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The reactions of *O*-(4-nitrophenyl) *S*-aryl dithiocarbonates with anilines: Effects on the relative nucleofugality

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Abstract

Kinetic and high-performance liquid chromatography studies were investigated for the reactions of *S*-phenyl, *S*-(4-chlorophenyl), and *S*-(4-nitrophenyl) *O*-(4-nitrophenyl) dithiocarbonates with anilines. These were performed in the presence of 0.1M borate buffer in 44 wt% aqueous ethanol. For reactions of the 3 substrates, the mechanism is stepwise with 2 tetrahedral intermediates, one zwitterionic ($T^{\pm}$), and the other anionic (T^{-}), where the intermediate T^{-} is formed by proton transfer from $T^{\pm}$ to the borate buffer. The nonleaving group is not passive, playing an important role in the relative nucleofugality of the groups, which depend largely on its electron withdrawing capability. The nucleofugacity of 4-nitrophenolate ion and of 4-nitrophenylthiolate from the same tetrahedral intermediate is similar, despite the differences in their basicities (3 pK_a units). In the reactions of *S*-(4-nitrophenyl) *O*-(4-nitrophenyl) dithiocarbonate, the change of nucleophile from pyridines (only 4-nitrophenolate ion is nucleofuge) to anilines (2 nucleofuges) shows that the nature of the amine impacts on the relative nucleofugality of groups.

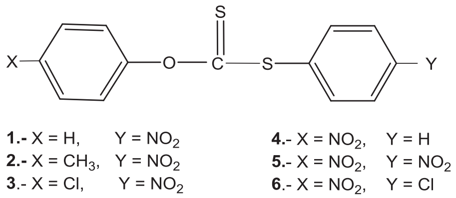
KEYWORDS
diaryl dithiocarbonates, nucleofugality

1 | INTRODUCTION

The kinetics and mechanisms of the aminolysis of alkyl aryl and diaryl carbonates and some of their sulfur derivatives, such as *O*-alkyl *S*-aryl dithiocarbonates, are well documented.[1–7] On the other hand, the mechanism of the aminolysis of *O*-aryl *S*-aryl dithiocarbonates has been extensively studied by us (Scheme 1).[8] The reaction of a series of secondary alicyclic (SA) amines with *O*-phenyl *S*-(4-nitrophenyl) dithiocarbonate (**1**), *O*-(4-methylphenyl) *S*-(4-nitrophenyl) dithiocarbonate (**2**), and *O*-(4-chlorophenyl) *S*-(4-nitrophenyl) dithiocarbonate (**3**),[8a, b] the pyridinolysis[8c] and the anilinolysis[8e] of **2** and **3**, all occur by a stepwise mechanism. This mechanism is initiated by the nucleophilic attack of amine to the thiocarbonyl group, leading to the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$). Depending on the basicity and nature of the amine, the $T^{\pm}$ decomposes directly to products expelling the nucleofuge or can be deprotonated forming an anionic tetrahedral intermediate (T^{-}) and then expelling the nucleofuge.[8] The deprotonating agent of $T^{\pm}$ can be a second amine molecule or an external buffer.[8b, e] If the agent is a second amine molecule, plots of k_{obs} versus free amine concentration at constant pH are nonlinear upwards, but if the proton transfer is to the external buffer, these plots are linear.[8b, e]

In all the studied reactions of dithiocarbonates **1** to **3** with SA amines,[8a, b] pyridines,[8c] and anilines,[8e] the *S*-(4-nitrophenyl) group was the nucleofuge; this behavior was explained considering the lower pK_a of the conjugated acid of *S*-(4-nitrophenyl) compared with phenol as a nonleaving group in the substrates. On the other hand, in the pyridinolysis reaction of *O*-(4-nitrophenyl) *S*-phenyl dithiocarbonate **4** and *O*-(4-nitrophenyl) *S*-(4-nitrophenyl) dithiocarbonate **5**,[8d] the nucleofuge was the 4-nitrophenolate ion in spite of the fact that the pK_a of 4-nitrophenol is greater than that of benzenethiol and that of 4-nitrobenzenethiol. Apparently, the basicity is not the exclusive reason to determine the nucleofugality of groups, and the nonleaving group probably plays an important role in this behavior. More recently, the kinetic study of **5** with SA amines showed that the mechanism is concerted and both groups attached to the thiocarbonyl group are nucleofuges.[8f]

