Received: 20 May 2021 | Revised: 6 August 2021 | Accepted: 6 August 2021

DOI: 10.1002/kin.21531

INTERNATIONAL JOURNAL OF CHEMICAL KINETICS WILEY

RESEARCH ARTICLE

Nucleophilicities of para-substituted aniline radical cations in acetonitrile: Kinetic investigation and structure–reactivity relationships

Ghabi Amira[1] | **Souissi Salma**[1] | **Gabsi Wahiba**[1,2] | **Boubaker Taoufik**[1]

[1] Laboratoire de Chimie Hétérocyclique, Produits Naturels et Réactivité (LR11ES39), Faculté des Sciences, Université de Monastir, Monastir, Tunisia

[2] Chemistry Department, College of Sciences and Arts, Jouf University, Algrayat, Saudi Arabia

Correspondence
Taoufik Boubaker, Laboratoire de Chimie Hétérocyclique, Produits Naturels et Réactivité (LR11ES39), Faculté des Sciences, Université de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia.
Email: boubaker_taoufik@yahoo.fr

Abstract

The kinetics of the coupling of 2-bromo-3,5-dinitrothiophene **1** with various anilines **2a–f** were studied in CH_3CN at 20°C. The derived second-order rate constants of anilines possessing an electron-withdrawing group (e.g., **2d–f**) were employed to determine the electrophilicity parameter E of the thiophene **1** according to the correlation equation $\log k_{20°C} = s_N (E + N)$, where N and s_N are nucleophile-specific parameters. Nonlinear Brønsted and Hammett relationships are discussed, and it is shown that the reactions for donor anilines **2a–d** proceed through a single-electron transfer mechanism. Further support for this assumption was given by the observation that the nucleophilicity parameters N and $E°$ values of oxidation potential constants are linearly related in a direct relationship with a correlation parameter of $R^2 = 0.9914$. The effect of aniline nucleophilicity on reactivity was examined quantitatively on the basis of kinetic measurements, leading to a nonlinear relationship of $\log (k_{20°C})$ with nucleophilicity parameters (N). It is suggested that the observed nonlinear Mayr correlation can be effectively explored to evaluate the nucleophilicity parameters N of four-substituted aniline radical cations $XC_6H_4NH_2^{+\bullet}$ (X = OH, OMe, Me) and studying their reactivity patterns. On the other hand, it is confirmed that the N values of $HOC_6H_4NH_2^{+\bullet}$ (15.60), $MeOC_6H_4NH_2^{+\bullet}$ (15.23) and $MeC_6H_4NH_2^{+\bullet}$ (14.19) thus obtained can be used to predict the second-order rate constants for their reactions with N1-methyl-4-nitro-2,1,3 benzothiadiazolium tetrafluoroborate of known electrophilicity E. This study was one of the first that employed the Mayr approach for determining nucleophilicity parameters of radical cations.

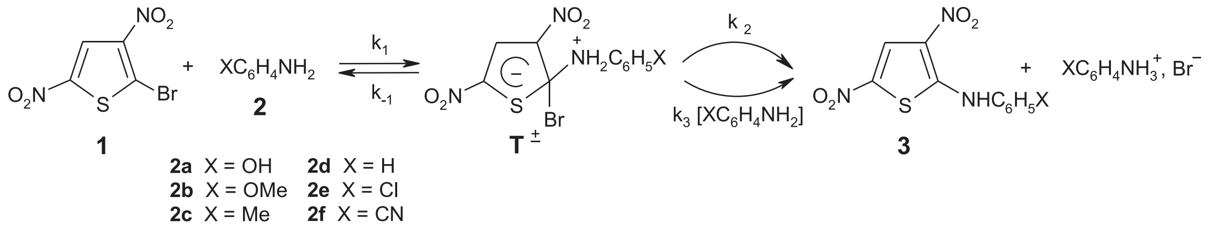
KEYWORDS

aniline radical cations, electrophilicity, kinetics, linear free-energy relationships, Mayr correlation, nucleophilicity, p-X-aniline, single-electron transfer mechanism, thiophene

1 | INTRODUCTION

In the past decade, aromatic azo compounds have emerged as an important structural class with diverse applications in chemistry. Anilines, as the parent molecules of aromatic amines, are essential building blocks in organic synthesis,[1,2] which has lead, in turn, to research on methods to synthesize primary anilines.

Recently, Maeda and coworkers have reported the synthesis of anilines from cyclohexanones using a



SCHEME 1 The reaction of 2-bromo-3,5-dinitrothiophene with 4-X-substituted anilines in CH_3CN at 20°C

Pd/C–ethylene system under nonaerobic conditions.[3] Molecules containing the aniline motif are vital building blocks used in the creation of a range of agrochemicals[4] and pharmaceuticals, this chemical fragment is present in the core of important commercialized drugs, including those with antidepressant,[5] anticancer,[6] antiviral,[7] and anti-inflammatory properties.[8] Additionally, anilines are now extensively used in the field of materials science as electron-donor units, notably for organic light-emitting diode devices[9] and semiconducting polymers.[10] They have been employed as fluorescent materials,[11] and in some types of hollow micro/nanospheres, which have applications in environmental as environment cleanup, energy storage, and medical diagnostics.[12] Moreover, they have recently been proven particularly effective in other areas like photocatalysis,[13] sensors,[14] and detection of oxidants in the air.[15]

The behavior of anilines in S_NAr and sigma complexation reactions has been examined extensively by several research groups with the aim of understanding the electronic, basicity, and nucleophilic effects of the aniline group.[16–19] More recently, Ben Salah and coworkers[16] have shown that the reactions of N1-methyl-4-nitro-2,1,3-benzothiadiazolium tetrafluoroborate **4** with a series of para-X-anilines possessing an electron-withdrawing group (X = H, Cl, and CN) in acetonitrile at 20°C can be described by the linear free-energy relationship equation (1), where E is the electrophilicity parameter, N is the nucleophilicity parameter, and s_N is the nucleophile-specific slope parameter.[20–28] While the Ben Salah work revealed that a Mayr-type plot[16] with aniline donors (X = OH, OMe, Me, and H) exhibited an abnormally high slope value, ca. >1. Data on related systems is therefore of interest in order to confirm and further test this finding.

$$(\log k\,(20^\circ\mathrm{C}))\,/S_N = E + N. \qquad (1)$$

To this end, we now expand our study to the coupling reactions of 2-bromo-3,5-dinitrothiophene **1** with a series of 4-X-substituted anilines **2a–f** (X = OH, OMe, Me, H, Cl, and CN) as shown in Scheme 1 in acetonitrile at 20°C. As will be seen, nonlinear free-energy relationships have been obtained and analyzed. The present work is also intended to examine the origin of the large values of Brønsted coefficient (β_{nuc}) and reaction constant (ρ) obtained for aniline donors (X = OH, OMe, and Me) and at the same time provide more data on which an interpretation of these anilines nucleophilicity effects on reactivity can eventually be based. The paper concludes with a discussion of exploitation of the nonlinear Mayr relationship to evaluate the nucleophilicity parameters N of aniline radical cations in acetonitrile.

