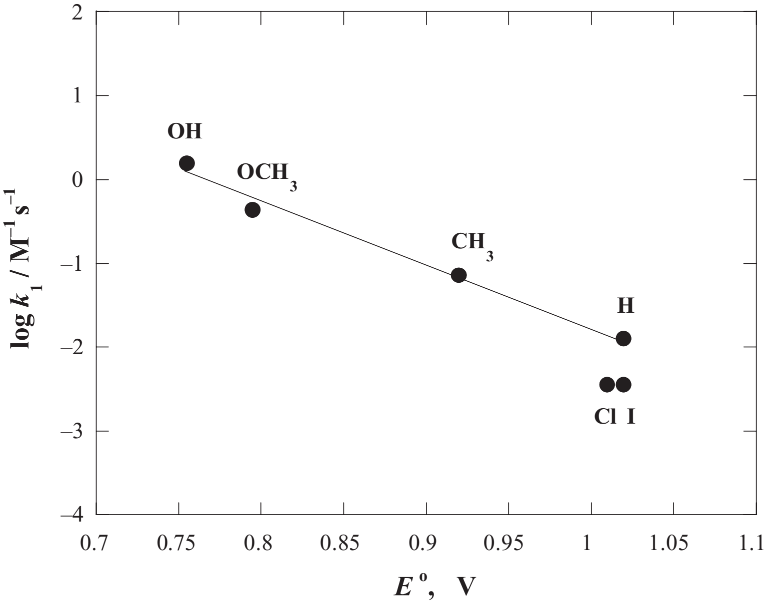


Figure 3 Influence of the oxidation potential, E^o, of anilines on the rate constants of reactions of 4-chloro-7-nitrobenzofurazan **1** with anilines **2a–f** in Me_2SO at 25°C. The identity of points is given in Tables I and II.

acceptor and subsequent (slow) coupling of the resulting cation and anion radicals within the solvent cage via the transition state **3**.

To support the above argument of a system proceeding through a SET mechanism, the measured rate constants, k_1, for the reactions of 4-chloro-7-nitrobenzofurazan **1** with anilines **2** have been plotted against the oxidation potential E° values of the 4-substituted aniline radical cations, as measured by Jonsson and coworkers in aqueous solution [29] (see Table II). As seen from Fig. 3, the plot of log k_1 versus E° is quite good and the corresponding relationship is

$$\log k_1 = 5.76 - 7.51\ E^\circ \quad (R_2 = 0.9935) \qquad (4)$$

The points for 4-iodoaniline **2e** and 4-chloroaniline **2f**, deviating from the linear plot, were not included in the determination of Eq. (4). This is a very significant result because this result is consistent with the preceding argument that the reaction of **2e** and **2f** proceeds through a different mechanism, for example, through a polar S_NAr mechanism. The same conclusion has been drawn from reactions of 4-chloro-7-nitrobenzofuranzan **1** with a series of 4-X-substituted in 30–70 (v/v) and 20–80 (v/v) H_2O-Me_2SO mixtures at 25°C [1].

Thus, it can reasonably be concluded that the linear log k_1 versus E^o plot associated with reactions of 4-chloro-7-nitrobenzofurazan **1** with 4-X-substituted anilines **2a–d** is more consistent with a SET than for a polar mechanism.

Substituent Effects and Origin of the Nonlinear Hammett Correlation

The susceptibility of the reaction of 4-chloro-7-nitrobenzofurazan **1** with para-X-substituted anilines **2a–g** can be highlighted by the study of the slopes of the Hammett plots (log k_1 vs. σ) [30]. In fact, the effect of substituent X on reactivity has been graphically illustrated in Fig. 4. As can be seen, the Hammett plot is nonlinear but consists of two intersecting straight lines, with a negative slope, $\rho = -5.75$ when $\sigma < 0$ and with a larger negative slope, $\rho = -1.97$ when $\sigma > 0$. We note that the kinetics of the same reactions performed in 20–80 and 70–30 (v/v) H_2O-Me_2SO mixtures have been reported by Terrier and coworkers, and in this latter case linear Hammett plots are obtained [1].

The magnitudes of ρ obtained in this present system are clearly consistent with the development of a positive charge at the nitrogen atom of the aniline moiety in the transition state for formation of the zwitterionic intermediate $ZH^{\pm}$ and appears to be highly dependent on the nature of the substituent X. In fact, the transmission of electronic effects is more significant for the reactions with electron-donating X-substituents ($\rho = -5.75$) than for electron-acceptor X-substituents ($\rho = -1.97$), clearly indicating a mechanistic change at $\sigma \approx 0$.

