Reactivity and Mechanism of Phenoxide Anions Addition to 4-nitrobenzofurazan in Aqueous Solution

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Kinetic and Mechanism of Phenoxide Anions Addition to 4-nitrobenzofurazan in Aqueous Solution

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Abstract
Second-order rate constants \( (k_1) \) for the \( \sigma \)-complexation of 4-nitrobenzofurazan 1 with four 4-X-substituted phenoxide anions 2a-d \( (X = OCH_3, CH_3, H \) and Cl) were measured in aqueous solution at 20 °C. Using this series of phenoxide anions as reference, the electrophilicity parameters \( E \) of this electrophile 1 has been evaluated according Mayr’s approach. With the \( E \) value of -9.42, equation of Mayr was found to correctly predict the rate constants for the reactions of the 4-nitrobenzofurazan 1 with hydroxide ion in H\(_2\)O and 50% H\(_2\)O - 50% CH\(_3\)CN. On the other hand, the large \( \beta_{\text{nuc}} \) value of 1.12 obtained in the present work is clearly consistent with a single transfer electrons mechanism (SET).

Résumé
Les constantes de vitesse du second-order \( (k_1) \) afférentes à la réaction de \( \sigma \)-complexation du 4-nitrobenzofurazan 1 avec quatre anions phénate para-X-substitués 2a-d \( (X = OCH_3, CH_3, H \) et Cl) ont été mesurées en solution aqueuse à 20 °C. Ainsi, le paramètre d’électrophilie \( E \) du 4-nitrobenzofurazan 1 a été évalué selon l’approche de Mayr. Sur la base de la valeur de \( E \) obtenue (-9.42), les constantes de vitesse relatives à la réaction du 4-nitrobenzofurazan 1 avec l’ion hydroxyde dans H\(_2\)O and 50% H\(_2\)O - 50% CH\(_3\)CN ont été calculées et comparées à celles obtenues expérimentalement. Une réponse très anormale de la constante de vitesse \( k_1 \) aux changements de basicité \( (pK_{aH}) \) des anions phénates a été mise en évidence, avec une pente \( \beta_{\text{nuc}} = 1,12. \) A cet égard, un mécanisme de transfert d’électrons (SET) a été suggéré pour ce type de couplage.

Keywords: Mayr relationship, kinetics, electrophilicity, nucleophilicity, SET mechanism, \( \sigma \)-complexation, benzofurazan.

Introduction

We have recently reported that the rate constants of a series of 4-X-substituted phenoxide anions \( (X = CH_2O, CH_3, H \) and Cl) with a various substituted benzotriazoles chosen as reference electrophiles (1) are nicely described by the linear free energy relationship (Eq. (1)) (2). In this equation, \( E \) and \( N \) are the electrophilicity and nucleophilicity parameters, respectively, \( s_N \) is the nucleophile specific slope parameter and \( k \) is the second-order rate constant.

\[
\log k (20 \, ^\circ C) = s_N (E + N)
\]  

We now report a kinetic investigation in aqueous solution of the reaction of 4-nitrobenzofurazan 1 with four 4-X-substituted phenoxide anions 2a-d according Scheme I, in
order to evaluate the $E$ parameter of 4-nitrobenzofurazan 1 and to include it into the comprehensive electrophilicity scale. In addition, the effect of phenoxide anions basicity on reactivity and reaction mechanism is discussed.

Scheme I. $\sigma$-complexation reactions of the 4-nitrobenzofurazan 1 with the 4-X-substituted phenoxide anions 2a-d in aqueous solution at 20 °C.

Results and discussion

Structural Studies

The $^1$H nmr spectrum of 4-nitrobenzofurazan 1 in DMSO-d$_6$ at ambient temperature exhibits a triplet at 7.88 (H6) and two doublets at 8.70 (H5) and at 8.60 (H7) (see Table 1) (3). When mixing 1 equiv. of potassium phenoxide 2c (0.121 mmol) with 1 equiv. of 4-nitrobenzofurazan 1 (0.121 mmol) in DMSO-d$_6$ at ambient temperature a number of new resonances appear which allows the detection of two doublets at 5.36 and 4.94 ppm. These bands can be attributed to H-6 and H-7, respectively. Nevertheless, detection of H-5 was not possible because of overlapping resonance signals at averaged positions of 6.36 and 7.84 ppm corresponding to the aromatic protons of phenoxide anion.