2 | EXPERIMENTAL

2.1 | Materials

The various 4-X-substituted anilines **2a–f** (X = OH, OCH_3, CH_3, H, Cl, and CN) were commercially available products that were purified, as appropriate, by recrystallization or distillation prior to use. Acetonitrile (Aldrich, HPLC: 99.9%) was available of the highest quality and used without further purification. 2-Bromo-3,5-dinitrothiophene **1** used in this work was prepared according to a literature procedure.[29,30]

A stock solution of 2-bromo-3,5-dinitrothiophene **1** ($\approx 5 \times 10^{-3}$ mol L^{-1}) was prepared and diluted before use to $\approx 5 \times 10^{-5}$ mol L^{-1}.

UV–visible spectra and kinetic measurements were made on a Shimadzu spectrophotometer equipped (model 1650 PC) with a Peltier temperature controller (model TCC-240 A), which is able to keep to temperature within 0.1 K.

2.2 | Kinetic measurements

All the reactions were carried out in triplicate under pseudo–first-order conditions with a thiophene **1** concentration of approximately 5×10^{-5} mol L^{-1} and aniline concentrations in the range 2×10^{-3} to 8×10^{-1} mol L^{-1}. The k_{obsd} values were determined from the slope of the plot of ln ($A_\infty - A_t$) versus time. The kinetic constants measured were found to be reproducible to ±3–5%. Correlation coefficients of the linear regressions were usually higher than 0.99. Measured first-order rate constants k_{obsd}

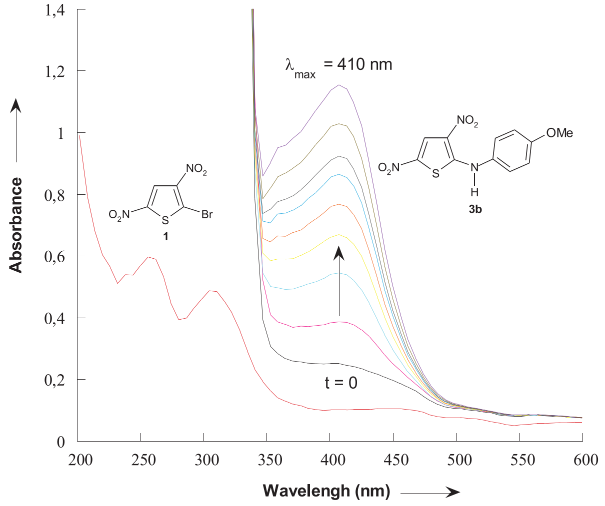


FIGURE 1 UV–visible absorption spectra describing the progressive conversion of the thiophene **1** (5×10^{-5} mol L^{-1}) to the substitution product **3b** in CH_3CN at 20°C

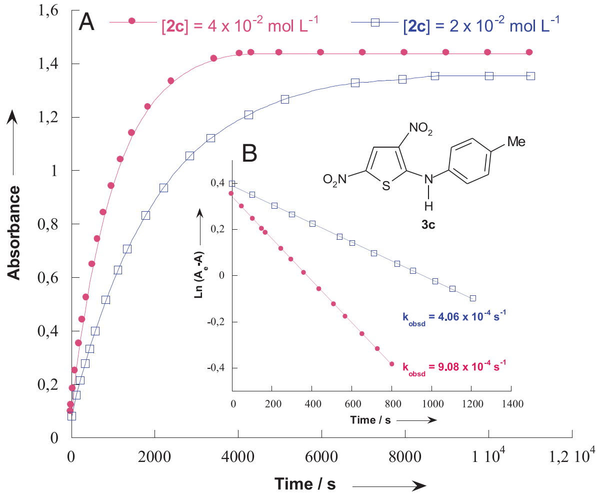


FIGURE 2 Plots of the absorbance at λ_{max} = 408 nm versus time observed for the reaction of thiophene **1** (5×10^{-5} mol L^{-1}) with 4-methylaniline **2c** and correlation ln ($A_\infty - A_t$) versus time in acetonitrile solution at 20°C

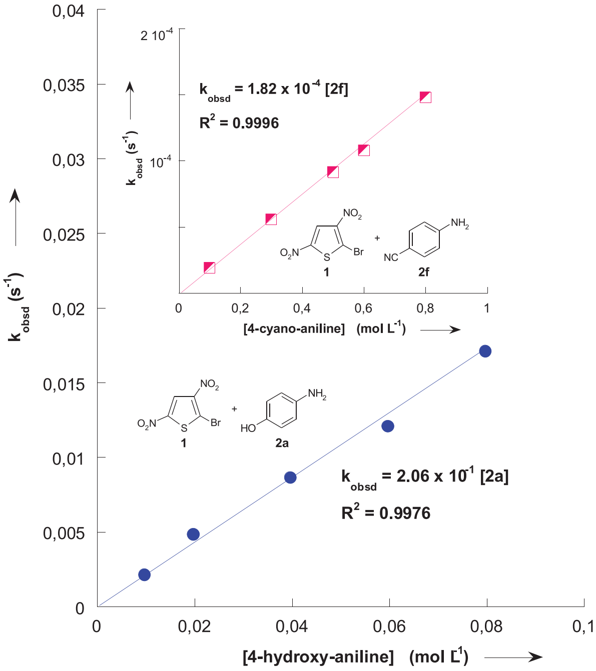


FIGURE 3 Effect of para-substituted aniline concentration on the rate constant k_{obsd} for the formation of the products **3a** and **3f** in CH_3CN solution at 20°C

obtained at aniline concentrations are given for all substrates in Tables S1 in the Supporting Information, together with the derived second-order rate constants.

3 | RESULTS AND DISCUSSION

3.1 | Kinetic studies

The kinetics of 2-bromo-3,5-dinitrothiophene **1** with the series of 4-X-substituted anilines **2** (X = CN, Cl, H, OH, OCH_3, and CH_3) according to Scheme 1 were performed in CH_3CN at 20°C under pseudo–first-order conditions with a large excess of the aniline concentration and monitored by UV–vis spectroscopy at or close to the absorption maxima of the substitution products **3a–f** ($364\text{ nm} < \lambda_{max} < 410\text{ nm}$) (Figure 1).

