Kinetics of the Reaction of *para*-Substituted Nitrosobenzenes with Methoxide Ion in Methanol

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The kinetics of the reaction of RC_6H_4NO with MeO^- to yield $RC_6H_4N{=}N(O)C_6H_4R$ (R = H, *p*-NMe_2, *p*-OMe, or *p*-Cl), or $RC_6H_4NO_2$ in the presence of oxygen (R = H, *p*-OMe, or *p*-Cl) were studied as a function of temperature and MeO^- concentration. ρ Values (3·9 and 4·0 at 25 °C, for azoxy formation and oxidation respectively) are consistent with the presence of a negative charge in the transition state, the rate-determining steps being the formation of $RC_6H_4NOH\cdot$ from RC_6H_4NO and MeO^- for azoxy formation and the reduction of $RC_6H_4NO_2^{\cdot-}$ by MeOH for oxidation. Activation parameters are discussed in the light of the proposed mechanism.

THE role of nitroso-derivatives in the electron-transfer mechanism for the reduction of the nitro-group in nitroaromatic compounds by alkoxide ions has been clarified in previous work [1,2] [*cf.* equations (1)—(12) of the proposed reaction scheme [2]]. In this paper attention is drawn particularly to reaction of substituted nitrosobenzenes with methoxide ion [reaction (1)]. This reaction has long been known in preparative chemistry to yield the corresponding azoxy-derivatives.[3] We found, however, in accord with Ayscough *et al.*,[4] that, when the concentration of substrate was as low as that

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[1] I. R. Bellobono, A. Gamba, G. Sala, and M. Tampieri, *J. Amer. Chem. Soc.*, 1972, **94**, 5781.

[2] I. R. Bellobono, P. Govoni, and F. Zavattarelli, preceding paper.

[3] For references, see S. R. Sandler and W. Karo, ' Organic Functional Group Preparations,' Academic Press, New York, vol. 12, chs. 15—16.

[4] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.* (*B*), 1966, 903.

of oxygen in methanol solution,[5] oxidation of the nitroso- to a nitro-group [reaction (2)] was a concurrent and sometimes predominant reaction in methoxide solutions. The kinetics of both reactions (1) and (2) have now been examined in methanol solution (k_A and

$$2RC_6H_4NO + \tfrac{1}{2}CH_3O^- \xrightarrow{k_A} RC_6H_4N{=}N(O)C_6H_4R + \tfrac{1}{2}HCO_2^- + \tfrac{1}{2}H_2O \quad (1)$$
$$(R = H,\ p\text{-}NMe_2,\ p\text{-}OMe,\ \text{or}\ p\text{-}Cl)$$

$$RC_6H_4NO + \tfrac{1}{2}CH_3O^- + O_2 \xrightarrow{k_N} RC_6H_4NO_2 + \tfrac{1}{2}HCO_2^- + \tfrac{1}{2}H_2O \quad (2)$$
$$(R = H,\ p\text{-}OMe,\ \text{or}\ p\text{-}Cl)$$

k_N denote experimental rate constants for the production of azoxy- or nitro-compound respectively). Reaction (1) occurred easily and quantitatively, with the given stoicheiometry, provided oxygen was rigorously excluded. Reaction (2) could be studied by a suitable choice of experimental conditions so as to keep the oxygen in solution at a concentration greater than that of the substrate.

EXPERIMENTAL

Materials.—RC_6H_4NO (R = *p*-NMe_2,[6,7] R = H,[7] R = *p*-OMe,[8,9] and R = *p*-Cl [7]) were prepared and purified by literature methods. All other reagents and solvents were prepared and/or purified as described previously.[1,10] Identification of products was on the basis of elemental analyses and existing literature data.

Kinetics.—Kinetic runs were carried out directly in thermostatted spectrophotometric cells, following the standard procedure.[2] When studying reaction (1), particular care was devoted to oxygen exclusion even during spectrophotometric measurements: a stream of purified oxygen-free nitrogen was circulated in the cell compartment. When studying reaction (2), on the other hand, all solutions and solvents were saturated with oxygen.

RESULTS AND DISCUSSION

The stoicheiometry of reactions (1) and (2) has been established by titration of methoxide, chemical and spectrophotometric analysis of reagents and products, as well as by g.l.c. detection of formic acid.