Due to the competitive nucleophilic addition at both unsubstituted C-5 and C-7 positions (see structure in Table 1), the $^1$H NMR results obtained appears to be insufficient to discriminate between the two competitive pathways. However, comparison of the observed chemical shifts with those previously reported for the analogous $\sigma$-adducts (3-5), such as 3-Me and 3'-Me (3) (Table 1) facilitated structural characterization of the phenoxy-adduct 3c or 3c'. In fact, Table 1 clearly shows that, the chemical shifts obtained in the present work are close to those of corresponding protons in the methoxy-adduct 3-Me, i.e., phenoxide anion reacted with 1 to give an oxygen-bonded adduct by reaction at C-7 position.

It is interesting to note that the greater stability of the adduct 3c relative to her isomer 3c' can be explained in terms of an extensive delocalization of the negative charge through the NO$_2$ group in the position para to the sp$^3$ carbon C-7(6).
Another factor in favor of the addition of phenoxide anions on carbon C-7 preferentially than carbon C-5 of the 4-nitrobenzofurazan 1 is the recently proved change in the regioselectivity displayed by the aryloxide nucleophiles (ArO). In fact, Buncel and co-workers strongly favor the straightforward interpretation that C-7 ArO-adducts of 4-nitrobenzofuroxan are the products of both thermodynamic and kinetic control (7).

Table 1. $^1$H Chemical shifts (parts per million) for 4-nitrobenzofurazan $^1$ and related σ-adducts $^{3c}$, 3-Me$^b$ and 3'-Me$^b$.

<table>
<thead>
<tr>
<th>δ$^a$</th>
<th>1</th>
<th>3c' or 3c</th>
<th>3'-Me</th>
<th>3-Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>H7</td>
<td>8.60</td>
<td>5.36</td>
<td>7.02</td>
<td>5.33</td>
</tr>
<tr>
<td>H6</td>
<td>7.88</td>
<td>4.94</td>
<td>6.53</td>
<td>5.13</td>
</tr>
<tr>
<td>H5</td>
<td>8.70</td>
<td>-</td>
<td>5.50</td>
<td>7.16</td>
</tr>
</tbody>
</table>

$^a$ δ in ppm, internal reference TMS (tetramethylsilane).

$^b$ Chemical shifts taken from Ref. (3)

$^c$ This work.

Kinetic Measurements

The kinetics of the reactions of 4-nitrobenzofurazan 1 with phenoxide ions 2a-d according to Scheme I have been studied by UV-vis spectroscopy in aqueous solution at 20 °C. All experiments were carried out under pseudo-first-order conditions with a 5 x 10$^{-5}$ mol L$^{-1}$ concentration of 1 and a large excess of the phenoxide buffers (1 x 10$^{-3}$ to 1 x 10$^{-2}$ mol L$^{-1}$). Note that for a given buffer, two [4-X-phenoxide anion]/[ 4-X-phenol] buffer ratios have been used. In all cases, only one relaxation process corresponding to the formation of the σ-adducts 3a-d (325 nm < $\lambda_{\text{max}}$ < 340 nm) was observed. The observed pseudo-first-order rate constants, $k_{\text{obsd}}$, measured in aqueous solution at different phenoxide anion concentrations and different pH for the four reactions studies are summarized in Tables S1-S4 given as supplementary Information.