As discussed in previous studies of the S_NAr reactions,[31–36] the application of the steady-state approximation with respect to zwitterionic intermediate $\mathbf{T}^{\pm}$ to Scheme 1 gives the following relationship. On the other hand, if the rate-determining step is the formation of zwitterionic intermediate $\mathbf{T}^{\pm}$ (i.e., $k_{-1} << (k_2 + k_3[\text{aniline}])$), Equation (2) simplifies to Equation (3):

$$k_{obsd} = \frac{k_1(k_2 + k_3[\text{aniline}])}{k_{-1} + k_2 + k_3[\text{aniline}]}[\text{aniline}], \tag{2}$$

$$k_{obsd} = k_1\,[\text{aniline}]\,. \tag{3}$$

In all experimental measured in the kinetic investigations, only one relaxation process was identified (Figure 2). Pseudo–first-order rate constants, k_{obsd}, are summarized in Table S1 (see the Supporting Information), and k_{obsd} versus [aniline] plots for some of these data are shown in Figures 3. The fact that the k_{obsd} data were found to obey Equation (3) confirmed that the formation of the zwitterionic intermediate $\mathbf{T}^{\pm}$ is the rate-limiting step of the uncatalyzed reaction. The slopes of these plots gave the second-order rate constants (k_1) for the S_NAr reaction of thiophene **1** by anilines **2**, which are listed in Table 1.

TABLE 1 Second-order rate constants k_1 for the reactions of the reference nucleophiles **2a–f** with thiophene **1** in CH_3CN at 20°C

4-X-Substituted aniline		k_1 ($mol^{-1}\,L\,s^{-1}$)	σ	σ^+	pK_a	$E(XC_6H_4NH_2^{\bullet+}/XC_6H_4NH_2)$ (V vs. NHE)
2a	X = OH	2.06×10^{-1}	−0.37	−1.70	12.10	0.76
2b	X = OMe	1.03×10^{-1}	−0.27	−0.78	11.80	0.79
2c	X = Me	2.09×10^{-2}	−0.17	−0.31	11.25	0.92
2d	X = H	2.29×10^{-3}	0	0	10.62	1.02
2e	X = Cl	1.10×10^{-3}	0.23	0.11	9.89	1.01
2f	X = CN	1.82×10^{-4}	0.66	0.61	8.07	–

Values of k_1 are determined in this work from the slope of plots of (k_{obsd} vs. [4-X-aniline]). The σ and σ^+ values were taken from Refs. 41 and 42, pK_a values for anilinium ions in CH_3CN solution taken from Ref. 37, and oxidation potentials, E^o, values in aqueous solution, were taken from Ref . 43.

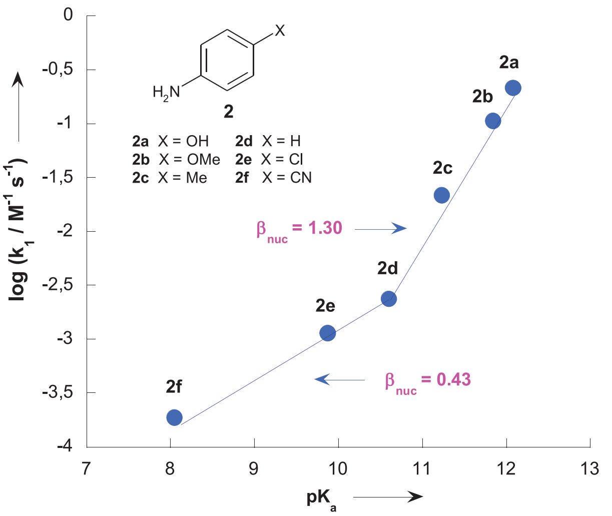


FIGURE 4 Brønsted plot for the reactions of anilines **2a–f** with thiophene **1** in CH_3CN at 20°C. The pK_a values are given in Table 1

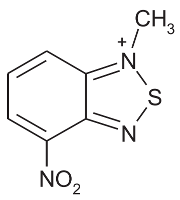
3.2 | Effect of the nucleophile nature on reactivity and mechanism

The effect of aniline basicity on reactivity is demonstrated in Figure 4, which shows that the Brønsted (log k_1 vs. pK_a values for the acid dissociation equilibria of anilinium ions in CH_3CN [Ref. 37] listed in Table 1) plot is biphasic concave upwards with a breakpoint at X = H (pK_a = 10.62). The straight lines obtained for acceptor substituents (X = H, Cl, CN) and for donor substituents (X = OH, OMe, Me) are given by Equations (4) and (5), respectively:

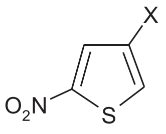
$$\log k_1 = -7.21 + 0.43\,\mathrm{p}K_a \quad \left(R^2 = 0.9989\right), \tag{4}$$

$$\log k_1 = -16.46 + 1.30\,\mathrm{p}K_a \quad \left(R^2 = 0.9957\right). \tag{5}$$

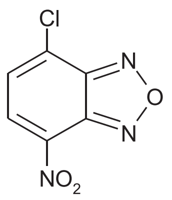
As can be seen, a normal Brønsted coefficient β_{nuc} value of 0.43 is observed for acceptor substituents, while large $\beta_{nuc} = 1.30$ is obtained for donor substituents. As discussed in previous studies,[16–19,34] the magnitude of β_{nuc} values obtained in the present work indicates a change in mechanism from a polar process to a single-electron transfer process (SET). The distinction between polar S_NAr and the SET process is that, in the first case, the β_{nuc} values are known between 0.5 and 0.7.[34,38] In the second case, the β_{nuc} values are near or greater unity.[16–19] It has to be noted that large β_{nuc} values have also been reported for the σ-complexation process,[39,40] for example, reactions of 3,5-dinitrothiophene **5a** and 3-cyano-5-nitrothiophene **5b** with a series of para-substituted phenoxide anions in aqueous solution at 20°C ($1.08 < \beta_{nuc} < 1.15$).[40]



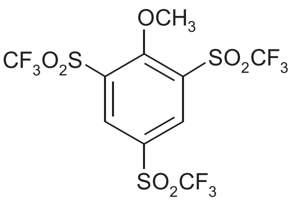
4



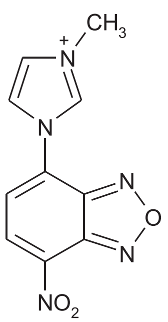
5a : X = NO_2
5b : X = CN



6



7



8

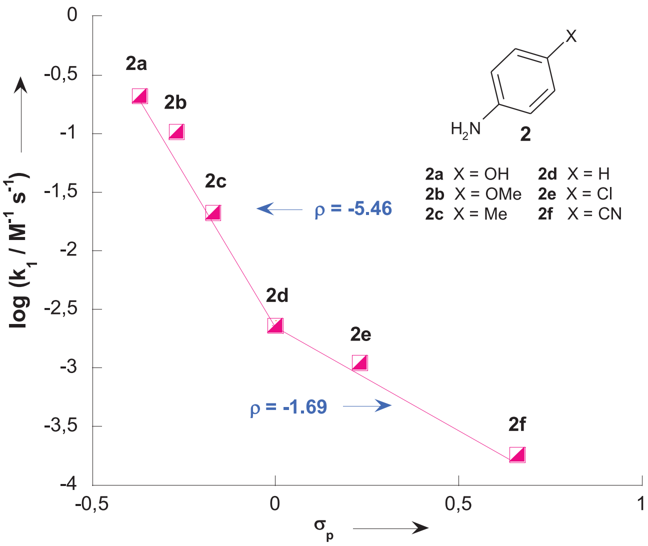


FIGURE 5 The Hammett plot (log k_1 vs. Hammett's constant σ) of the reactions of anilines **2a–f** with thiophene **1** in CH_3CN at 20°C. The σ values are given in Table 1

