Reactivity of phenolic nucleophiles towards nitroso compounds. Part 2.[1] Reaction with alkyl nitrites (*O*-nitroso compounds)

J. Ramón Leis,* Ana Ríos and Luisa Rodríguez-Sánchez

*Departamento de Química Física, Facultad de Química, Universidad de Santiago,
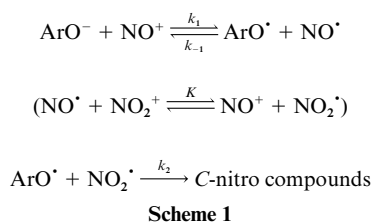15706 Santiago de Compostela, Spain*

Second-order rate constants, k, have been measured for the reaction of substituted phenolate ions with alkyl nitrites in aqueous solution at 25 °C. The final products of this reaction were identified as aromatic *C*-nitroso compounds and/or NO_2^-. Nitrosation of the phenolate ion yields *ca.* 90% of the *p*-nitroso product. However, methylation of the activated position of the ring (as in 4-methylphenol) does not result in the decrease in the overall reaction rate that would be expected. The reactivity of all the phenolate ions studied correlates well with their basicity, with the Hammett σ^- constant and with their reactivity in other reactions in which they are known to act as O-nucleophiles. All these facts suggest that the reaction of aryloxide ions with alkyl nitrites always occurs through the oxygen atom to yield an unstable *O*-nitroso compound. This intermediate is likely to undergo an internal rearrangement of the NO group to give the corresponding *C*-nitroso product, competing with homolysis of the O–NO bond to yield nitric oxide. Oxidation of NO in the presence of O_2 gives N_2O_3, which could act as a nitrosating agent towards ArO^-. Hydrolysis of N_2O_3 in basic media accounts for the presence of the nitrite ion as one of the products.

Introduction

Nitrosation of phenols in acidic media by nitrous acid has been widely studied by Challis and co-workers.[2–4] The products of this reaction are *C*-nitroso compounds† formed *via* a neutral dienone intermediate, from which proton loss is usually rate limiting. Nitro compounds are sometimes the final products due to rapid oxidation of the initially formed nitrosoaromatic species.

It is also known that nitrous acid acts as a catalyst in the nitration of certain aromatic systems including phenols.[5,6] A detailed investigation into the mechanism of this reaction provides evidence for an electron-transfer pathway, which in some cases is accompanied by a conventional nitrosation–oxidation reaction. Kinetic studies of the nitrous acid-catalysed nitration of phenol[7] and *p*-nitrophenol[8] are consistent with the mechanism given in Scheme 1.

$$ArO^- + NO^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArO^\bullet + NO^\bullet$$

$$(NO^\bullet + NO_2^+ \overset{K}{\rightleftharpoons} NO^+ + NO_2^\bullet)$$

$$ArO^\bullet + NO_2^\bullet \overset{k_2}{\longrightarrow} \textit{C}\text{-nitro compounds}$$

<div align="center">

Scheme 1

</div>

Formation of the phenoxy radical and nitric oxide could occur by homolysis of a small equilibrium concentration of phenyl nitrite (ArONO), which in the case of phenol can also form *p*-nitrosophenol (which is readily oxidised to *p*-nitrophenol).

Phenolic substrates can also be nitrosated in basic media although the mechanism of this reaction has not been studied

in detail. An investigation of the nitrosation of a large number of phenols by isoamyl nitrite in dimethylformamide (DMF) and in the presence of potassium carbonate showed that this reaction yields the corresponding *p*-quinone monoxime, unless the *para*-position is blocked.[9] We have recently reported a kinetic study of the reaction of phenolate ions with the ambient electrophile *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS).[1] The products of this reaction are consistent with two competitive pathways corresponding to reaction at both electrophilic centres of MNTS (the −NO and −SO_2− groups) (Scheme 2). Methylation of the activated position of