Because the reactions were carried out in water, competing reactions of electrophile 1 with hydroxide and water have to be considered. In these instances, the observed pseudo-first-order rate constants, $k_{\text{obsd}}$, reflect the sum of the reactions of the electrophile 1 with the phenoxide anion ($k_1$), OH$^-$ ($k_{\text{OH}}$), water ($k_{\text{H}_2\text{O}}$) and decomposition of adducts 3 ($k_1$) (Eq. (2)).
\[ k_{\text{obsd}} = k_1 [2a-d] + k_{\text{OH}} [\text{OH}^-] + k_{\text{H}_2\text{O}} + k_- \]  

(2)

As is apparent from Figure 1 for the reactions of phenoxide anions 2a and 2c with 1, the plots of \( k_{\text{obsd}} \) versus \([2a-d]\) were linear for any given phenoxide/phenol buffer with points determined at different pH falling on the same straight line. A similar result has been obtained for the corresponding reactions of phenoxide anions 2b and 2d (Figure S1). These results indicate that the contribution of \( \text{H}_2\text{O} \) and \( \text{OH}^- \) to \( k_{\text{obsd}} \) is negligible so that Eq. (2) reduces to Eq. (3).

\[ k_{\text{obsd}} = k_1 [2a-d] + k_- \]  

(3)

Accordingly, the \( k_1 \) and \( k_- \) values associated with the \( \sigma \)-complexation reactions of 4-nitrobenzofurazan 1 with these series of phenoxide 2a-d were determined from the slopes and intercepts of the linear plots and reported in Table 2.

---

**Fig. 1.** Effect of the phenoxide anions 2a and 2c concentration and pH on the observed first-order rate constants, \( k_{\text{obsd}} \), for formation of adducts 3a and 3c in aqueous solutions at 20 °C.
Table 2. Second-order rate constants, $k_1$, for coupling of 4-nitrobenzofurazan 1 with phenoxide anions 2a-d in aqueous solution at 20 °C.

<table>
<thead>
<tr>
<th>4-X-substituted phenoxide anion</th>
<th>$k_1^a$ / (M$^{-1}$ s$^{-1}$)</th>
<th>$k_1^a$ / (s$^{-1}$)</th>
<th>$N / s_N^b$</th>
<th>pK$_{aH}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a (X = CH$_3$O)</td>
<td>2.82</td>
<td>6.00 x 10$^{-3}$</td>
<td>10.22 / 0.62</td>
<td>10.27$^c$</td>
</tr>
<tr>
<td>2b (X = CH$_3$)</td>
<td>1.66</td>
<td>4.50 x 10$^{-3}$</td>
<td>9.69 / 0.61</td>
<td>10.19$^d$</td>
</tr>
<tr>
<td>2c (X = H)</td>
<td>5.74 x 10$^{-1}$</td>
<td>2.20 x 10$^{-3}$</td>
<td>9.00 / 0.60</td>
<td>9.88$^e$</td>
</tr>
<tr>
<td>2d (X = Cl)</td>
<td>2.38 x 10$^{-1}$</td>
<td>7.45 x 10$^{-4}$</td>
<td>8.45 / 0.62</td>
<td>9.35$^e$</td>
</tr>
</tbody>
</table>

$^a$ This work.

$^b$ Reactivity parameters $N$ and $sN$ taken from Ref. (1).

$^c$ Values of pK$_{aH}$ taken from Ref. (28).

$^d$ Value taken from Ref. (29).

Quantification of Electrophilicity Parameter $E$ of 4-nitrobenzofurazan

Examination of the data in Table 2 show that the second-order rate constants ($k_1$) for the σ-complexation reaction (Scheme I) appear to be significantly dependent on the nucleophilicity parameters $N$ of the phenoxide anions 2a-d. In fact, the effect of nucleophilicity $N$ on reactivity has been graphically illustrated in Figure 2. As can be seen, the relationship between $(\log k_1)/s_N$ and $N$ is linear and results in the following equation

$$(\log k_1)/s_N = -9.377 - 0.995 N \quad (r^2 = 0.9957) \quad (3)$$

From the intercept of this line with the abscissa axis, the electrophilicity parameter $E = -9.42$ has been derived for this electrophile 1. It is interesting to note that this value is in good agreement with that theoretically estimated ($E = -9.85$) from pK$_{aH}^{H_2O}$ via the relationship $E = -0.662$ pK$_{aH}^{H_2O} - 3.20$ (8, 9).