To get more information about the SET process observed for the electron-donating group, the effect of substituent on reactivity has also been investigated. As observed in Figure 5, the plot of log k_1 against the Hammett's constant σ_p is nonlinear,[41,42] but the data can be described by two straight lines that intersect at the boundary between electron-withdrawing and electron-donating groups. The two linear free energy relationships are expressed as Equations (6) and (7), for the electron-withdrawing (X = H, Cl, CN) group and for the electron-donating group (X = OH, OMe, Me), respectively:

$$\log k_1 = -2.61 - 1.69 s_p \quad \left(R^2 = 0.9979\right), \tag{6}$$

$$\log k_1 = -2.61 - 5.46 s_p \quad \left(R^2 = 0.9929\right). \tag{7}$$

As shown in Figure 5, the magnitude of the ρ value obtained with the electron-donating group (ρ = −5.46) appears to be much smaller than the ρ value of −1.69 obtained with the electron-acceptor group, clearly indicating a mechanistic change over at $\sigma \approx 0$. On the other hand, the ρ value of −1.69 is in agreement with those reported for polar S_NAr reactions in which the nucleophilic attack is the rate-determining step.[17,19] For example, ρ of −1.97 [Ref. 17] and −1.40 [Ref. 19] has been reported for reactions of benzofurazan **6** and anisole **7** with a series of 4-X-substituted anilines (X = H, I, Cl, and CN) in dimethyl sulfoxide at 25°C. However, in the present work, the much smaller negative ρ value of = −5.46 for the more basic anilines is not ascribed to a polar S_NAr mechanism.

In previous work, Terrier and coworkers have concluded that S_NAr reactions of cation **8** with a series of para-substituted anilines in 20–80 (v/v) H_2O-Me_2SO at 25°C proceed through a SET mechanism and proposed the existence of a radical cation $XC_6H_4NH_2^{+\bullet}$ in order to explain the large negative ρ value observed (−5.27).[18] A similar result has also been obtained for the corresponding S_NAr reactions with electrophiles **6** and **7** with ρ values of −5.75 [Ref. 17] and −3.26,[19] respectively.

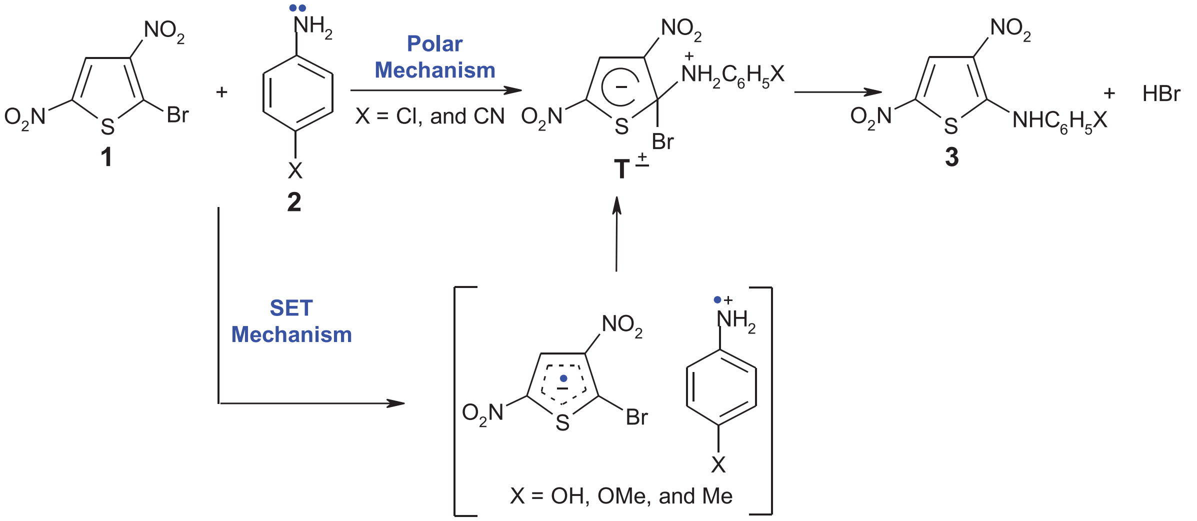
From the present data and that previously reported, the SET mechanism shown in Scheme 2 is proposed to be responsible for the nonlinear free energy relationships observed for the S_NAr reactions of 2-bromo-3,5-dinitrothiophene **1**.

The proposed SET mechanism for the reaction of thiophene **1** with anilines **2a–c** (X = OH, OMe, Me) can be supported from the following results: (1) Satisfactory correlation (R^2 = 0.9914) has been obtained between the second-order rate constants (log k_1) derived for the reaction of thiophene **1** with anilines possessing an electron-donating group **2a–d** and the oxidation potentials $E°$ (in volts vs. NHE) values of the para-substituted aniline radical cations measured by Jonsson and coworkers[43] (Figure 6A). This indicates that these anilines exist as a radical cation $XC_6H_4NH_2^{+\bullet}$ and hence justifies to a possible transition from the polar to the SET mechanism in this field. (2) As shown in Figure 6B, the Yukawa–Tsuno[44–46] plot given by Equation (8) for the reaction of thiophene **1** with anilines **2a–f** is linear (R^2 = 0.9912) with an extent of resonance contribution *r*-value of 1.39. Therefore, the present result clearly suggests that stabilization of the radical cation $XC_6H_4NH_2^{+\bullet}$ through resonance or hyperconjugation interaction between the electron-donating substituent X and the $-NH_2$ functionality as illustrated by resonance structures I–IV (Scheme 3) is responsible for the positive deviation shown by donor substituents from the Hammett plot:

$$\log k_1^X / k_1^H = \rho \quad (\sigma + r(\sigma^+ - \sigma)). \tag{8}$$

3.3 | Quantification of electrophilicity *E* of 2-bromo-3,5-dinitrothiophene 1

The behavior of para-substituted anilines **2** nucleophilicity on the reactivity is illustrated by Figure 7, which shows that the Mayr plot of (log k_1)/s versus the reference nucleophilicity parameters N of anilines **2a–f**[47,48] listed in Table 2 is nonlinear with a break observed for the unsubstituted aniline **2d** (N = 12.64). As can be seen, the effect of aniline nucleophilicity on reactivity is normal (slope = 1.04, Equation 9) for weaker anilines (e.g., X = Cl, CN), and abnormally effect (slope = 2.95, Equation 10) for