The ρ value of -1.97 shown in Fig. 4 is comparable to that reported for reactions that have been suggested to proceed through a polar nucleophilic aromatic substitution mechanism, for example, $\rho = -1.84$

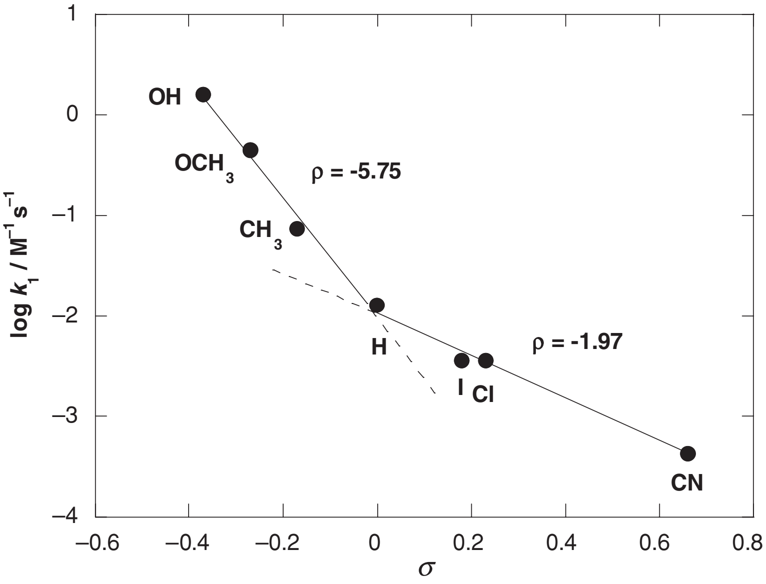


Figure 4 Hammett plot for the reactions of 4-chloro-7-nitrobenzofurazan **1** with 4-X-substituted anilines **2a–g** in dimethyl sulfoxide at 25°C. The identity of points is given in Table I.

for a reaction of 2,6-bis(trifluoromethanesulfonyl)-4-nitroanisole with anilines in acetonitrile [4] and $\rho = -1.70$ for a reaction of 2-chloro-5-nitropyridine with various arenethiolates in methanol [31]. However, the $\rho = -5.75$ value obtained with anilines **2a–c** appears to be a huge value for reactions that proceed through a polar nucleophilic aromatic substitution mechanism. Nevertheless, a similar ρ value has also been reported ($\rho = -5.27$) by Terrier and coworkers for substitution of 3-methyl-1-(4-nitrobenzofurazanyl)-imidazonium ions with a series of 4-X-substituted anilines (X = NH_2, OCH_3, CH_3 and H) in the 20–80 (v/v) H_2O-Me_2SO mixture [1].

It is interesting to note that our value of $\rho = -5.75$ obtained in Me_2SO is more negative than those measured for the same reaction in the H_2O-Me_2SO mixture: $\rho = -3.82$ and $\rho = -2.68$ in 80% and 30% Me_2SO, respectively [1]. This result agrees with the fact that the reaction must proceed through a dipolar transition state. On the other hand, the decrease in the ρ value from the H_2O-Me_2SO mixture to pure Me_2SO provides evidence that the solvation by H_2O through hydrogen bonding reduces the positive charge on the nitrogen atom in the transition state [32].

Deviations from Hammett plots based on standard σ galues have been rarely reported in S_NAr reactions, but have been commonly observed in the S_N2 process [33, 34]. Koh and coworkers, for example, investigated the reactions of substituted phenacyl bromides with pyridines in acetonitrile at 45°C and the curved Hammett plots have been interpreted in terms of a change in the rate-determining step from breakdown to formation of a tetrahedral intermediate [33a]. Recently, Um and coworkers have reported nonlinear Hammett plots for nucleophilic substitution reactions of *o*-4-nitrophenyl X-substituted thionobenzoates with benzylamine in 80% H_2O-20% Me_2SO at 25°C, which is interpreted as a stabilization of the groundstate of the substrate through a resonance interaction between the electron-donating substituent X and the thionocarbonyl moiety [34a].