To shed more light on the mechanisms and selectivity of the anilinolysis of *O*-aryl *S*-aryl dithiocarbonates, in this work, we report both a kinetic and an analytic study of the reactions of **4**, **5**, and *O*-(4-nitrophenyl) *S*-(4-chlorophenyl) dithiocarbonate (**6**) with a series of anilines. A comparison between the kinetic results and product analyses obtained in this work and with other substrates previously published will permit to determine the influence of the amine and of the nonleaving group on the nucleofugality of the potential leaving groups in these reactions.



SCHEME 1 Structure of a series of diaryl dithiocarbonates

2 | MATERIALS AND METHODS

2.1 | Materials

Anilines were purified by recrystallization or distillation. Dithiocarbonates **4** and **5** were prepared as described.[8d]

Dithiocarbonate **6** was prepared in the same way and presents the following analytical properties:

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 (d, 2H, *J* = 9.2 Hz); 7.46 (d, 2H, *J* = 8.8); 7.53 (d, 2H, *J* = 8.4 Hz); 8.30 (d, 2H, *J* = 9.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 123.7; 125.8; 128.5; 130.4; 137.0; 137.8; 146.4; 158.9; 212.1.

Elem. Anal. Calcd. for $C_{13}H_8ClNO_3S_2$: C: 47.93; H: 2.48; N: 4.30; S: 19.68. Found: C: 48.10; H: 2.08; N: 4.01; S: 18.31.

2.2 | Kinetic measurements

The kinetics of the reactions were analyzed through a diode array spectrophotometer in 44 wt% ethanol-water, at 25.0 ± 0.1°C and an ionic strength of 0.2M (maintained with KCl). The reactions were followed in a wavelength range between 300 and 500 nm and studied under at least 10-fold excess of amine over the substrate. The initial concentration of the substrate was 2.5×10^{-5}M. Under these conditions, pseudo–first-order rate coefficients (k_{obs}) were found throughout and the kinetics were measured for at least 5 half-lives, following the formation of the 4-nitrophenoxide ion. The pH was maintained constant by using a 0.1M borate buffer. The k_{obs} values obtained and the experimental conditions for the studied reactions are detailed in Tables S1 to S3.

2.3 | Product studies

2.3.1 | UV-vis analysis

For all the reactions, 4-nitrophenoxide anion was identified as one of the products. This was achieved by comparison of the UV-vis spectra after the reactions end with those of an authentic sample of 4-nitrophenol, under the same reaction conditions.

2.3.2 | High-performance liquid chromatography analysis

These were performed by high-performance liquid chromatography (HPLC) with a diode array detector, provided with LiChroCART 250-4 HPLC-RP-18e (5 μm), mobile phase of 50% CH_3CN/acetate buffer (0.01M, pH 5.0), and flow rate of 1.2 mL/min. 4-Nitrophenol, benzenethiol, and 4-chlorobenzenethiol were identified by comparison of their spectra and retention times (r.t.) with those of authentic samples. Thionocarbonates and dithiocarbonates were identified through comparison of the spectra and r.t. of the products obtained in the reactions of 4-nitrophenyl thionochloroformate, phenyl dithiochloroformate, and 4-chlorophenyl dithiochloroformate with aniline.

The reactions of **4** with aniline show the presence of 4-nitrophenol (r.t. = 3.1 min, λ = 330 nm) and phenyl aniline dithiocarbamate (r.t. = 5.4 min, λ = 280 nm). The presence of *O*-(4-nitrophenyl) aniline thionocarbamate (r.t. = 6.5 min, λ = 270 nm) was not observed.

The reactions of **6** with aniline show the presence of 4-nitrophenol (r.t. = 3.1 min, λ = 330 nm) and 4-chlorophenyl aniline dithiocarbamate (r.t. = 5.1 min, λ = 260 nm). Aniline *O*-(4-nitrophenyl) thionocarbamate (r.t. = 6.5 min, λ = 270 nm) was not detected.