<div align="center">
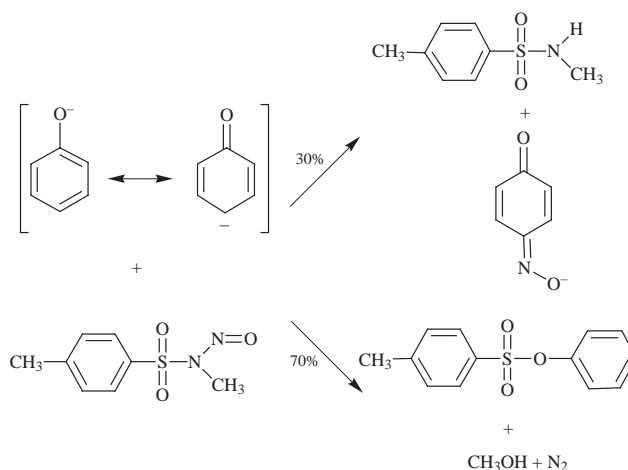
Scheme 2

</div>

the ring did not decrease the reactivity of the corresponding phenolate ion. Furthermore, methylation does not increase the proportion of attack through the oxygen atom at the −SO_2− group of MNTS, but increases the amount of reaction at the nitroso group. All these experimental observations led us to propose a mechanism in which phenolates act only as oxygen nucleophiles towards MNTS. However, it is not clear how the *O*-nitroso compound initially formed evolves to give the final products (*C*-nitroso compounds and/or NO_2^-).

---

† The term *C*-nitroso compound is used to describe both the quinone monoxime, and the nitrosophenol as a general indication of the tautomeric compounds: it does not necessarily indicate the form, quinonoid or benzenoid, which prevails in the tautomeric equilibrium in solution [based upon the usage of A. Kraaijeveld and E. Havinga, *Rec. Trav. Chim.*, 1954, **73**, 537].

In this paper we describe the results obtained in the study of the reaction of substituted phenols with alkyl nitrites, which, like MNTS, are known to transfer the nitroso group directly to a large number of nucleophiles.[10–12] The experimental results allow the discussion of different mechanistic possibilities for the nitrosation of phenols in basic media.

Experimental

Alkyl nitrites were synthesized by treating the corresponding alcohols with sodium nitrite in an acidic medium,[13] and the products were stored in the dark at a low temperature over molecular sieves. Phenols were obtained from Aldrich and purified by recrystallization or redistillation.[14] All other reagents (Aldrich or Merck) were used as supplied. Alkyl nitrite solutions were made up in dioxane to prevent their hydrolysis[15] and a small volume of these solutions was added to the reaction mixtures to initiate the reaction. The percentage of organic solvent in the medium was always ≤5%.

The kinetics of the reaction of phenolate ions with alkyl nitrites were studied at 25 °C under pseudo-first-order conditions, *i.e.* with the nucleophile always in great excess with respect to RONO. In most cases the pH was controlled using buffer solutions of the nucleophile itself, which were made up with the corresponding phenol and NaOH. However, for the less basic phenols (2-Cl-, 4-CHO- and 2-CN-phenol) reactions were carried out in 0.1 M carbonate/bicarbonate buffer at pH 9.9. The ionic strength was not kept constant in the kinetic studies since the reaction rates were found to be independent of this parameter in preliminary studies. pH was measured with a Radiometer pHM82 pH-meter equipped with a GK2401B combined glass electrode and calibrated using commercial buffers of pH 7.02 (Crison) and 10.01 or 12.45 (Beckman).

Reaction kinetics were followed spectrophotometrically using Kontron Uvikon 930 or Milton Roy Spectronic 3000 diode array spectrophotometers with thermostatted cell carriers. The reaction spectra were generally clean and experiments were monitored at wavelengths corresponding to the formation of the *C*-nitroso compound. Particular care was taken to ensure that decomposition of the phenols in basic media and in the presence of light was not significant and did not compete with the process under study. Absorbance–time data always fitted the first-order integrated equation and values of the observed pseudo-first-order rate constant, k_{obs}, were reproducible to within 5%.

Reaction products were identified by UV–VIS spectroscopy and, in all cases, released nitrite was quantified by a modified form of Shinn's method.[10]

Results

The reaction of phenol with different alkyl nitrites in basic media led to the formation of *p*-nitrosophenol, as shown by the UV–VIS spectrum of the final reaction mixture. Quantification of this product, which at basic pH exists as the *p*-quinone monoxime ($\lambda_{max} = 400$ nm, $\varepsilon = 27\ 100$ M^{-1} cm^{-1}),[16] showed a 90% yield in all cases. No evidence was found of the presence of significant amounts of the 2-nitroso isomer. Analysis of the reaction mixtures at the end of the reaction by Shinn's method showed ≤10% formation of NO$_2^-$ (see Table 1).