The experimental pseudo-first-order rate constants k_A and k_N for reactions (1) and (2) were found to be non-linear functions of sodium methoxide concentration for the concentration range investigated (0·12—1·65M-MeO^-). Consistent second-order rate constants k_A' and k_N' were obtained by use of 'kinetic activities' (a_{MeO^-}) of methoxide ion instead of concentrations, as previously.[1,2] The second-order rate constants at various temperatures in the range 0·8—67·9 °C are reported in Tables 1 and 2 for reactions (1) and (2) respectively.

For reaction (1), only in the case of *m*- or *p*-nitronitrosobenzene was an intermediate (I; R = *m*- or *p*-NO_2) observed. Rate constants for the formation (k_6) and decomposition (k_3) of these species [equations (6)—(12) of ref. 2] are reported in the preceding paper.[2] With the exception of the substrate bearing the nitro-group as substituent in the *meta*- or *para*-position, and for which $k_3 \ll k_6$, rate constants for the disappearance of the nitroso-compound and for the formation of the corresponding azoxy-derivative are numerically coincident.

TABLE 1

Second-order rate constant for reaction (1) between substituted nitroso-compounds and methoxide ion to yield the corresponding azoxy-derivative

Substituent R	Temp. (°C)	k_A'/l mol^{-1} s^{-1}
p-NMe_2	34·0	$4{\cdot}838 \times 10^{-7}$
p-NMe_2	51·3	$2{\cdot}289 \times 10^{-6}$
p-NMe_2	55·0	$3{\cdot}024 \times 10^{-6}$
p-NMe_2	59·4	$4{\cdot}391 \times 10^{-6}$
p-OMe	41·4	$3{\cdot}703 \times 10^{-5}$
p-OMe	46·1	$6{\cdot}615 \times 10^{-5}$
p-OMe	51·0	$1{\cdot}111 \times 10^{-4}$
p-OMe	56·3	$2{\cdot}304 \times 10^{-4}$
p-OMe	61·1	$4{\cdot}790 \times 10^{-4}$
p-OMe	67·9	$1{\cdot}212 \times 10^{-3}$
H	25·0	$7{\cdot}412 \times 10^{-4}$
H	40·0	$2{\cdot}321 \times 10^{-3}$
H	50·0	$6{\cdot}430 \times 10^{-3}$
p-Cl	34·5	$4{\cdot}798 \times 10^{-3}$
p-Cl	41·0	$8{\cdot}910 \times 10^{-3}$
p-Cl	45·3	$1{\cdot}634 \times 10^{-2}$
p-Cl	50·5	$2{\cdot}394 \times 10^{-2}$
p-Cl	57·1	$4{\cdot}637 \times 10^{-2}$
p-Cl	61·6	$8{\cdot}277 \times 10^{-2}$

TABLE 2

Second-order rate constants for reaction (2) between substituted nitroso-compounds and methoxide ion in the presence of oxygen to yield the corresponding nitro-derivative

Substituent R	Temp. (°C)	k_N'/l mol^{-1} s^{-1}
p-OMe	15·6	$2{\cdot}726 \times 10^{-6}$
p-OMe	31·9	$9{\cdot}757 \times 10^{-6}$
p-OMe	38·4	$1{\cdot}383 \times 10^{-5}$
p-OMe	45·3	$2{\cdot}463 \times 10^{-5}$
p-OMe	50·6	$2{\cdot}678 \times 10^{-5}$
p-OMe	55·2	$3{\cdot}918 \times 10^{-5}$
p-OMe	60·2	$5{\cdot}360 \times 10^{-5}$
H	34·0	$8{\cdot}000 \times 10^{-5}$
H	41·4	$3{\cdot}300 \times 10^{-4}$
H	52·4	$5{\cdot}710 \times 10^{-4}$
H	60·5	$1{\cdot}260 \times 10^{-3}$
p-Cl	11·0	$2{\cdot}191 \times 10^{-4}$
p-Cl	21·2	$3{\cdot}711 \times 10^{-4}$
p-Cl	24·8	$5{\cdot}008 \times 10^{-4}$
p-Cl	28·2	$7{\cdot}334 \times 10^{-4}$
p-Cl	31·5	$8{\cdot}334 \times 10^{-4}$
p-Cl	32·2	$8{\cdot}500 \times 10^{-4}$
p-Cl	34·7	$1{\cdot}055 \times 10^{-3}$
p-Cl	41·4	$1{\cdot}271 \times 10^{-3}$
p-Cl	50·5	$2{\cdot}300 \times 10^{-3}$

The proposed mechanism [2] seems therefore to be generally valid, k_A' values of Table 1 representing second-order rate constants (k_6') for the rate-determining step [equation (6) of ref. 2] in the reaction of all sub-

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[5] For solubilities of oxygen in methanol at various temperatures and pressures see G. R. Levi, *Gazzetta*, 1901, **31**, 11, 513; C. B. Kretschmer, G. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, 1946, **38**, 506.