The HPLC study of the reactions of **5** with aniline (Figure 1) shows the presence of 4-nitrophenol (r.t. = 3.1 min, λ = 330 nm), *O*-(4-nitrophenyl) aniline dithiocarbamate (r.t. = 5.2 min, λ = 270 nm),

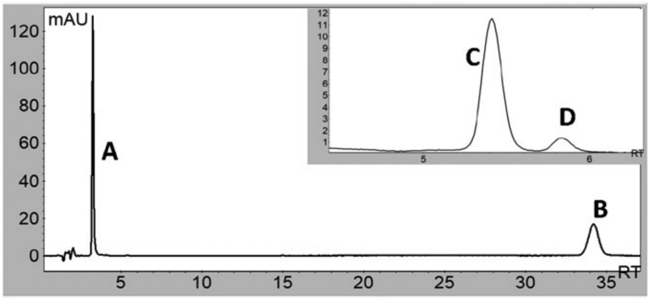


FIGURE 1 High-performance liquid chromatography analysis of the reaction of **5** with aniline (from 0 to 37 min, at λ = 316 nm). A, 4-nitrophenol. B, Dimer of 4-nitrobenzenethiol. The insert is a small part of the same chromatogram (4.5-6.5 min at λ = 270 nm). C, 4-Nitrobenzenethiol aniline dithiocarbamate. D, 4-Nitrophenyl aniline thiocarbamate

O-(4-nitrophenyl) aniline thionocarbamate (r.t. = 6.5 min, λ = 270 nm), and the dimer of 4-nitro benzenethiolate (r.t. = 34 min, λ = 330 nm).

3 | RESULTS AND DISCUSSION

3.1 | Chromatographic study of the anilinolysis reaction

Figure 1 shows the HPLC results for the reaction of **5** with aniline. The presence of 4-nitrophenol (first chromatographic peak, at r.t. = 3.1 min) and the dimer of 4-nitrobenzenethiol (second chromatographic peak, at r.t. = 34 min) can be observed. This result suggests that in this reaction, both groups linked to the thiocarbonyl moiety of **5** are nucleofuges. This is confirmed by the presence of the 2 aniline carbamates as products (see the insert of the Figure 1).

The HPLC study of the reactions of **4** shows that 4-nitrophenol and the phenyl aniline dithiocarbamate were the products, indicating that in these reactions, only the 4-nitrophenolate ion is the nucleofuge.

In the case of the HPLC study for the reactions of **6**, results show that 4-nitrophenol and aryl aniline dithiocarbamate were the products, indicating that in these reactions, the 4-nitrophenolate ion is the main nucleofuge. It is important to point out that although traces of 4-chlorobenzethiol and of *O*-(4-nitrophenyl) aniline thionocarbamate (less than 1%) were found in this analysis, they could be due to the expulsion of 4-chlorobenzenethiolate; however, in this study, we will consider that 4-nitrophenolate ion is the main nucleofuge.

3.2 | Kinetics and mechanism

For all the studied reactions, pseudo–first-order rate constants (k_{obs}) were obtained under aniline excess. These rate constants and the experimental conditions are found in Tables S1 to S3.

In some of the studied anilinolysis, it has been described that anilines play 2 roles, one as nucleophile and the other as base.[9] To preclude the participation of a second aniline molecule as deprotonating agent of the possible tetrahedral intermediate formed in a stepwise mechanism, the reactions were performed in the presence of 0.1M borate buffer.

Under these experimental conditions, plots of k_{obs} against free amine concentration [N] were linear (Equation 1). In Equation 1, k_0 and k_N are solvolysis and the nucleophilic rate constants.

$$k_{\mathrm{obs}} = k_0 + k_N[\mathrm{N}]. \tag{1}$$

In all cases, $k_N[\mathrm{N}] \gg k_0$; therefore, the solvolysis reaction is disregarded. Table 1 exhibits a summary of the k_N values obtained for the anilinolysis of dithiocarbonates **4** to **6**.