The products formed in the nitrosation of substituted phenols were identified as the corresponding *C*-nitroso compounds by their typical absorption bands [2,6-dimethyl-4-nitrosophenol, 2-chloro-4-nitrosophenol (see Fig. 1), 2-cyano-4-nitrosophenol and 3-chloro-4-nitrosophenol, λ_{max} ~400 nm; 4-chloro-2-nitrosophenol, 4-methyl-2-nitrosophenol and 4-hydroxy-3-nitrosobenzaldehyde, λ_{max} ~470 nm; 3-

Table 1 Yields of nitrite obtained in the reaction of substituted phenolates with alkyl nitrites

Phenolate	RCH$_2$ONO, R	NO$_2^-$ (%)^a
2,6-(CH$_3$)$_2$^{b}	Cl$_2$CH–	25 ± 8
4-CH$_3$^{b}	BrCH$_2$–	76 ± 6
	Cl$_2$CH–	82 ± 3
H^b	BrCH$_2$–	8 ± 1
	Cl$_2$CH–	7 ± 2
	F$_3$C–	11 ± 1
3-CH$_3$O^b	Cl$_2$CH–	10 ± 1
4-Cl^c	BrCH$_2$–	74 ± 7
	Cl$_2$CH–	74 ± 10
2-Cl^d	Cl$_2$CH–	86 ± 9
3-Cl^e	Cl$_2$CH–	48 ± 8
2-CN^d	Cl$_2$CH–	68 ± 1
4-CHO^d	Cl$_2$CH–	72 ± 1

^{a} Average of the values obtained at different phenol concentrations and constant pH. ^{b} [ArO$^-$]/[ArOH] = 1. ^{c} [ArO$^-$]/[ArOH] = 4. ^{d} pH = 9.90 (carbonate/bicarbonate buffer 0.1 M). ^{e} [ArO$^-$]/[ArOH] = 3.
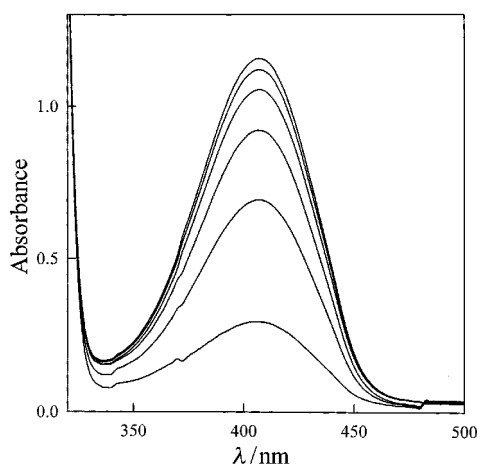

Fig. 1 Typical absorption spectra for the reaction of 2-chlorophenol (9.3×10^{-2} M) with 2,2-dichloroethyl nitrite (1.8×10^{-4} M) at 25 °C showing the increase in absorbance at 408 nm due to the formation of 2-chloro-4-nitrosophenolate ion. 0.1 M carbonate/bicarbonate buffer (pH = 9.90). Scans were taken at 60 s intervals.

methoxy-4-nitrosophenol, λ_{max} ~350 nm]. For most of these phenols *C*-nitrosation was accompanied by the formation of large amounts of NO$_2^-$. The nitrite yields are summarized in Table 1. Analysis of NO$_2^-$ at different phenol concentrations and constant pH showed a small decrease in the percentage of this product on increasing the nucleophile concentration for 2-, 3- and 4-chlorophenol (see Table 2 for representative data). In addition, the final absorbance at λ_{max} for the product was consistent with the formation of a larger amount of *C*-nitroso compound at high concentrations of phenol. Experiments carried out with 4-methylphenol and 2-bromoethyl nitrite at two different pH values showed the same product ratios in the final reaction mixtures (Table 2).

