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Proton and Electron Transfer Processes in the Reactions of Nitroaromatics with Alkoxides

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Chimica fisica. — *Proton and Electron Transfer Processes in the Reactions of Nitroaromatics with Alkoxides.* Nota di IGNAZIO RENATO BELLOBONO [*] e MICHELE RIVA [**], presentata [***] dal Socio G. SARTORI.

RIASSUNTO. — Sono state valutate le costanti di equilibrio a 25 °C, relativamente alle soluzioni acquose, per il comportamento « acido » (equilibrio con gli anioni fenilici) ed « antibasico » (equilibrio con i complessi di addizione di ione idrossido) di una serie di polinitroderivati aromatici. I valori di tali costanti sono stati estrapolati nella scala acquosa, partendo da misure spettrofotometriche e potenziometriche in soluzioni di etilendiammina. Alla luce di questa scala di « acidità » e di « antibasicità », facendo uso delle relazioni lineari di energia libera, e con particolare riguardo al ruolo degli intermedi, vengono discusse criticamente le reazioni di scambio idrogeno–deuterio, di sostituzione nucleofila del nitrogruppo, e di ossido–riduzione del nitrogruppo, che si producono in soluzione metanolica, in presenza di ioni metossido.

A major problem which arises when the reactivity of nitroaromatics is considered is the variety of different types of behaviour exhibited on treatment with alkoxide bases in primary alcohols:

a) nucleophilic addition to the ring [1–11]; *b*) hydrogen exchange [12–19]; *c*) nucleophilic substitution of the nitro group [20–22]; *d*) electron transfer [23] and reduction of the nitro group to an azoxy derivative [24–30].

In order to know just why a certain type of reaction predominates in a given system, it is important to understand thoroughly the various possible interactions and particularly:

1) the influence of nitro (and other) substituents on the nature of the reaction;

2) the influence of nucleophile concentration and solvent effects;

3) the relationship between rate processes (e.g. nucleophilic substitution, hydrogen exchange, electron transfer) and equilibrium processes (e.g. formation of σ-complexes or phenyl anions).

The general subject of the interaction of aromatic nitro compounds with bases has been treated in detail in the literature. Rather than analyzing systematically the various aspects of these interactions, we shall focus our attention on the discussion of the latest results obtained in our laboratory concerning proton and electron transfer processes, with emphasis on the evidence of intermediates and reactivity relationships.

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INFLUENCE OF METHOXIDE ION CONCENTRATION

A problem dealing with all kinds of reactions is the determination of kinetic order with respect to alkoxide ions.

For reactions involving the methoxide ion in methanol solution, such as nucleophilic substitution of the nitro group [21, 22], hydrogen exchange [17–19], electron transfer [27–30] between nitro group and methoxide ion, it was commonly found that pseudo-first order kinetic coefficients k_1 determined in excess of alkoxide ion were not a linear function of methoxide ion concentration, nor of any simple power of methoxide ion concentration. Examples of similar behaviour were first described by Schaal and coworkers [31–37], who correlated log k_1 with the function H_M defined for concentrated methoxide solutions ($> 0.15\,M$) by

$$\text{(1)} \qquad H_M = -\log a_{CH_3OH_2^+} \, (f_{A^-}/f_{HA}) \cong \log a_{CH_3OCH_2^+} \cdot f_{\pm}$$

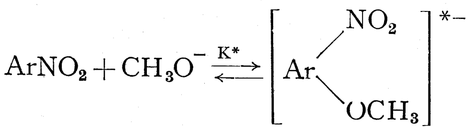
where $a_{CH_3OCH_2^+}$ is the activity of $CH_3OH_2^+$ ion and f are molar activity coefficients of acid-base couples (HA/A^-) which were used to establish the H_M function and $f_{\pm}$ is the mean ionic activity coefficient.

The alternative use of acidity functions other than H_M has been recently discussed [38].