Figure 2 shows the Brønsted plots obtained. The k_N values of Table 1 as well as those of the pK_a of the conjugate acids of the anilines were statistically corrected

TABLE 1 k_N values obtained for the reactions of *S*-phenyl *O*-(4-nitrophenyl) dithiocarbonate (**4**), *S*-(4-nitrophenyl) *O*-(4-nitrophenyl) dithiocarbonate (**5**), and *S*-(4-chlorophenyl) *O*-(4-nitrophenyl) dithiocarbonate (**6**) with anilines at 25°C, ionic strength 0.2M (KCl), and borate buffer 0.1M, in 44 *w*/w% ethanol-water

		$10^2\ k_N/\mathrm{s^{-1}\ M^{-1}}$		
Amine	**pK_a**	**4**	**5**	**6**
1,4-Phenylenediamine	6.45	...	233 ± 5	220 ± 7
4-Methoxyaniline	5.29	3.5 ± 0.1	53 ± 2	50 ± 1
4-Methylaniline	4.90	2.12 ± 0.07	27.6 ± 0.4	27.4 ± 0.4
Aniline	4.46	0.77 ± 0.04	12.5 ± 0.6	15.4 ± 0.2
3-Methoxyaniline	4.26	0.44 ± 0.02	6.6 ± 0.2	6.1 ± 0.2
3-Aminoacetophenone	3.10	...	...	2.3 ± 0.2
4-Aminoacetophenone	1.73	...	0.48 ± 0.02	...

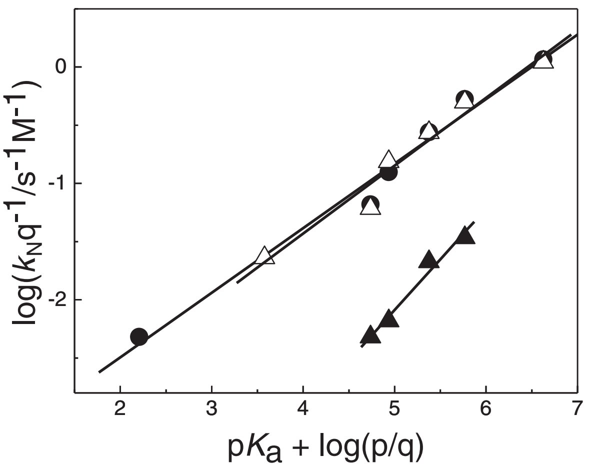


FIGURE 2 Corrected Brønsted-type plots for the anilinolysis of **4** (▲), **5** (●), and **6** (Δ)

with $q = 2$ for 4-phenylenediamine ($q = 1$ for all the other anilines) and $p = 3$ for all the conjugate acids of the anilines.[10] These plots are linear, with slopes $\beta = 0.87$, 0.55, and 0.58 for **4**, **5**, and **6**, respectively.

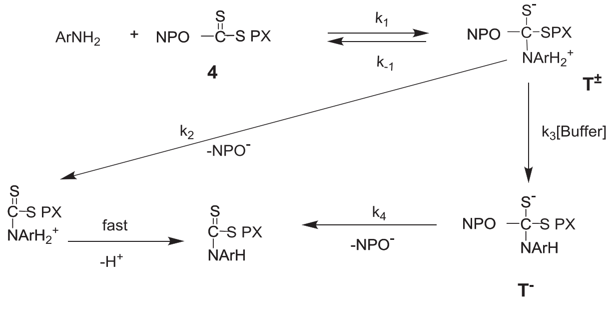
The value of $\beta = 0.87$ obtained for the anilinolysis of **4** is in accordance with those found in similar reactions where the mechanism is stepwise and the nucleofuge is expelled from the tetrahedral intermediate as the rate determining step (0.8-1.1).[1–8]

Scheme 2 (X=H) shows a possible mechanism for this reaction, considering that (1) 4-nitrophenolate ion is the unique nucleofuge (see Section 3.1) and (2) in the experimental conditions, plots of k_{obs} against aniline concentration are linear; therefore, the buffer is the deprotonation agent of $T^{\pm}$.