Pseudo-first-order rate constants, k_{obs}, were determined as described in the Experimental section. Plots of k_{obs} against total phenol concentration at constant pH are linear. Typical data are shown in Fig. 2 for phenol and 2-chlorophenol. A small but significant intercept was observed in some of these plots due to the competing hydrolysis of the alkyl nitrite in basic media. The dependence on pH of k_{obs} (Fig. 3) for the reaction of phenol with 2-bromoethyl nitrite shows that the phenolate ion is the only reactive form of the nucleophile. The expression for the pseudo-first-order rate constant is given by eqn. (1), where k is the second-order rate constant for reaction of the corresponding phenolate ion with RONO and K_a the acid dissociation constant for the phenol.

Table 2 Influence of the total nucleophile concentration and pH on the yields of nitrite formed in the reaction of substituted phenols with alkyl nitrites

Phenolate	RONO	[Phenol]$_{total}$/M	pH	NO$_2^-$ (%)	$\Delta A_{478\,nm}$
4-Cl	BrCH$_2$CH$_2$ONO[a]	0.1	10.02	66	0.41
		4.1×10^{-2}	10.02	75	0.25
		1.0×10^{-2}	10.02	80	0.16
	Cl$_2$CHCH$_2$ONO[b]	0.1	9.98	62	0.19
		4.1×10^{-2}	9.98	76	0.12
		1.0×10^{-2}	9.98	84	0.07
4-CH$_3$	BrCH$_2$CH$_2$ONO[c]	2.5×10^{-2}	10.87	70	0.25
		2.5×10^{-2}	9.67	76	0.21

[a] [RONO] = 2.4×10^{-4} M. [b] [RONO] = 1.2×10^{-4} M. [c] [RONO] = 2.6×10^{-4} M.
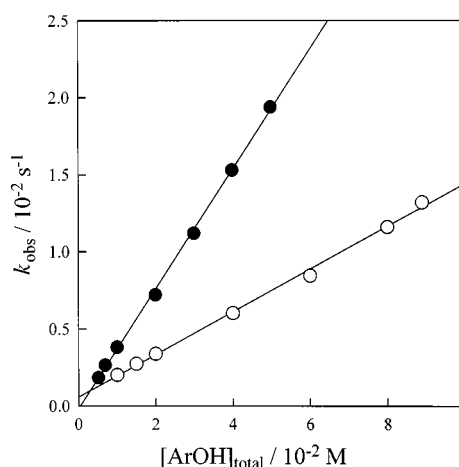

Fig. 2 Dependence of the observed rate constants for the reaction of phenol (●) and 2-chlorophenol (○) with 2,2-dichloroethyl nitrite on the total concentration of the nucleophile. (●) [ArO$^-$]/[ArOH] = 1; (○) 0.1 M carbonate/bicarbonate buffer, pH = 9.90.
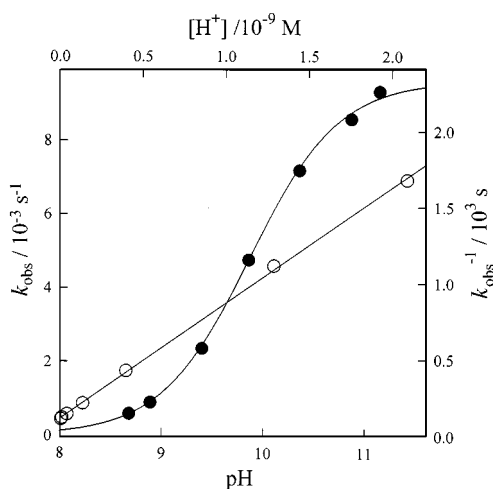

Fig. 3 Influence of pH on the observed rate constant for reaction of phenol with 2-bromoethyl nitrite. [phenol]$_{total}$ = 0.5 M. (●) k_{obs} vs. pH; (○) $1/k_{obs}$ vs. [H$^+$].

$$k_{obs} = \frac{kK_a[\text{ArOH}]_{total}}{K_a + [\text{H}^+]} \quad (1)$$

A value of 9.84 for the pK_a of phenol is obtained from the slope and the intercept of a linear plot of $1/k_{obs}$ vs. [H$^+$] (Fig. 3). The value of k, obtained from the intercept of this plot, for the nitrosation of phenol by 2-bromoethyl nitrite is listed in Table 3 together with values for the nitrosation by alkyl nitrites of the different substituted phenols studied.