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[10] A. Gamba and I. R. Bellobono, *Gazzetta*, 1972, **102**, 445.

strates, for which $k_3 \gg k_6$ at all tested concentrations of sodium methoxide.

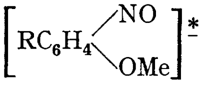
Activation enthalpies (ΔH^*) and entropies (ΔS^*) of reaction (1) are shown in Table 3, in which values [2] for the formation of intermediate (I; $R = p\text{-}NO_2$) are also reported. Enthalpy and entropy factors partially compensate each other to give a free energy of activation ΔG^*, which is a linear function of the substituent constant σ. The value of ρ^*, the slope of the graph $\log K^*$ ($\equiv -\Delta G^*/2{\cdot}303RT$) *vs.* σ, where K^* is the 'thermodynamic' equilibrium constant between reagents and transition state, is $2{\cdot}91 \pm 0{\cdot}59$ (correlation coefficient r 0·8867) over the range 298—328 K (range of mean reaction temperatures). At 298·2 K, the usual Hammett plot of $\log k_A'$ *vs.* σ yields $\rho = 3{\cdot}88 \pm 0{\cdot}46$ (r 0·9573) for reaction (1).

TABLE 3

Activation parameters for reactions (1) and (2)

Substituent R	Reaction (1) Mean temp. (K)	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal mol^{-1} K^{-1}	ΔG^*/ kcal mol^{-1}	Reaction (2) Mean temp. (K)	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal mol^{-1} K^{-1}	ΔG^*/ kcal mol^{-1}
p-NMe$_2$	319·9	16·96 ± 0·11	−32·3 ± 0·3	27·28				
p-OMe	327·8	27·47 ± 0·72	8·2 ± 2·2	24·78	311·1	11·93 ± 0·29	−42·5 ± 0·9	25·16
H	310·7	15·69 ± 1·14	−20·3 ± 3·4	22·00	320·4	18·63 ± 2·82	−16·1 ± 8·8	23·78
p-Cl	321·2	20·53 ± 0·51	−2·5 ± 1·6	21·35	304·0	10·42 ± 0·34	−38·6 ± 1·1	22·14
p-NO$_2$	289·2	11·10 ± 0·09	−28·3 ± 0·3	19·29				

The magnitude of these ρ and ρ^* values is fully consistent with the presence of a negative charge in the transition state, which can be visualized, as in aromatic nucleophilic substitution, as (A) leading to



$$\left[RC_6H_4 \begin{matrix} NO \\ OMe \end{matrix} \right]^{*}_{-}$$

(A)

$RC_6H_4NOH\cdot + CH_2O^{-\cdot}$. The similarity of ρ and ρ^* indicates that substituent effects mainly influence K^* values. These facts further substantiate the proposed mechanism [2] with equation (6) of ref. 2 as the rate-controlling step.

For reaction (2), e.s.r. evidence [4] of paramagnetic species formed from nitroso-compounds and methoxide ion in the presence of oxygen may be taken into account to formulate the mechanism (3)—(8). The second-order

$$RC_6H_4NO + CH_3O^- \xrightarrow{k_4} RC_6H_4NOH\cdot + CH_2O^{-\cdot} \quad (3)$$

$$CH_2O^{-\cdot} + CH_3OH \rightleftharpoons CH_2OH\cdot + CH_3O^- \quad (4)$$

$$RC_6H_4NO + CH_2OH\cdot \xrightarrow{\text{fast}} RC_6H_4NOH\cdot + CH_2O \quad (5)$$

$$2RC_6H_4NOH\cdot + O_2 \xrightarrow{\text{fast}} 2RC_6H_4NO_2H\cdot \quad (6)$$

$$2RC_6H_4NO_2H\cdot + 2CH_3O^- \rightleftharpoons 2RC_6H_4NO_2^{-\cdot} + 2CH_3OH \quad (7)$$

$$2RC_6H_4NO_2^{-\cdot} + 2CH_3OH \longrightarrow RC_6H_4NO + RC_6H_4NO_2 + 2CH_3O^- + H_2O \quad (8)$$

rate constants (first-order with respect to methoxide ion in terms of kinetic activity, first-order with respect to nitroso-compound) may be explained if elementary steps of reaction (8) such as (8a) and (8b) are considered.