Comparison of Figure 3 shows that the 4-nitrobenzofurazan 1 displays an electrophilicity that compares well with that of benzyldienemalononitril (4, $E = -9.42$) (10), ion p-methoxybenzylidenemethyliminium (5, $E = -9.64$) (11) and 2-N-(4′-nitrophenyl)-4,6-dinitrobenzotriazole 1-oxide (6, $E = -9.56$) (1). On the other hand, our electrophile 1 is less reactive than the 4,6-dinitrobenzofuroxan (7, $E = -5.22$) (8) and 4,6-dinitrobenzofurazan (8, $E = -5.46$) (8) by more than 4 units of $E$. Figure 2 also shows that compound 1 is considerably more electron deficient structure than the 2-Methoxy-5-nitro-thiophene-3-carboxylic acid methyl ester (9, $E = -18.48$) (12), the ion N1-methyl-4-nitro-2,1,3-
benzothiadiazolium \((10, E = -15.77)\) (13) and the 1,3,5-trinitrobenzene \((11, E = -13.19)\) (8), the conventional aromatic electrophile in \(\sigma\)-complexation processes (14-19).

We note in particular that the small value of \(\Delta E = 0.62\) observed on going from 4-nitrobenzofurazan \(1\) to 4-nitrobenzofuroxan \((12, E = -10.04)\) (8) is similar to those estimated value of 0.40 going from 4,6-dinitrobenzofurazan \(8\) to 4,6-nitrobenzofuroxan \(7\). On the other hand, addition of a second nitro group on the carbocyclic ring of 4-nitrobenzofurazan \(1\) to form 4,6-dinitrobenzofurazan \(8\) is accompanied by a relatively strong increase in electrophilicity \(\Delta E \approx 3.96\), while that introduction of an oxygen to a nitrogen of 4-nitrobenzofurazan \(1\) to give 4-nitrobenzofuroxan \(12\) is slightly affected \(\Delta E \approx 0.62\). This result suggests that the effect of adding an N-oxide oxygen atom has a minor influence on electrophilic reactivity of the C7 position of 4-nitrobenzofurazan \(1\).

\[\text{Fig. 2. Correlation of the rate constants (log } k_1/s_N \text{) for the reactions of the 4-nitrobenzofurazane 1 with phenoxide anions 2a-d versus their nucleophilicity parameters } N \text{ in aqueous solution at 20 °C. The rate constants used for this Figure are given in Table 1.}\]
Fig. 3. Comparison of the electrophilic reactivity $E$ of the 4-nitrobenzofurazan 1 with those of other types of neutral and positively charged electrophiles.

**Reactions of 4-nitrobenzofurazan 1 with hydroxide ion**

The obtained $E$ parameter of 4-nitrobenzofurazan 1 can be used for semiquantitative prediction of rates constants of other organic reactions. In this context, we measured the rates of the reactions of the electrophile 1 with the hydroxide ion in 50% water - 50% acetonitrile at 20 °C. Some pertinent kinetic and $^1$H NMR data obtained for hydroxy adduct derived from 1 are available in Tables S5 and S6. On the other hand, using the electrophilicity parameters $E$ of the 4-nitrobenzofurazan 1 determined in this work ($E = -9.42$) and the nucleophilicity parameters $N$ and $s_N$ hydroxide ion in water and 50% water - 50% acetonitrile (20), the second-order rate constants values for the coupling reactions have been calculated by Eq. (1). The results are shown in Table 3 which also includes the experimental rate constants previously reported by Crampton and Co-workers (19) for the $\sigma$-complexation reaction of 1 with OH$^-$ in water.
Table 3 shows that Eq. (1) predicts the second-order rate constants for the C-O coupling of 4-nitrobenzofurazane 1 with hydroxide ion within a factor of < 22. It should be noted that here the agreement between calculated and experimental rate constants is satisfactory, because the validity confidence limit of linear free energy relationship (Eq. (1)) is generally a factor of 10-100 (21-23).

The deviations between calculated rate constants from the three parameters Eq. (1) and experimental rate constants have been observed by many authors (21-27). For example, the reactivities of series p-X-substituted benzylidenemalononitriles with hydroxide ions in 50% water-50% acetonitrile at 20 °C, Dhahri and co-workers (24) have been investigated and these authors have shown that experimental rate constants are 10 to 23 orders of magnitude higher than those calculated from Eq. (1). Appel and Mayr (27) have shown that Eq. (1) predicts the rate constants for the olefination reactions of the benzaldehydes with phosphoryl-stabilized carbanions and phosphorus ylide in dimethyl sulfoxide solution within a factor of 2-65.