Table 3 Bimolecular rate constants for the nitrosation of substituted phenols by alkyl nitrites at 25 °C

Phenolate	pK_a	RONO	k/M^{-1} s^{-1}
2,6-(CH$_3$)$_2$	10.63[a]	Cl$_2$CHCH$_2$ONO	5.45
4-CH$_3$	10.09[b]	BrCH$_2$CH$_2$ONO	5.00×10^{-2}
		Cl$_2$CHCH$_2$ONO	1.57
H	9.81[b]	BrCH$_2$CH$_2$ONO	1.96×10^{-2}
		Cl$_2$CHCH$_2$ONO	0.77
3-CH$_3$O	9.65[c]	Cl$_2$CHCH$_2$ONO	2.65
4-Cl	9.26[b]	BrCH$_2$CH$_2$ONO	8.59×10^{-3}
		Cl$_2$CHCH$_2$ONO	0.36
3-Cl	8.87[b]	Cl$_2$CHCH$_2$ONO	0.15
2-Cl	8.32[b]	Cl$_2$CHCH$_2$ONO	0.14
4-CHO	7.66[a]	Cl$_2$CHCH$_2$ONO	3.00×10^{-2}
2-CN	7.22[c]	Cl$_2$CHCH$_2$ONO	1.32×10^{-2}

[a] Ref. 17. [b] Ref. 18. [c] Ref. 19.

Discussion

Nitrosation of phenol in acid media proceeds by an aromatic electrophilic substitution mechanism involving a neutral dienone intermediate. Phenol acts as a carbon nucleophile and the reaction takes place mainly at the *para*-position to give ≥95% *p*-nitrosophenol and a small amount of the *ortho*-isomer as the only products.[4] However, phenols are ambient nucleophiles and their reaction with the nitroso group could also take place at the oxygen atom. Thus, Challis *et al.* have suggested that nitrosation of the 2-naphtholate ion at pH < 5 occurs by reversible formation of an unstable aryl nitrite.[4] This same species has been proposed as an intermediate in the nitrous acid-catalyzed nitration of phenols.[7,8,17]

Reaction of phenol with alkyl nitrites in basic media gives a high yield of the *p*-nitrosophenolate ion (*ca.* 90%) as the only *C*-nitroso product, along with a small amount of NO$_2^-$. Analysis of the reaction products for *ortho*-substituted phenols shows an increase in the percentage of NO$_2^-$ formed with respect to the unsubstituted compound, in spite of the fact that the *para*-position is free (Table 1). A mechanism similar to that proposed by Challis *et al.* in 1971 for nitrosation of phenols in acid media[2] (see Scheme 3) would not explain the presence of NO$_2^-$ in the final products.
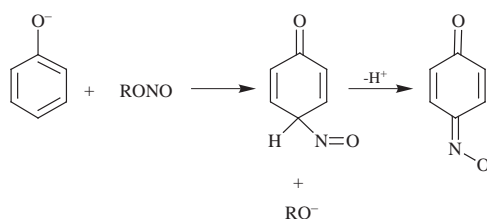
Scheme 3

Furthermore, methylation of the activated position of the ring results in an increase in the overall reaction rate (Table 3),
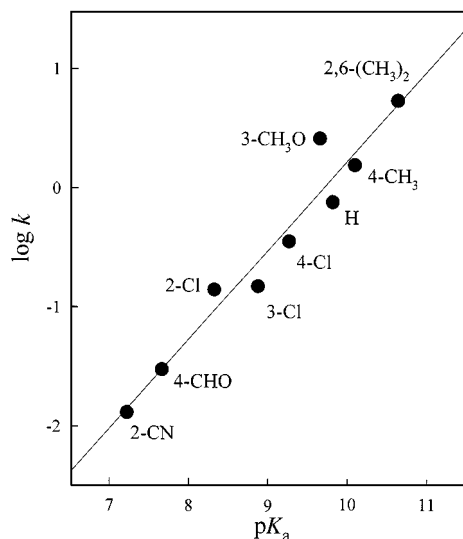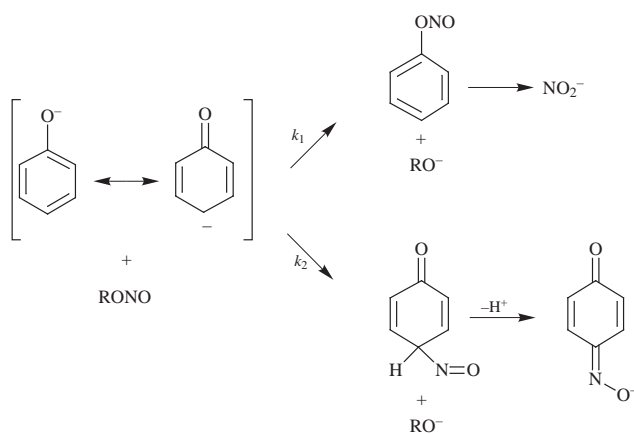
Fig. 4 Brønsted plot for the reaction of substituted phenolate ions with 2,2-dichloroethyl nitrite. Data are from Table 3.