SCHEME 2 Proposed pathway for the reactivity of para-substituted anilines **2** at the C-2 position of thiophene **1** in CH_3CN at 20°C

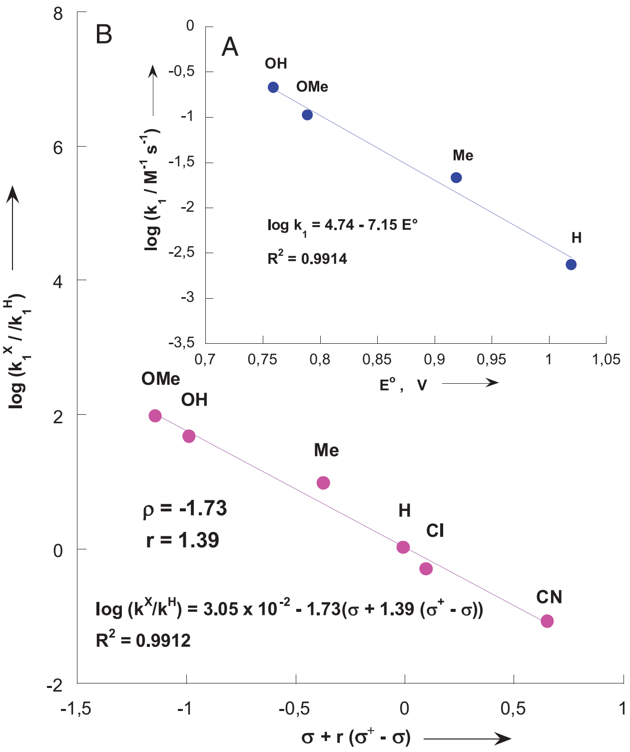
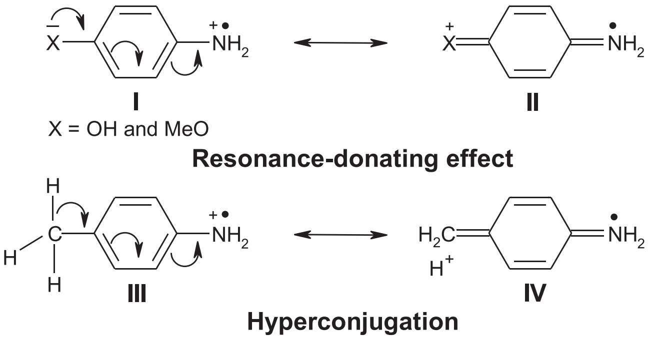


FIGURE 6 (A) Experimental log k_1 versus oxidation potential, E, (vs. SCE, AN) plot for the reactions of thiophene **1** with anilines **2a–d** in CH_3CN at 20°C. (B) Yukawa–Tsuno correlation for reactions of thiophene **1** with anilines **2a–f** in CH_3CN at 20°C. The E, σ, and σ^+ values are given in Table 1



SCHEME 3 Resonance and hyperconjugation effects of aniline radical cations

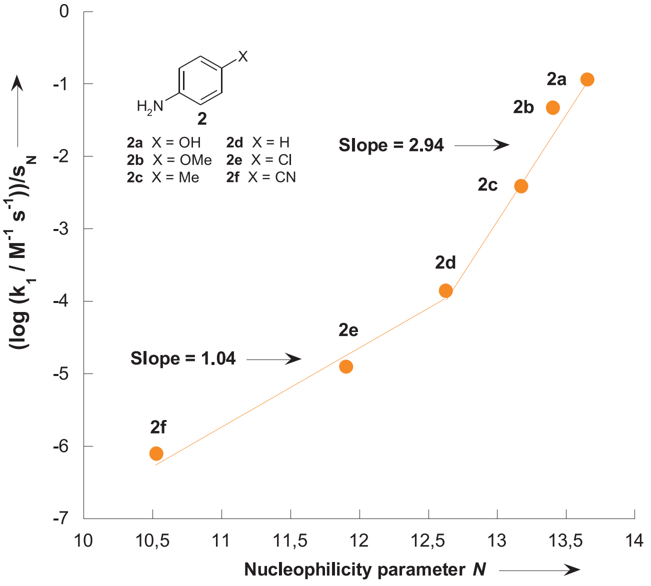


FIGURE 7 Plot of the (log k_1)/s_N for the reactions of thiophene **1** with reference anilines **2a–f** in CH_3CN at 20°C versus their nucleophilicity parameters N

strongly anilines (e.g., X = OH, OMe, Me). We note that such a large slope value has also been recently found by Ben Salah and coworkers (slope = 2.73)[16] in the reaction of N1-methyl-4-nitro-2,1,3 benzothiadiazolium tetrafluoroborate **4** with donor anilines (e.g., X = OH, OMe, Me) under

TABLE 2 Nucleophilicity specific parameters N and s_N of the para-X-substituted anilines **2a–f** as reference nucleophiles employed in this work

Para-X-substituted aniline		N	s_N
2a	X = OH	13.67[a]	0.71[a]
2b	X = OMe	13.42[b]	0.73[b]
2c	X = Me	13.19[b]	0.69[b]
2d	X = H	12.64[b]	0.68[b]
2e	X = Cl	11.92[b]	0.60[b]
2f	X = CN	10.54[a]	0.61[a]

[a] From Ref. 47.

[b] From Ref. 48.

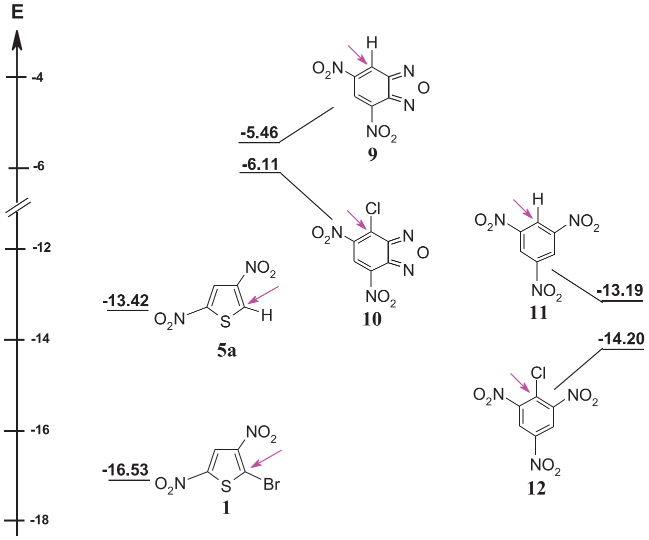


FIGURE 8 Reactivity at unsubstituted versus substituted ring carbon atoms

the same conditions.