Applying the steady-state condition to both intermediates, Equation 2 can be obtained.

$$k_{obs} = (k_1\ (k_2 + k_3[\text{Buffer}]))/(k_{-1} + k_2 + k_3[\text{Buffer}])[\text{Aniline}]. \tag{2}$$

The deprotonation rate constant (k_3), which is diffusion controlled, is greater than that for the 4-nitrophenolate ion expel from $T^{\pm}$ (k_2). Considering this fact, and the buffer concentration used, $k_3[\text{Buffer}] >> k_2$, Equation 3 is obtained.



SCHEME 2 Proposed mechanism for the anilinolysis reactions of dithiocarbonate **4**, (X=H)

$$k_{obs} = (k_1\ k_3[\text{Buffer}])/(k_{-1} + k_3[\text{Buffer}])[\text{Aniline}]. \tag{3}$$

If $k_{-1} >> k_3[\text{Buffer}]$, the k_{obs} is simplified to Equation 4.

$$\begin{aligned} k_{obs} &= (k_1\ k_3[\text{Buffer}])/(k_{-1}))[\text{Aniline}] \\ &= K_1\ k_3[\text{Buffer}][\text{Aniline}]. \end{aligned} \tag{4}$$

As the term $k_3[\text{Buffer}]$ is a constant independent of the aniline used, there is no change in the slope of the Brønsted plot.

On the other hand, the obtained β values, 0.55 and 0.58, for the reactions of **5** and **6**, respectively, are in the described range for concerted mechanisms (0.4-0.7)[11]; nevertheless, it is necessary to disregard the presence of the break of the plot due to a possible stepwise mechanism.[11] For the pyridinolysis of the dithiocarbonate **6**, the break must be greater than 9.5[8d]; for the anilinolysis, the $pK_a°$ must be at a greater pK_a than for the pyridinolysis (out of the pK_a studied range); consequently, it is not possible to confirm the concerted mechanism by using this argument.

For the anilinolysis reaction of **6**, we are prone to accept a stepwise mechanism as for substrates represented in Scheme 1 (X=Cl) (where only 4-nitrophenolate ion is the nucleofuge, see above), considering (1) the SA aminolysis reaction of **6** is stepwise (unpublished results) and (2) the change of SA amine by aniline stabilizes a tetrahedral intermediate.[12] Therefore, if the mechanism is stepwise with the SA aminolysis, it is even more justified that it would be so for the aniline series.

It is noticeable that although the reactions of dithiocarbonates **4** and **6** proceed through the same mechanism of Scheme 2, they present different values of β. A possible reason is that in the reactions of **6**, the greater electron withdrawing capacity of chlorobenzenethiol would favor the reestablishment of the double bond of the thiocarbonyl group and the expel of 4-nitrophenolate ion. No effect on the deprotonation step because it is diffusion controlled in the reactions of both substrates. Under these conditions, it is possible that the used assumption $k_3[\text{Buffer}] >> k_2$ is not valid and the more complex Equation 2 must then be used.

If $k_{-1} >> (k_3[\text{Buffer}] + k_2)$, Equation 2 is simplified to Equation 5.

$$\begin{aligned} k_{obs} &= ((k_1\ (k_2 + k_3[\text{Buffer}])/k_{-1})[\text{Aniline}] \\ &= K_1(k_2 + k_3[\text{Buffer}])[\text{Aniline}]. \end{aligned} \tag{5}$$

Due to the sum in the k_N expression is not possible to use the Brønsted equation, therefore, the β values obtained for the reaction of **6** do not have physical sense.