Fig. 5 Hammett plot for the reaction of substituted phenolate ions with Cl_2CHCH_2ONO.

which is contrary to what would be expected for a mechanism involving direct *C*-nitrosation of the aromatic ring.

An alternative mechanism for nitrosation of phenols in basic media would involve reaction with the nitrosating agent along two competitive pathways (Scheme 4): (i) an *O*-nitrosation

Scheme 4

reaction to yield an aryl nitrite and (ii) reaction through the carbon atom of the phenol to give *C*-nitrosated products. The overall reaction rate would be the sum of the second-order rate constants for both processes. Formation of 90% *p*-nitrosophenol during the nitrosation of the unsubstituted phenolate ion would indicate that the C atom at the *para*-position of the ring is more nucleophilic than the O atom. When a methyl group is blocking the *para*-position (as in the anion of 4-methylphenol) the final products correspond to almost 80% NO_2^-, suggesting that the O atom is now the preferential site of reaction and, therefore, a decrease in the overall reaction rate with respect to the unsubstituted anion would be expected. However, experimental results show that the overall reactivity increases upon methylation of the *para*-position of the ring.

All these facts suggest that phenolate ions react with alkyl nitrites only through the O atom to initially give an unstable aryl nitrite. A similar conclusion was reached in a previous study of the reaction of phenolate ions with a different nitrosating agent, MNTS, in basic media.[1]

Fig. 4 shows a plot of the reactivities of the various phenolate ions with 2,2-dichloroethyl nitrite (log k) against the pK_a values for the corresponding phenols. The existence of a good
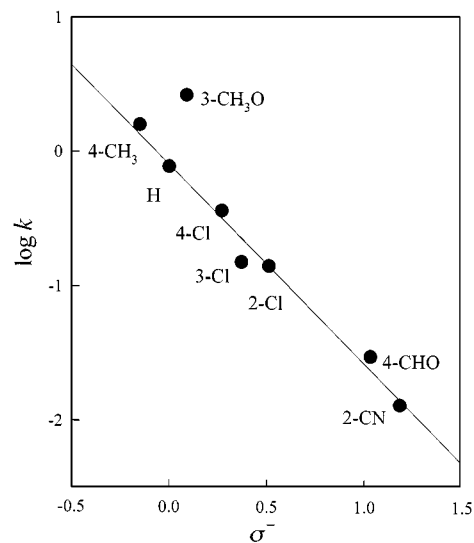
linear correlation between reactivity and basicity over 4 pK_a units ($\beta = 0.75 \pm 0.07$) is consistent with the phenolate ions always acting as O-nucleophiles.

Analysis of the bimolecular rate constants, k, given in Table 3 shows that the reaction is accelerated by the presence of electron-donating groups. Attack by substituted phenolate ions on the nitroso group of the alkyl nitrite has a linear σ^- dependence‡ with a slope $\rho = -1.5$ (Fig. 5). This behavior can be explained by considering that the resonance interaction present in aromatic oxyanions bearing electron-withdrawing substituents, such as −CHO or −CN, in *ortho*- or *para*-positions is mostly lost on going from reactants to the transition state.