Table 3. Comparison between experimental and calculated second-order rate constants, $k_1$, for the reactions of 4-nitrobenzofurazan 1 with hydroxide ion in H$_2$O and 50% H$_2$O-50% MeCN.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Solvent</th>
<th>$N/s_N$ a</th>
<th>$k_1^{exp}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_1^{calc}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_1^{calc}/k_1^{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>H$_2$O</td>
<td>10.47 / 0.61</td>
<td>0.2 b</td>
<td>4.37</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>50% H$_2$O-50% MeCN</td>
<td>10.19 / 0.62</td>
<td>12.9 c</td>
<td>3.00</td>
<td>0.23</td>
</tr>
</tbody>
</table>

a $N$ and $s_N$ values taken from Ref. (20).
b T = 25 °C see Ref. (19).
c This work.
d The values of $k_{calc}$ were calculated in this work from known $E$, $N$ and $s_N$ values indicated in the table through the log $k$ vs. $s_N$ ($E + N$) (2).

Brönsted Behaviour and Mechanistic Interpretation

As shown in Table 2, the second-order rate constant, $k_1$, value for the reactions of 1 with the phenoxide anions 2a-d decreases as the basicity of phenoxide decreases, e.g., $k_1$ decreases from 2.82 M$^{-1}$ s$^{-1}$ to 2.38 x 10$^{-1}$ M$^{-1}$ s$^{-1}$ as the pK$_{aH}$ of the conjugated acid of phenol increases from 9.35 to 10.27. The effect of phenoxide anion basicity on the reactivity is illustrated in Figure 4 by the satisfactory linear correlation obtained in plotting the logarithm rate constants, $k_1$, versus the pK$_{aH}$ values for the conjugate acids of phenol in aqueous solution (28, 29).
The $\beta_{\text{nuc}}$ value of 1.12 obtained in the present work is distinctly larger than that values observed in the range of polar $\sigma$-complexation and $S_N$Ar reactions (from 0.50 to 0.70) (30). This suggested that the reaction between the 4-nitrobenzofurazan 1 and these series of phenoxide anions 2a-d might not be a simple $\sigma$-complexation process. We note that similar $\beta_{\text{nuc}}$ value of 1.22 for the reaction of 2-chloro-5-nitropyridine 13 with various phenoxide anions in methanol has also been reported (31). Recently, various para-substituted anilines have been used as reference nucleophiles in various types of reaction (13, 32-34) to determine Brönsted $\beta_{\text{nuc}}$ values, which were proposed to proceed through a single electron transfer mechanism (SET). For example, $\beta_{\text{nuc}}$ of 1.60 and 1.24 have been reported for reaction of acceptor-substituted anilines, respectively, with 4-chloro-7-nitrobenzofurazan 14 in dimethyl sulfoxide solution (32), and benzothiadiazolium cation 10 in acetonitrile (13).

A possible explanation for such $\beta_{\text{nuc}}$ value of 1.12, is to assume that the C-O couplings proceed through a single electron transfer mechanism (Scheme II). The formation of the $\sigma$-adducts 3a-d proceed through initial (fast) electron transfer from the 4-X-substituted

\[ \log k_1 = -11.12 + 1.12 \log K_{\text{aH}} \]  
\[ R^2 = 0.9719 \]
phenoxide anions 2a-d to the 4-nitrobenzofurazan 1 acceptor and subsequent (slow) coupling of the resulting neutral radical 2• and anion radical 1• within the solvent cage via the transition state 15.