The HPLC study of the anilinolysis reactions of **4** shows the presence of 4-nitrophenol and anilinium phenyl dithiocarbamate, and in the reactions of **6**, 4-nitrophenol and 4-chlorophenyl aniline dithiocarbamate were found. These results and the presence of traces of *O*-(4-nitrophenyl) aniline thionocarbamate in the reactions of dithiocarbonate **6** confirm that 4-nitrophenolate ion is the principal (or unique) nucleofuge in these reactions. This result is in accordance with the fact that, at the isobasic point, RO^- is a better nucleofuge than RS^-.[8d, 13] The pK_a of 4-nitrophenol is 7.5,[14] that of benzenethiol is 7.2,[8d] and that of 4-chlorobenzenethiol is 7.0.[8d]

To propose a mechanism for the anilinolysis of **5**, it is not possible to use the same argument above-mentioned for **6**, considering the stabilization of the tetrahedral intermediate by change of the amine nature. In fact, by going from pyridines to SA amines as nucleophiles, the reaction mechanism of **5** changes from stepwise to concerted,[8f] but, as is known, anilines stabilize a tetrahedral intermediate relative to SA amines but destabilize it relative to pyridines.[12]

Regarding the close similarity of the k_N values of both substrates (**5** and **6**) in Table 1, it is possible to assume that both go by the same stepwise mechanism.

The HPLC study of the reactions of **5** with aniline shows the presence of 4-nitrophenol, the dimer of 4-nitrobenzenethiol, 4-nitrophenyl aniline thionocarbamate, and 4-nitrophenyl aniline dithiocarbamate. This result shows that both groups attached to thiocarbonyl group are nucleofuges. A possible reaction mechanism is shown in Scheme 3.

Applying the steady-state condition to both intermediates, Equation 6 can be obtained.

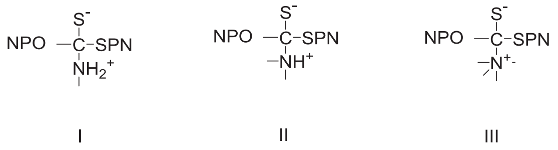
$$k_{\text{obs}} = \left(k_1\left(k_2 + k_2' + k_3[\text{Buffer}]\right)/\left(k_{-1} + k_2 + k_2' + k_3[\text{Buffer}]\right)\right)[\text{Aniline}]. \qquad (6)$$

The same mechanism has been reported for the anilinolysis of *O*-(4-cyanophenyl) *O*-(3-nitrophenyl) thionocarbonate.[9] The presence of the 2 nucleofuges in the anilinolysis reaction of **5** shows that the nucleofugacity of 4-nitrophenolate ion is similar to that of 4-nitrophenylbenzenethiolate from the tetrahedral intermediate I (Scheme 4), despite the differences in their basicities (pK_a values of 4-nitrophenol and 4-nitrobenzenethiol are 7.5 and 4.5, respectively).[14]

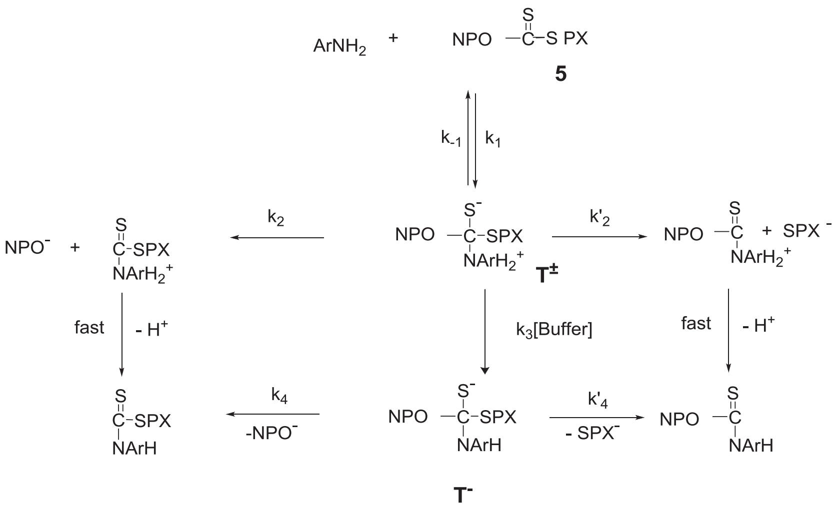
3.3 | Influence of amine nature on the nucleofugality of groups

To determine the influence of the amine nature on the relative nucleofugality of groups, we compare the behavior of the reactions of **5** with 3 amines families. In the anilinolysis, both groups are nucleofuges from the tetrahedral intermediate I (Scheme 4); also in the reaction of **5** with SA amines,[8f] both groups are nucleofuges; but in the last, the mechanism is concerted (tetrahedral intermediate II could not exist).