Phenolate ions are known to react as O-nucleophiles with esters of carboxylic acids. Fig. 6 shows a plot of log k for the reaction of different phenolic nucleophiles with 2,2-dichloroethyl nitrite against log k for their reaction with 4-nitrophenyl acetate[18] and 2,4-dinitrophenyl acetate.[19] These electrophiles

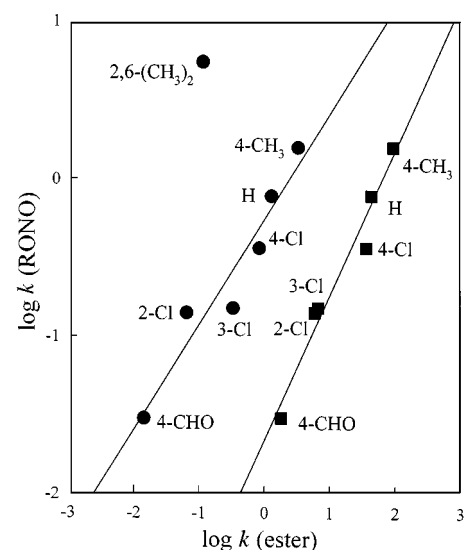**Fig. 6** Reactivities of substituted phenolate ions with Cl_2CH-CH_2ONO plotted *vs.* those of the same nucleophiles with (●) 4-nitrophenyl acetate and (■) 2,4-dinitrophenyl acetate.

---

‡ σ^- values are from: C. Hansch and A. Leo, *Substituent Constants For Correlation Analysis in Chemistry and Biology*, Wiley-Interscience, John Wiley and Sons, New York, 1979. In the case of the 3-Cl substituent, for which no σ^- value is available, an estimation was made by considering $\sigma_m^- \cong \sigma_m$ for this nonconjugated substituent.

are believed to react with aromatic oxyanions through a concerted mechanism in which attack of the nucleophile and departure of the leaving group take place simultaneously.[18–20] A satisfactory correlation is observed in both cases and the slopes of the regression lines are 0.7 and 0.9 respectively. The marked deviation observed for the anion of 2,6-dimethylphenol is due to a large steric requirement in the transition state for its reaction with carboxylic esters, which is not present in the transition state for its reaction with alkyl nitrites.

The results reported previously for the reaction of phenolates with MNTS[1] and those shown in this work for their reaction with alkyl nitrites, lead to the conclusion that the oxygen atom is the only reactive center of these ambident nucleophiles in nitrosation reactions in basic media. However, it is difficult to determine the mechanism by which the initially formed unstable ArONO rapidly decomposes to give the final products.

Formation of the nitrite ion in the reaction mixtures could take place by hydrolysis of the O-nitroso intermediate. However, yields of NO_2^- were found to be independent of pH at constant nucleophile and RONO concentration (Table 2), showing that its formation from the ArONO species corresponds to a homolytic process rather than to a hydrolysis reaction.

In reaction mixtures containing large concentrations of reactants ($\approx 5 \times 10^{-2}$ M 2,4,6-trimethylphenolate and $BrCH_2$-CH_2ONO), highly colored species are formed that are probably derived from the tri-substituted phenoxy radical. Similar colors are observed during the oxidation of 2,4,6-trimethylphenol by potassium ferricyanide in basic solution. This reagent is known to generate high yields of phenoxy radicals.[21] This behavior provides evidence for the homolytic cleavage of the O-NO bond to give the aryloxide radical and nitric oxide. Furthermore, in our previous study[1] NO was identified as one of the products of the reaction between MNTS and 2,4,6-trimethylphenol by the ABTS [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)] test. Experiments carried out under the same conditions for phenol, 2,6-dimethylphenol, 4-methylphenol and 2-chlorophenol lead to similar conclusions.