$$RC_6H_4NO_2^{-\cdot} + CH_3OH \xrightarrow{k_{8a}} RC_6H_4NO + CH_2O^{-\cdot} + H_2O \quad (8a)$$

$$RC_6H_4NO_2H\cdot + CH_2O^{-\cdot} \xrightarrow{\text{fast}} RC_6H_4NO_2 + CH_3O^- \quad (8b)$$

The rate (v) equation (9) is obtained for the limiting reaction (8a) when the equilibrium constant K_7 ($\equiv c_{RC_6H_4NO_2^{-\cdot}}/c_{RC_6H_4NO_2H}\cdot a_{MeO^-}$) is introduced. For $k_{8a} < k_6$, if equilibrium (7) is shifted to the left, $c_{RC_6H_4NO} \simeq c_{RC_6H_4NO_2H\cdot}$, and equation (9) reduces to (10), which has the same form as that found experimentally.

$$v = k_{8a}c_{RC_6H_4NO_2^{-\cdot}} = k_{8a}K_7c_{RC_6H_4NO_2H\cdot}\,a_{MeO^-} \quad (9)$$

$$v \simeq k_{8a}K_7c_{RC_6H_4NO}a_{MeO^-} = k_N'c_{RC_6H_4NO}\,a_{MeO^-} \quad (10)$$

The kinetic parameters of reaction (2) are shown in Table 3. The Hammett plot of $\log k_N'$ *vs.* σ yields a ρ value of $3{\cdot}97 \pm 0{\cdot}31$ at 298 K (r 0·9932) denoting the presence of a negative charge in the transition state, in agreement with the suggested reaction scheme. The low entropy of activation further supports equation (8a) as the rate-determining step, since it is evident from e.s.r. data [1] that the radical anion of nitroaromatic compounds is strongly solvated in methanol solutions.

Experimental evidence indicating that the rate-limiting step of reaction (2) is auto-oxidation–reduction of the radical anion of the nitro-derivative is found in the following observations. The specific rate constant for the decomposition of m-(NO$_2$)C$_6$H$_4$NO$_2^{-\cdot}$ was measured at 40·0 °C [1] (k_5 in ref. 1 $\equiv k_{8a}$ of this paper): from its value, the initial rate for $6{\cdot}0 \times 10^{-4}$M-substrate can be calculated as $4{\cdot}82 \times 10^{-3}$ mol l^{-1} s^{-1}. This value should be the same as that of the initial rate of reaction (2), measured at an equal concentration of m-(NO$_2$)C$_6$H$_4$NO, but in highly concentrated methoxide solutions, so as to shift equilibrium (7) to the right. This latter rate is very difficult to measure experimentally as equation (11) occurs together with equation (6) for this substrate.

$$2m\text{-}(NO_2)C_6H_4NO^{-\cdot} \xrightarrow{\text{fast}} m\text{-}(NO_2)C_6H_4N(O^-)N(O^-)C_6H_4(NO_2)\text{-}m \quad (11)$$

Nevertheless, it has been evaluated at 40 °C in oxygen-saturated solutions containing 4·5M-MeO$^-$, with 6·0 ×

10^{-4}M-substrate, as $(4{\cdot}27 \pm 0{\cdot}45) \times 10^{-3}$ mol l^{-1} s^{-1}. The agreement between the two values, within the limits of the approximations involved, may be considered satisfactory.

Furthermore, at $c_{\mathrm{MeO^-}} < 1{\cdot}5$M in the presence of oxygen, k_N' for m-$(NO_2)C_6H_4NO$ has been measured at 40 °C, even if with some difficulty due to the parallel formation of the azoxy-derivative. Its value ($7{\cdot}08 \times 10^{-2}$ mol l^{-1} s^{-1}) satisfactorily fits the Hammett plot of k_N' *vs.* σ at this temperature.

An alternative pathway, composed from equations (3), (6), and (8b) only, may be considered for the oxidation of nitroso-compounds. The possibility of this scheme occurring in preference to that expressed by equations (3)—(8b) is linked to the relative rates of reactions (4), (5), and (8b). This pathway, however, does not produce formaldehyde. The stoicheiometry of reaction (2), on the contrary, clearly shows the formation of formic acid, corresponding to the disproportionation of the expected amount of formaldehyde. Finally, the different rates for the formation of nitro- and azoxy-derivatives imply different rate-limiting steps. Therefore, the steady-state concentration of $CH_2O^{\cdot -}$ must be very low in the concentration range of methoxide ion examined in this paper, and the mechanism based on reactions (3), (6), and (8b) only is not supported by the experimental data.

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