On the other hand, it is important to mention that in both reactions, pyridinolysis[8d] and anilinolysis (this study), the mechanism is stepwise. Nevertheless, in the pyridinolysis reactions, only 4-nitrophenolate ion is expelled from the tetrahedral intermediate III,[8d] while in the anilinolysis, from the tetrahedral intermediate I,



SCHEME 4 Zwitterionic tetrahedral intermediates in the reactions of **5** with anilines (I), SA amines (II), and pyridines (III)



SCHEME 3 Proposed mechanism for the anilinolysis reactions of dithiocarbonate **5**, (X=NO_2)

both 4-nitrophenolate and 4-nitrobenzenethiolate are nucleofuges. This result reinforces the idea that the amine nature changes the relative nucleofugality of groups.

3.4 | Influence of nonleaving group on the nucleofugality

An important question arises from the comparison of results for the anilinolysis of **5** (this study) with those of the same reactions of **2** and **3** in the same experimental conditions.[8e] Although for these substrates the mechanism is stepwise, the kinetic behavior is different. In fact, for the reactions of **2** and **3**, the plots of k_{obs} versus aniline concentrations are curved up and those for **5** are linear. To explain the upward curve in the plots, it was supposed that the deprotonating agents were both the buffer anion and a second amine molecule. In all these reactions, the aniline and buffer concentrations are similar; therefore, the deprotonation rate constants must be similar. In the case of **2** and **3**, the rate equation is $k_{\mathrm{obs}} = K_1(k_2 + k_3[\mathrm{A}^-])\ \mathrm{N} + K_1 k_3 \mathrm{N}^2$ (eq. 3 in Castro et al[8e]), where N corresponds to the amine and A^- represents the anionic form of the buffer. Nevertheless, in the reaction of **5**, the second term disappears probably because k_2 for the reaction of **5** is greater than that for **2** and **3**. This is probably due to the greater electron withdrawing of the 4-nitrophenoxy group favoring the 4-nitrobenzenethiolate expel.

In the anilinolysis reactions of **2** and **3**, only 4-nitrobenzenethiolate is the nucleofuge, whereas in the reaction of **5**, the 4-nitrophenolate ion is also the nucleofuge. This can be explained by the greater electron withdrawing capacity of the 4-nitrophenolate moiety compared with 4-chloro or 4-methyl phenolate moieties in the tetrahedral intermediate. In the same way, in the anilinolysis of **4** and **6**, 4-nitrophenolate ion is the unique nucleofuge, while in the reactions of **5**, 4-nitrobenzenethiolate is also a leaving group. This can be explained in part due to the different electron withdrawing capabilities of the *S*-(4-nitrophenyl) group compared with benzenethiolate group, which diminish the expulsion of 4-nitrophenolate and compete as a nucleofuge. These results strongly support the idea that the nonleaving group is not passive and plays an important role in the relative nucleofugality of groups.

4 | CONCLUSIONS

The reaction of *O*-(4-nitrophenyl) *S*-aryl dithiocarbonates (**4-6**) with anilines has been examined. The analysis based on the kinetic study demonstrates that these reactions occur through a stepwise mechanism with 2 tetrahedral intermediates, one zwitterionic ($\mathrm{T}^{\pm}$) and the other anionic (T^{-}), with the borate buffer as the proton transfer agent.

The nucleofugacity of 4-nitrophenolate ion is similar to that of 4-nitrobenzenethiolate from the tetrahedral intermediate I, despite the differences in their basicities (3 $\mathrm{p}K_{\mathrm{a}}$ units).

In the reactions of *O*-(4-nitrophenyl) *S*-(4-nitrophenyl dithiocarbonate (**5**), the change of nucleophile from pyridines (one nucleofuge, 4-nitrophenolate ion) to anilines (2 nucleofuges, 4-nitrophenolate and benzenethiolate ions) shows that the nature of the amine affects the relative nucleofugality of groups.

The nonleaving group is not passive and plays an important role in the relative nucleofugality of groups depending largely on its capability of electron withdrawing.

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