Kinetics of Auto-oxidation–Reduction of Substituted Nitrosobenzenes in Cyclohexane

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Auto-oxidation–reduction of substituted nitrosobenzenes RC_6H_4NO (R = H, *p*-NMe_2, *p*-OMe, *p*-Cl, *m*-NO_2, and *p*-NO_2) has been studied kinetically at 70—100° in cyclohexane solution. Experimental data and the influence of substituents are discussed on the basis of an equilibrium between monomer (M) and dimer (D), and of the reaction $2M \longrightarrow D$ being the rate-determining step.

THE role of nitrosobenzenes in the electron-transfer mechanism for the reaction of nitroaromatic compounds with methoxide ion in methanol solution has been previously studied.[1-4] The auto-oxidation–reduction of the radical anion of the nitro-compounds, which leads to nitroso-derivatives, the kinetic precursors of the *NN'*-dihydroxy-*NN'*-diphenylhydrazine intermediates, and finally yields azoxy-derivatives, has been clarified.[1-4]

We deemed it interesting to examine the auto-oxidation–reduction of nitrosoaromatic compounds, which occurs by heating appropriate solutions. The thermal decomposition of nitroso-compounds has long been known[5] and yields nitro- and azoxy-derivatives. Kinetic studies for this reaction, by Gowenlock *et al.*,[6-8] have been mainly confined to the dimers of *trans*-nitrosoalkyl or aryl nitrosoalkyl derivatives.

In this paper, a kinetic study of reaction (1) at 70—100 °C in cyclohexane solution is reported. The

$$3RC_6H_4NO \longrightarrow RC_6H_4NO_2 + RC_6H_4N{=}N(O)C_6H_4R \quad (1)$$

$$R = \mathrm{H}, p\text{-}NMe_2, p\text{-}OMe, p\text{-}Cl, m\text{-}NO_2, \text{ and } p\text{-}NO_2$$

choice of solvent was made to minimize solute–solvent interactions and to emphasize the influence of parameters such as the effect of substituents and the equilibrium[9,10] between monomer and dimer, which largely favours the former in solution.

EXPERIMENTAL

Materials.—Nitrosobenzenes RC_6H_4NO (R = H, *p*-NMe_2, *p*-OMe, *p*-Cl, *m*-NO_2, and *p*-NO_2) were prepared and purified as previously described;[4,11] commercial samples were also used in some instances. Identification of products, after their separation by t.l.c., was on the basis of elemental analyses and existing literature data. The stoicheiometry of reaction (1) was ascertained within the limits of analytical error. Spectrograde cyclohexane was employed.

Kinetics.—Solutions ($1—20 \times 10^{-3}$M) of RC_6H_4NO in cyclohexane were placed in nitrogen-filled tubes equipped with pressure plugs. The reaction was initiated by immersing the tubes in a constant-temperature bath and was stopped, when desired, by quenching. Reaction tubes were removed at regular intervals for spectrophotometric analysis, which was carried out after appropriate dilution. The ' infinity time ' absorption was calculated; when measured experimentally, it agreed with the calculated values within the limits of analytical uncertainty. The reaction order n was obtained both by the method of half-reaction time and by the integrated equation (2) where k

$$1/(A_\infty - A_t)^{n-1} = (n - 1)ktC_0^{n-1}/(A_\infty - A_t)^{n-1} + 1/(A_\infty - A_0)^{n-1} \quad (2)$$

is the kinetic constant, t the time, A_0, A_t, A_∞ absorbances at ' zero,' t, and ' infinite time,' respectively, and C_0 the initial concentration of nitroso-derivative. The upper limit of the concentration range investigated was imposed by the solubility of the material; the lower limit by the necessity of not employing unreasonably long reaction times.

RESULTS AND DISCUSSION

A kinetic study of reaction (1) at the different temperatures in cyclohexane solution was carried out by

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following spectrophotometrically, at various wavelengths, both the rate of disappearance of reagents and that of formation of products. A kinetic order of two was found in all instances.

All kinetic runs showed an induction period, which remained unaffected by the presence of oxygen, or other radical scavengers, such as 1,1-diphenyl-2-picrylhydrazyl. In some experiments scavengers were added to check the possible effects of radical reactions. The existence of an induction period was shown particularly by plotting equation (2): the ordinate $1/(A_t - A_\infty)$ equals $1/(A_0 - A_\infty)$ at a time equal to the induction period.

The mean values of the second-order rate constants at various temperatures in the range 70—100 °C are reported in Table 1. The influence of substituents is illustrated in the Figure, where the logarithm of rate constants at 90 °C, over the concentration range studied, is plotted against substituent constants σ[12] or σ^+.[13]

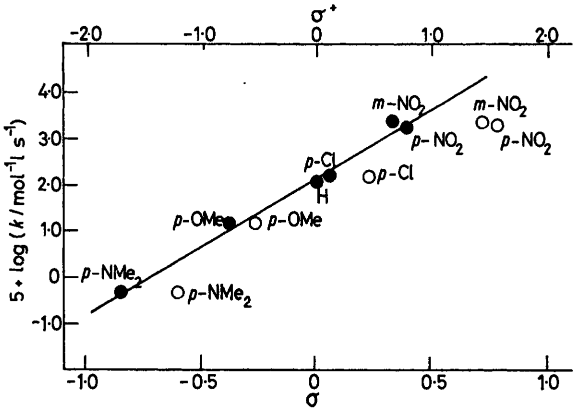
TABLE 1

Second-order rate constants *k* and probable errors for reaction (1) at different temperatures