$$(\log\ k_1)/s_N = -17.19 + 1.04N \quad \left(R^2 = 0.9901\right) \tag{9}$$

$$(\log\ k_1)/s_N = -41.15 + 2.95N \quad \left(R^2 = 0.9906\right) \tag{10}$$

The magnitude of slope close to unity obtained for donor anilines **2d–f** indicates that Equation (9) can be used to calculate the electrophilicity parameter E of 2-bromo-3,5-dinitrothiophene **1**. From the intercepts of these lines with the ordinate axis, a value of $E = -16.53$ is found. The present value reveals that thiophene **1** exhibits an electrophilicity more than three units lower than the E value of 3,5-dinitrothiophene **5a** ($E = -13.42$) previously reported by Gabsi and coworkers (Figure 8).[40] This result supports the view that the nucleophilic attack at an activated unsubstituted ring position is, in general, kinetically more reactive compared to that at an equally activated substituted position.[34,49] Representative examples are shown in Figure 8, which compares the reactivity between C–H and C–Cl positions for 4,6-dinitrobenzofurazan **9** / 7-chloro-4,6-dinitrobenzofurazan **10** and 1,3,5-trinitrobenzene **11** / 2-chloro-1,3,5-trinitrobenzene **12** systems.[49]

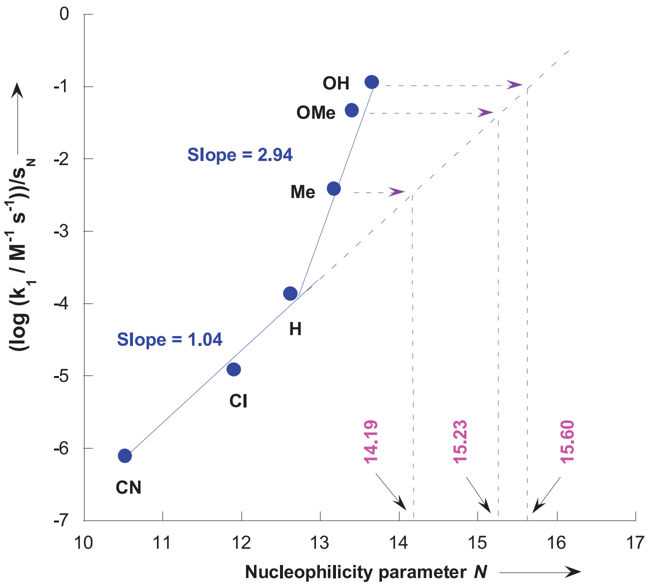


FIGURE 9 Determination of nucleophilicity parameters N of aniline radical cations in acetonitrile at 20°C from the nonlinear Mayr's correlation

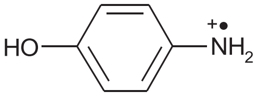
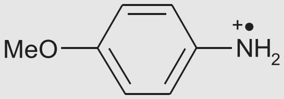
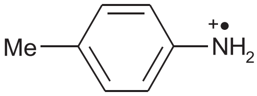
3.4 | Quantification of nucleophilicities of para-substituted

3.4.1 | Aniline radical cations in acetonitrile

Considering that, in acetonitrile, the series of anilines donors exists as radical cations, we now discuss how the nonlinear Mayr relationship observed in the present work can be explored to evaluate the nucleophilicity parameters of para-X-aniline radical cations (X = OH, OMe, Me). On the basis of the linear correlation given by Equation (9), which was obtained from points for p-cyano, p-chloro, and unsubstituted aniline, a new set of N values describing the nucleophilicities of these para-X-aniline radical cations can be derived from the rates in acetonitrile solution (Figure 9). The data obtained are given in Table 3.

To examine if the nucleophilicity parameters N of the series of aniline radical cations given in Table 3 are suitable for the prediction of rate constants of reactions with other types of electrophiles, we considered the reactions of the anilines donors **2a–d** with N1-methyl-4-nitro-2,1,3 benzothiadiazolium tetrafluoroborate **4** in acetonitrile at 20°C, in which the rate constants have been recently reported by Ben Salah and coworkers.[16] Table 3 compares the experimental rate constants with values calculated according to

TABLE 3 Comparison of measured and calculated second-order rate constants, k_1, for the reactions of cation 4 with donor anilines **2a–c** in CH_3CN at 20°C

Aniline radical cation	N [a]	k_1^{exp} [b] $(\mathrm{M^{-1}\,s^{-1}})$	k_1^{calcd} [c] $(\mathrm{M^{-1}\,s^{-1}})$	$k_1^{\text{calcd}}/k_1^{\text{exp}}$
	15.60	6.40×10^{-1}	7.54×10^{-1}	1.17
	15.23	3.66×10^{-1}	4.03×10^{-1}	1.10
	14.19	6.80×10^{-2}	8.12×10^{-2}	1.19

[a] This work.

[b] The k_1^{exp} values were taken from Ref. 16.

[c] The values of k_{calcd} were calculated in this work from known E, N, and s_N values indicated in the table through the log k versus s_N $(E + N)$.

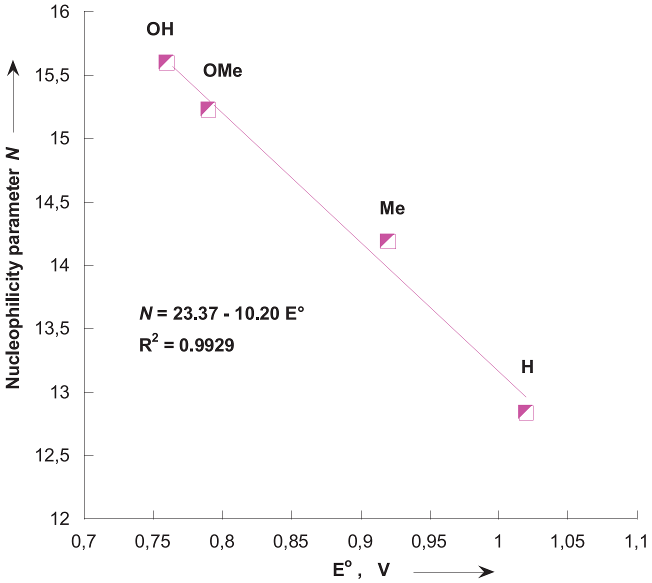


FIGURE 10 Nucleophilicity parameters (N) of the para-X-aniline radical cations versus their oxidation potentials E° in acetonitrile at 20°C

the linear free energy relationship (1) from the E value of **4** $(E = -15.77)$[16] and the N values determined in this work. As shown the calculated and experimental values agree in all cases to within 20%. It is interesting to note that to the best of our knowledge no such study has been reported elsewhere.