The nonlinear Hammett plot shown in Fig. 4 has been analyzed using a Yukawa–Tsuno equation (Eq. (5)) in which r and $(\sigma^+ - \sigma)$ represent the relative extended value of the resonance contribution and the resonance substituent constant measuring the capacity for π-delocalization of a given π-electron donor substituent, respectively [35].

$$\log k_1^X / k_1^H = \rho(\sigma + r(\sigma^+ - \sigma)) \qquad (5)$$

As can be seen, the Yukawa–Tsuno plot (Fig. 5) for the reactions of 4-chloro-7-nitrobenzofurazan **1** with anilines **2a–g** exhibits a straight line ($R^2 = 0.9930$) with $\rho = -2.19$ and $r = 1.05$. Such a linear plot clearly indicates that the mesomeric stabilization is responsible for the nonlinear Hammett plot shown in Fig. 4. These results suggest that the structure of the aniline moiety in the transition state should be closely related to the radical cation ($XC_6H_4\overset{+\bullet}{N}H_2$).

It has to be noted that radical cations $R_1R_2\overset{+\bullet}{N}H$, have also been obtained in the reactions of picryl

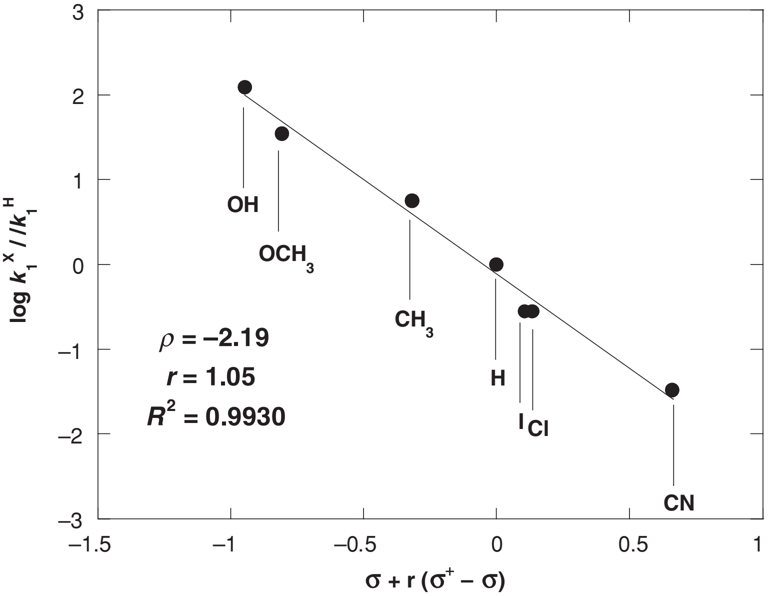


Figure 5 Yukawa–Tsuno correlation for reactions of 4-chloro-7-nitrobenzofurazan **1** with anilines **2a–g** in Me_2SO at 25°C. The σ and σ^+ values are taken from [30].

chloride with primary and secondary amines in dimethyl sulfoxide [20].

Thus, the results of the nonlinear Hammett plot in Fig. 4 reinforce the conclusions drawn above on the basis of the nonlinear Brønsted plot with a large $\beta_{\mathrm{nuc}} = 1.60$ value in Fig. 2.

CONCLUSION

The kinetic studies of the reactions of 4-chloro-7-nitrobenzofurazan **1** with substituted anilines **2a–g** have been carried out in a dimethyl sulfoxide solution at 25°C. The Hammett plot exhibits two intersecting straight lines, whereas the Yukawa–Tsuno plot for the same reaction is linear with ρ and r values of -2.14 and 1.10, respectively, indicating that the nonlinear Hammett plot is due to the stabilization of the transition-state through resonance between the radical moiety $XC_6H_4\overset{+\bullet}{N}H_2$ and the electron-donating 4-X-substituent ($X = OH, OCH_3$, and CH_3). The Brønsted-type plot is also nonlinear, i.e. the slope (β_{nuc}) changes from a small value ($\beta_{\mathrm{nuc}} = 0.56$) to a large value ($\beta_{\mathrm{nuc}} = 1.60$) at $pK_a = 3.82$. These results are consistent with a change in the mechanism from a polar S_NAr process to a SET. The excellent correlation of the reaction rates with the oxidation potential ($E°$) values is further evidence that reactions between **1** and anilines **2a–d** are proceeding by initial electron transfer. On the other hand, our larger $\beta_{\mathrm{nuc}} = 1.60$ value supports the proposal that values of β_{nuc} close to or greater than 1 may be an indicator of electron transfer in nucleophilic aromatic substitution reactions.

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