10^3C_0/M	Temperature (°C)	10^3k/ls^{-1} mol^{-1}
RC_6H_4NO (R = H)		
12.46	100	2.47 ± 0.08
12.11	90	1.16 ± 0.03
17.99	80	0.554 ± 0.01
12.05	80	0.528 ± 0.02
12.09	70	0.227 ± 0.003
RC_6H_4NO (R = *p*-Cl)		
11.78	100	2.16 ± 0.04
12.14	90	1.41 ± 0.02
11.94	80	0.709 ± 0.004
17.98	80	0.646 ± 0.01
6.00	80	0.666 ± 0.03
12.09	70	0.359 ± 0.008
RC_6H_4NO (R = *m*-NO_2)		
0.98	90	23.2 ± 0.9
1.99	90	22.6 ± 0.9
3.99	90	21.6 ± 0.9
RC_6H_4NO (R = *p*-NO_2)		
1.20	90	19.7 ± 0.6
1.40	90	21.2 ± 0.8
1.60	90	21.2 ± 0.7
3.60	90	21.4 ± 0.8
RC_6H_4NO (R = *p*-MeO)		
7.78	90	0.133
20.4	90	0.132
RC_6H_4NO (R = *p*-NMe_2)		
4.13	90	0.005 7

The non-linearity of the plot against σ seems to be significant, beyond the standard deviations of the kinetic runs. A change of behaviour appears when proceeding from electron-accepting to electron-donating substituents, and the ' step ' of the Figure for the σ plot may be indicative of an intermediate electron donor–acceptor effect of chlorine in this reaction.

A straight line of slope 1.46 ± 0.06 is obtained, on the other hand, by using the set of σ^+ values, which is entirely reasonable in view of the high electron demand for this reaction and of the stabilization of the monomer by electron-donating substituents. This is consistent with the results of some studies [14-16] on the influence of *para*-substituents of nitrosobenzenes in the equilibrium between monomer and dimer. An increase in the stability of the monomer was observed when changing from electron-accepting to electron-donating substituents. This greater thermodynamic stability was interpreted on the basis of the remarkable electron attraction by the nitroso-group and of resonance contribution by a quinonoid structure with separation of charge, favoured by electron-donating substituents.



log*k* at 90° for the kinetics of auto-oxidation–reduction of substituted nitrosobenzenes in cyclohexane, as a function of substituent constants σ (○) and σ^+ (●)

As the dimers of nitrosoaromatic compounds exhibit a non-planar crystal structure,[17,18] in contrast to the planar conformation of monomers, and as the resonance interaction, in a conjugated system, increases with planarity, the monomer is stabilized mainly by resonance interaction. In any case, therefore, apart from the effect of substituents on the dimer, it is quite reasonable to expect that the equilibrium between monomer and dimer will be directed towards the former in the presence of electron-donating substituents. A ρ constant of −1.5 [16] was found in effect for the dissociation equilibrium of the dimer. The ρ value obtained in the Figure for the σ^+ plot in the kinetic process agrees, both in magnitude and sign, with that obtained from thermodynamic data.

A kinetic scheme, able to account for experimental data of reaction (1), is represented by reactions (3) and (4), when M denotes the monomer, D the dimer of the nitroso-derivatives, and P the products. The differential

$$\mathrm{M} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D} \qquad (3)$$

$$\mathrm{D} + \mathrm{M} \xrightarrow{k_2} \mathrm{P} \qquad (4)$$

$$-\mathrm{d}C_\mathrm{M}/\mathrm{d}t = 2k_1C_\mathrm{M}^2 - 2k_{-1}C_\mathrm{D} + k_2C_\mathrm{M}C_\mathrm{D} \qquad (5)$$

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rate equation (5) for this mechanism, where C expresses concentration, with the hypothesis of a stationary state for the dimer concentration, yields equation (6). Two

$$-\mathrm{d}C_M/\mathrm{d}t = 3k_1k_2C_M^3/(k_2C_M + k_{-1}) \qquad (6)$$

limiting cases may occur. (a) If $k_2C_M \gg k_{-1}$, equation (6) simplifies to equation (7), with a kinetic order of 2, and the formation of the dimer represents the rate-determinstep.

$$-\mathrm{d}C_M/\mathrm{d}t = 3k_1C_M^2 \qquad (7)$$

(b) If $k_2C_M \ll k_{-1}$, equation (8) is obtained, with a kinetic order of three, and reaction (4) becomes the rate-limiting step.

$$-\mathrm{d}C_M/\mathrm{d}t = 3(k_1k_2/k_{-1})C_M^3 \qquad (8)$$

Possibility (b) is ruled out by the experimental kinetic order found in this paper. In cyclohexane solution, however, equilibrium is shifted towards the monomer (particularly when changing from the p-NO_2 to p-NMe_2 substituent), and equation (7) is valid only for steady-state conditions. The time necessary to reach these conditions, at the temperature of kinetic runs, is given by the induction period, after which the rate equals that of formation of the reactive dimer.

Activation parameters, calculated by the Eyring equation, for reaction (1; R = H and p-Cl) are reported in Table 2. These are not unrealistic values, in view of the greater thermodynamic stability of the monomers of nitrosoaromatic compounds with respect to the dimers in cyclohexane solution (the equilibrium being largely displaced in favour of the former).

TABLE 2

Enthalpy [a] and entropy [a] of activation for reaction (1; R = H and p-Cl)

	ΔH^*/ kcal mol^{-1}	ΔS^*/ cal mol^{-1} K^{-1}
RC_6H_4NO (R = H)	19.5 ± 0.03	−18.6 ± 0.9
RC_6H_4NO(R = p-Cl)	14.8 ± 0.6	−31.5 ± 1.7

[a] Uncertainties are probable errors calculated by least squares from the scattering of the Eyring plots.

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