ArO$^{\bullet}$ and $^{\bullet}$NO could combine to yield aromatic C-nitroso compounds. However, the fact that no ortho-product is formed during the nitrosation of unsubstituted phenol is not consistent with the ratio of spin densities at the ortho- and para-positions of the phenoxy radical (0.67).[7,22] It is known that oxidation of NO by oxygen in aqueous solution yields the nitrite ion quantitatively.[23,24] This fact would explain the presence of NO_2^- as a product in our final reaction mixtures. Nitric oxide is not itself a nitrosating species, but its reaction with oxygen generates ONOONO, NO_2 and N_2O_3 as strong oxidizing intermediates. Pires et al.[25] found that the NO/O_2 system is an efficient nitrosating agent that in the presence of phenol leads to the formation of 4-nitrosophenol. They concluded that N_2O_3 is the nitrosating intermediate and in basic solution hydrolysis of this species to give the nitrite ion competes with its reaction with phenol to yield the C-nitroso compound. However, nitrosation by N_2O_3 could not be the only C-nitrosation pathway in the reaction of phenolate ions with alkyl nitrites since 50% is the maximum yield of C-nitroso product that can be formed by this route, and higher yields were obtained in this work for phenol, 2,6-dimethylphenol and 3-methoxyphenol. The fact that the percentage of C-nitroso compound formed during nitrosation of 2-, 3- and 4-chlorophenol increases with the total concentration of nucleophile (Table 2) is consistent with this being a significant nitrosation pathway. Another possibility would be an internal rearrangement of the NO group, similar to the Fischer–Hepp rearrangement of aromatic N-nitrosoamines.[26,27]

In conclusion, it seems clear from all the kinetic results that phenolate ions react with alkyl nitrites through the oxygen atom to give the corresponding nitrite ester. This unstable intermediate evolves by a complex mechanism to generate the final products observed. We suggest that homolysis of the O-NO bond to give ArO$^{\bullet}$ and $^{\bullet}$NO occurs simultaneously with an internal rearrangement of the NO group to yield stable C-nitroso compounds. Oxidation of NO to form N_2O_3 and reaction of the latter with an aryloxide ion generates an additional C-nitrosation pathway. Competitive hydrolysis of N_2O_3 in basic media would explain the presence of the nitrite ion as one of the products.

References

1 Part 1, J. R. Leis and A. Ríos, *J. Chem. Soc., Perkin Trans. 2*, 1996, 857.
2 B. C. Challis and A. J. Lawson, *J. Chem. Soc. (B)*, 1971, 770.
3 B. C. Challis and R. J. Higgins, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2365.
4 B. C. Challis and R. J. Higgins, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1597.
5 D. L. H. Williams, *Nitrosation*, Cambridge University Press, 1988.
6 J. H. Ridd, *Chem. Soc. Rev.*, 1991, **20**, 149.
7 U. Al-Obaidi and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1985, 467.
8 M. Ali and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1986, 327.
9 T. Ishikawa, T. Watanabe, H. Tanigawa, T. Saito, K.-I. Kotake, Y. Ohashi and H. Ishii, *J. Org. Chem.*, 1996, **61**, 2774.
10 L. García-Río, E. Iglesias, J. R. Leis, M. E. Peña and A. Ríos, *J. Chem. Soc., Perkin Trans. 2*, 1993, 29.
11 J. R. Leis, M. E. Peña and A. Ríos, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1233.
12 J. R. Leis, M. E. Peña and A. Ríos, *J. Chem. Soc., Perkin Trans. 2*, 1995, 587.
13 W. A. Noyes, *Org. Synth., Coll. Vol. II*, 1943, 108.
14 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, 1988.
15 L. García-Río, E. Iglesias, J. R. Leis, M. E. Peña and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1673.
16 H. Schmid, G. Muhr and P. Riedl, *Monatsh. Chem.*, 1966, **97**, 781.
17 A. P. Gosney and M. I. Page, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1783.
18 S. Ba-Saif, A. K. Luthra and A. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6362.
19 S. A. Ba-Saif, M. Colthurst, M. A. Waring and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1901.
20 D. Stefanidis, S. Cho, S. Dhe-Paganon and W. P. Jencks, *J. Am. Chem. Soc.*, 1993, **115**, 1650.
21 E. R. Altwicker, *Chem. Rev.*, 1967, **67**, 475.
22 A. I. Scott, *Q. Rev.*, 1965, **19**, 1.
23 A. R. Butler and D. L. H. Williams, *Chem. Soc. Rev.*, 1993, 233.
24 S. Goldstein and G. Czapski, *J. Am. Chem. Soc.*, 1995, **117**, 12078.
25 M. Pires, M. J. Rossi and D. S. Ross, *Int. J. Chem. Kinet.*, 1994, **26**, 1207.
26 I. D. Biggs and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1976, 691.
27 I. D. Biggs and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1977, 44.

Paper 8/05373A