To support this hypothesis, the logarithmic values of second-order rate constants, k₁, measured in this work have been plotted against the oxidation potentials E° (in volts vs NHE) values of the para-substituted phenoxide radical reported by Li and co-workers in aqueous solution (E° (2a) = 0.58 V, E° (2b) = 0.71 V, E° (2c) = 0.86 V and E° (2d) = 0.85 V) (35). As is apparent from Figure 5, excellent log k₁ vs. E° correlation was obtained. The log k₁ vs. E° plot is described by the following relationships

\[ \log k_1 = 1.92 - 2.48 E^\circ \]  
\[ (R^2 = 0.9889) \]  
(4)

We note that the point for 4-chlorophenoxide anion 2d exhibit negative deviation from the linear plot was not included in determination of equation (4). This is because both phenoxide 2c and 4-chlorophenoxide 2d anions have very comparable redox potentials. A similar result has been obtained for the corresponding reactions of the 3,5-dinitrothiophene and 3-cyano-5-nitrothiophene (36).

Consequently, it is reasonable to conclude that the \( \sigma \)-complexation reactions of 4-nitrobenzofurazan 1 with these series of 4-X-substituted phenoxide anions 2 proceed through a SET mechanism.

**Scheme II.** Possible mechanistic pathway for the reactivity of 4-nitrobenzofurazan 1 with 4-X-substituted phenoxide anions 2a-d in aqueous solution at 20 °C.
Conclusion

The present study has allowed us to conclude following: (1) The $\sigma$-complexation reaction of 4-nitrobenzofurazane 1 with a series of 4-X-substituted phenoxide ions 2a-d (X = OCH$_3$, CH$_3$, H and Cl) is nicely described by Mayr’s equation (Eq. (1)). (2) The electrophilicity parameter $E$ value for this electrophile 1 has been determined in water at 20 °C: $E$ = -9.42. (3) The second-order rate constants for the reactions of 4-nitrobenzofurazane 1 with OH$^-$ in water and 50% water - 50% acetonitrile were calculated by the correlation log k (20 °C) = $s_N$ ($N$ + $E$) and found to agree with those measured. (4) The abnormally high Brønsted coefficient $\beta_{nuc}$ of 1.12 reveals that the reactions investigated in this work may proceed via single electron transfer (SET) process.

Experimental

Materials

Commercially (Aldrich products) available 4-methoxyphenol, 4-methylphenol, phenol and 4-chlorophenol were used as received.

4-nitrobenzofurazan 1 was synthesized by reacting 2,1,3-benzoxadiazole with sulfuric and nitric acids at 0 °C (37).

Fig. 5. Correlation of the log $k_1$ values for formation of the $\sigma$-adducts 3a-d with the oxidation potential of the phenoxide anions 2a-d in aqueous solution.
Kinetics Measurements

The reactions of 4-nitrobenzofurazane 1 with para-substituted phenoxide anions 2a-d in water at 20 °C were followed spectrophotometrically. UV-visible kinetic measurements were made on a Shimadzu Spectrophotometer equipped (model 1650). The temperature of the solutions during all of the kinetic studies was kept constant (20 ± 0.2 °C) by using a circulating bath thermostat. Absorbance measurements were made at range 325-340 nm (wavelength corresponding to the absorption maximum of the σ-adducts 3a-e). The observed first-order rate constants, \( k_{\text{obsd}} \), were evaluated from the correlation \( \ln (A_\infty - A_t) \) against time, where \( A_\infty \) and \( A_t \) are the values of equilibrium absorbance and the absorbance after time \( t \), respectively. Correlation coefficients of the linear regressions were usually higher than 0.9760 (see Tables S1-S4). Five different phenoxide anion 2a-d concentrations were used to determine the second-order rate constant (\( k_1 \)) from the slope of the linear plot of \( k_{\text{obsd}} \) versus \([2a-d]\).

Supporting Information Available

Tables S1-S4. Kinetics data for the reactions of the 4-nitrobenzofurazan 1 with phenoxide anions 2a-d in aqueous solution at 20 °C.

Table S5. Kinetics data for the reactions of the 4-nitrobenzofurazan 1 with OH⁻ in 50% H₂O-50% MeCN at 20 °C.

Table S6. \(^1\)H and \(^{13}\)C nuclear magnetic resonance parameters of 4-nitrobenzofurazan 1 and hydroxy-adduct in 60:40 (v/v) (CD₃)₂OD / D₂O.

Fig. S1. Effect of the phenoxide anions 2b and 2d concentration and pH on the observed first-order rate constants for formation of adducts 3b and 3d in aqueous solutions at 20 °C.

References