An important observation is that the nucleophilicity parameters N of para-X-aniline radical cations correlate well with their oxidation potentials E° given in Table 1 (see Figure 10), suggesting that Equation (11) can be used to obtain N values in acetonitrile for unstudied donor substituents:

$$N = 23.37 - 10.29E^\circ \quad \left(R^2 = 0.9929\right). \tag{11}$$

4 | CONCLUSION

The electrophilic reactivity of 2-bromo-3,5-dinitrothiophene **1** was determined by analyzing the kinetics of its reaction with a series of para-X-substituted anilines **2a–f** in CH_3CN at 20°C according to the linear free energy relationship $\log k_{20^\circ\mathrm{C}} = s_N\,(E + N)$. The effect of aniline para-X-substituents on the reaction rate was examined quantitatively on the basis of kinetic measurements, leading to the nonlinear structure–reactivity correlations. The origin of the nonlinear Brønsted and Hammett plots was interpreted in terms of a change in slope from a small ($\beta_{\text{nuc}} = 0.43$ and $\rho = -1.69$) to a large ($\beta_{\text{nuc}} = 1.30$ and $\rho = -5.46$) value, which can be attributed to a change in mechanism from a polar S_NAr process for acceptor anilines (X = H, Cl, CN) to the SET process for donor anilines (X = OH, OMe, Me, H).

In this paper, we also show that the observed nonlinear Mayr correlation can be effectively explored for evaluating the nucleophilicity parameters N of aniline radical cations. Finally, a fairly reasonable correlation is found between corresponding N and E° values of oxidation potential constant for the π-electron donor substituents. The correlation is proposed to be useful to predict N values of unstudied para-substituted aniline radical cations in acetonitrile solution.

CONFLICTS OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

ORCID

Boubaker Taoufik https://orcid.org/0000-0003-3670-7828

REFERENCES

1. Deng T, Mazumdar W, Ford RL, et al. Oxidation of nonactivated anilines to generate N-aryl nitrenoids. *J Am Chem Soc*. 2020;142:4456-4463.
2. Tsvelikhovsky D, Buchwald SL. Synthesis of heterocycles via Pd-ligand controlled cyclization of 2-chloro-N-(2-vinyl)aniline: preparation of carbazoles, indoles, dibenzazepines, and acridines. *J Am Chem Soc*. 2010;132:14048-14051.
3. Maeda K, Matsubara R, Hayashi M. Synthesis of substituted anilines from cyclohexanones using Pd/C-ethylene system and its application to indole synthesis. *Org Lett*. 2021;23:1530-1534.
4. Yang GZ, Zhang J, Peng JW, et al. Discovery of luotonin A analogues as potent fungicides and biological evaluation inspired by natural alkaloid. *Eur J Med Chem*. 2020;194:112253-112265.
5. Khan ZA. Effect of various cationic hydrotropes on association behaviour of imipramine hydrochloride at different temperatures. *J Mol Liq*. 2019;281:333-343.
6. Wang XZ, Sun X, Han Y, et al. Photothermal supramolecular vesicle's coassembled from pillar arene and aniline tetramer for tumor eradication in NIR-I and NIR-II biowindows. *Chem Eng J*. 2021;403:126423-126431.
7. Leiva R, Barniol-Xicota M, Codony S, et al. Aniline-based inhibitors of influenza h1n1 virus acting on hemagglutinin-mediated fusion. *Med Chem*. 2018;61:98-118.
8. Savjani JK, Mulamkattil S, Variya B, Patel S. Molecular docking, synthesis and biological screening of mefenamic acid derivatives as anti-inflammatory agents. *Eur J Pharmacol*. 2017;801:28-34.
9. Izumi S, Higginbotham HF, Nyga A, et al. Thermally activated delayed fluorescent donor-acceptor-donor-acceptor p-conjugated macrocycle for organic light-emitting diodes. *J Am Chem Soc*. 2020;142:1482-1491.
10. Gregory SA, Li Y, Monroe TD, Li J, Yee SK, Losego MD. Vapor phase infiltration doping of the semiconducting polymer poly(aniline) with $TiCl_4 + H_2O$: mechanisms, reaction kinetics, and electrical and optical properties. *ACS Appl Polym Mater*. 2021;3:720-729.
11. Karri SN, Ega SP, Srinivasan P. Synthesis of novel fluorescent molecule and its polymeric from with aniline as fluorescent and supercapacitor electrode materials. *Polym Adv Technol*. 2020;31:1532-1543.
12. Cheng Z, Dia Z, Li J, et al. Template-free synthesis of tunable hollow microspheres of aniline and aminocarbazole copolymers emitting colorful fluorescence for ultrasensitive sensors. *J Energy Chem*. 2019;357:776-786.
13. Hao CH, Guo XN, Sankar M, et al. Synergistic effect of segregated Pd and Au nanoparticles on semiconducting SiC for efficient photocatalytic hydrogenation of nitroarenes. *ACS Appl Mater Interfaces*. 2018;10:23029-23036.
14. Zhang W, Wu Z, Hu J, et al. Flexible chemiresistive sensor of polyaniline coated filter paper prepared by spraying for fast and non-contact detection of nitroaromatic explosives. *Sens Actuators B Chem*. 2020;304:127233-127264.
15. Pascual BS, Vallejos S, Ruiz JAR, et al. Easy and inexpensive method for the visual and electronic detection of oxidants in air by using vinylic films with embedded aniline. *J Hazard Mater*. 2019;364:238-243.
16. Salah SB, Boubaker T, Goumont R. Kinetic studies on nucleophilic addition reactions of 4-X-substituted anilines to N1-methyl-4-nitro-2,1-3 benzothiazolium tetrafluoroborate in acetonitrile: reaction mechanism and Mayr's approach. *Int J Chem Kinet*. 2015;47:461-470.
17. Jamaoui I, Boubaker T, Goumont R. Nonlinear Bronsted and Hammett correlations associated with reactions of 4-chloro-7-nitrobenzofurazan with anilines in dimethyl sulfoxide solution. *Int J Chem Kinet*. 2013;45:152-160.
18. Terrier F, Mokhtari M, Goumont R, Hallé JF, Buncel E. High Bronsted β_{nuc} values in S_NAr displacement. An indicator of the SET pathway. *Org Biomol Chem*. 2003;1:1757-1763.
19. El Guesmi N, Boubaker T, Goumont R. Single electron transfer in S_NAr process: reactions of 2,4,6-tris(trifluoromethanesulfonyl)anisole with anilines in dimethyl sulfoxide. *Prog React Kinet Mech*. 2013;38:130-142.
20. (a) Mayr H, Patz M. Scales of nucleophilicity and electrophilicity: a system for ordering polar organic and organometallic reactions. *Angew Chem Int Ed Engl*. 1994;33:938-957. (b) Mayr H, Kempf B, Ofial AR. p-Nucleophilicity in carbon-carbon bond-forming reaction. *Acc Chem Res*. 2003;36:66-77.
21. Lakhar S, Westermaier M, Terrier F, et al. nucleophilic reactivities of indoles. *J Org Chem*. 2006;71:9088-9095.
22. Zhang J, Yang JD, Zheng H, Xue XS, Mayr H, Cheng JP. Exploration of the synthetic potential of electrophilic trifluoromethylthiolating and difluoromethylthiolating reagents. *Angew Chem Int Ed*. 2018;57:12690-12695.
23. Eitzinger A, Mayer RJ, Hampel N, Mayer P, Waser M, Ofial AR. Electrophilic reactivities of vinyl p-quinone methides. *Org Lett*. 2020;22:2182-2186.
24. Li Z, Mayer RJ, Ofial AR, Mayr H. From carbodiimides to carbon dioxide: quantification of the electrophilic reactivities of heteroallenes. *J Am Chem Soc*. 2020;142:8383-8402.
25. Necibi F, Ben Salah S, Roger J, Hierso JC, Boubaker T. Ambident electrophilicity of 4-nitrobenzochalcogenadiazoles: kinetic studies and structure-reactivity relationships. *Int J Chem Kinet*. 2020;52:669-680.
26. Azaiez K, Dhahri N, Boubaker T. Reactivity of nitroalkyl anions addition to substituted benzlylidencyanoacetate: electrophilicity parameters and free energy relationships. *Int J Chem Kinet*. 2017;49:847-858.
27. Ben Salah S, Necibi F, Goumont R, Boubaker T. Electrophilicities of 4-nitrobenzochalcogenadiazoles. *ChemistrySelect*. 2020;5:7648-7657.
28. Ayachi H, Raissi H, Mahdhaoui F, Boubaker T. Electrophilic reactivities of 7-L-4-nitrobenzofurazans in σ-complexation processes: kinetic studies and structure-reactivity relationships. *Int J Chem Kinet*. 2020;52:655-668.
29. Spinelli D, Consiglio G, Noto R, Corrao A. Linear free energy ortho-correlations in the thiophen series. Part I. The kinetics of piperidino debromination of some 2-bromo-3-X-5-nitrothiophens in methanol. *J Chem Soc Perkin Trans*. 1975;2:620-622.
30. Baldini G, Doddli G, Illuminati G, Stegel F. On the role of electronic and steric factors upon the formation of Meisenheimer-type adducts. *J Org Chem*. 1976;41:2153-2157.
31. Bunnett JF, Sekiguchi S, Smith LA. Kinetics of reactions of cyclic secondary amines with 2,4-dinitro-1-naphthyl ethyl ether

in dimethyl sulfoxide solution. spectacular difference between the behavior of pyrrolidine and piperidine. *J Am Chem Soc*. 1981;103:4865-4871.

32. Orvik JA, Bunnett JF. Kinetics of the separately observable formation and decomposition of the intermediate complex in aromatic nucleophilic substitution. Reactions of 2,4-dinitro-1-naphthyl ethyl ether with *n*-butyl-and *t*-butylamine in dimethyl sulfoxide solution. *J Am Chem Soc*. 1970;92:2417-2427.
33. Souissi S, Gabsi W, Echaieb A, Hierso JC, Fleurat-Lessard P, Boubaker T. Influence of solvent mixture on nucleophilicity parameters: the case of pyrrolidine in methanol–acetonitrile. *RSC Adv*. 2020;10:28635-28643.
34. Terrier F. *Modern Nucleophilic Aromatic Substitution*. Hoboken, NJ: John Wiley & Sons; 2013.
35. Echaieb A, Gabsi W, Boubaker T. Nucleophilic substitution reaction of 2-methoxy-3-X-5-nitrothiophene: effect of substituents and structure-reactivity correlation. *Int J Chem Kinet*. 2014;46:470-476.
36. Souissi S, Gabsi W, Boubaker T. Kinetic and quantification of the electrophilic reactivities of substituted thiophenes and structure-reactivity relationships. *Int J Chem Kinet*. 2018;50:582-590.
37. (a) Coetzeel JF, Padmanabhan GR. Properties of bases in acetonitrile as solvent. IV. Proton acceptor power and homoconjugation of mono-and diamines. *J Am Chem Soc*. 1965;87:5005-5010. (b) Henry S. Reactions of picric acid with aromatic amines in acetonitrile medium. *Pol J Chem*. 1987;61:449-455.
38. Bordwell FG, Hughes DL. Nucleophilic aromatic substitution reactions with carbanions and nitranions in dimethyl sulfoxide solution. *J Am Chem Soc*. 1986;108:5991-5997.
39. Salah SB, Boubaker T, Goumont R. Kinetic and mechanism of phenoxide anions addition to 4-nitrobenzofurazan in aqueous solution. *Can J Chem*. 2017;95:723-728.
40. Gabsi W, Essalah K, Goumont R, Tangour B, Boubaker T. The ambident electrophilic behaviour of 5-nitro-3-X-thiophenes in σ-complexation processes. *Int J Chem Kinet*. 2018;50:659-669.
41. Hammett LP. *Physical Organic Chemistry; Reaction Rates, Equilibria and Mechanism*. 2nd ed. New York: Mc-Graw-Hill; 1970.
42. Hansch C, Leo A, Taft RW. A survey of Hammett substituent constants and resonance and field parameters. *Chem Rev*. 1991;91:185-195.
43. Jonsson M, Lind J, Eriksen TE, Merényi G. Redox and acidity properties of 4-substituted aniline radical cations in water. *J Am Chem Soc*. 1994;116:1423-1427.
44. Tsuno Y, Fujio M. The Yukawa-Tsuno relationship in carbocationic systems. *Adv Phys Org Chem*. 1999;32:267-385.
45. Fujiyama R, Alam MA, Aiko A, Munechika T, Fujio M, Tsuno Y. The β-silicon effect. 4: substituent effects on the solvolysis of 1-alkyl-2-(aryldimethylsilyl)ethyl trifluoroacetates. *J Phys Org Chem*. 2010;23:819-827.
46. Um IH, Chun SM, Chae OM, Fujio M, Tsuno Y. Effect of amine nature on reaction rate and mechanism in nucleophilic substitution reactions of 2,4-dinitrophenyl X-substituted benzenesulfonates with alicyclic secondary amines. *J Org Chem*. 2004;69:3166-3172.
47. Dhahri N, Boubaker T, Goumont R. Kinetics of alkaline hydrolysis of p-substituted benzylidenemalononitriles in 50% aqueous acetonitrile: substituent effects and quantification of the electrophilic reactivity. *J Phys Org Chem*. 2014;27:484-489.
48. Brotzel F, Chu YC, Mayr H. Nucleophilicities of primary and secondary amines in water. *J Org Chem*. 2007;72:3679-3688.
49. Raissi H, Jamaoui I, Goumont R, Boubaker T. Kinetic studies on S_NAr reactions of substituted benzofurazan derivatives: quantification of the electrophilic reactivities and effect of amine nature on reaction mechanism. *Int J Chem Kinet*. 2017;49:835-846.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Amira G, Salma S, Wahiba G, Taoufik B, Nucleophilicities of para-substituted aniline radical cations in acetonitrile: Kinetic investigation and structure–reactivity relationships. *Int J Chem Kinet*. 2021;1-10. https://doi.org/10.1002/kin.21531