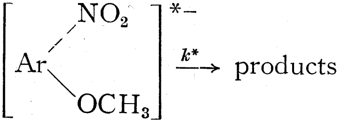
The linear correlation between log k_1 and H_M (or similar acidity functions), however, does not make it possible in itself to compare kinetic coefficients of different reactions, which may not be studied in the same range of methoxide ion concentration, or to obtain kinetic parameters in terms of true second order rate constants. Consistent values of these latter were calculated by expressing the rate r equation in terms of activities of methoxide ion

$$\text{(2)} \qquad r = k^* K^* c_{ArNO_2} c_{CH_3O^-} (f_{ArNO_2} f_{CH_3O^-}/f_*) \cong$$
$$\cong k c_{ArNO_2} c_{CH_3O^-} (f_{CH_3O^-}/f_{\pm}) \cong k c_{ArNO_2} a_{CH_3O^-}$$

where c are concentrations, f are activity coefficients of $ArNO_2$, CH_3O^- and activated complex (*) respectively, K^* is the equilibrium constant between reagents and activated complex



k^* is the first-order decomposition constant of the activated complex



and $a_{CH_3O^-}$ is the methoxide ion " kinetic activity " as expressed by equation (2). This latter was suitably evaluated by some approximations, such as considering $f_* = f_\pm$. Equation (3), then, gives

$$\log c_{CH_3O^-} f_{CH_3O^-} \cong H_M - pK_S + \log f_\pm \tag{3}$$

where K_S is the autoprotolysis constant of methanol. The ratio $a_{CH_3O^-}/c_{CH_3O^-}$, which is equal to the activity coefficient ratio $f_{CH_3O^-}/f_*$, may thus be calculated. For concentrations of methoxide greater than 1.5 M, equation (4) is, by interpolation from data by Schaal *et al.* treated by the above method, for CH_3ONa in CH_3OH

$$\log a_{CH_3O^-} = 1.015\, c_{CH_3O^-} - 0.395. \tag{4}$$

Strictly speaking, the computation of the activity coefficient ratio is possible only at temperatures of ca. 20 °C, at which the acidity function H_M has been measured. The variation of activity coefficients with temperature, however, may not be significant. The temperature dependence of the acidity function for the methanolysis of chloroform, for instance, was found to be apparently negligible in the range 20–80 °C [39].

A further approximation was necessary when studying hydrogen exchange reactions in CH_3OD, for which the same H_M values as for CH_3OH were adopted.

Even if this treatment is far from rigorous, it appears to be the only one accessible at present. In fact, despite the numerous assumptions and approximations, experimental k_1 values for the cited reactions were found to show a good linearity with $a_{CH_3O^-}$ evaluated by equation (3).

PROTON TRANSFER PROCESSES

The study of hydrogen exchange in polynitro compounds has thrown considerable light on the mechanism of proton transfer [40].

A concurrent process is represented by nucleophilic substitution of the nitro group [21–22] for which the relevant kinetic parameters are listed in Table I.

TABLE I

Kinetic parameters [21–22] *and second order rate constants* k *at* 90 °C *for the nucleophilic substitution of nitro group in nitroaromatics* $R_1R_2C_6H_3NO_2$ *by methoxide ion in methanol solution*

R_1	R_2	log (k/l mol^{-1} s^{-1}) at 90 °C	ΔH^*/kcal mol^{-1}	ΔS^*/kcal mol^{-1} °K^{-1}	$\Sigma\sigma$
$m-NO_2$	$m-NO_2$	0.34	20.9	−0.1	$2\sigma_m(NO_2)$
$p-NO_2$	H	−0.58	21.7	−1.7	$\sigma_p(NO_2)$
$o-NO_2$	H	−0.79	19.3	−8.3	$\sigma_o(NO_2)$

In order to study the kinetics of single processes, a careful choice of conditions must be made: thus hydrogen exchange in 1,3,5-trinitrobenzene [17] could be appropriately studied in the absence of appreciable nucleophilic substitution of the nitro group. Hydrogen exchange in positions 2 and 4,6 of 1,3-dinitrobenzene [18, 19], on the contrary, could be easily examined separately, owing to the rate differences. The generalized mechanism [19] for proton transfer by the methoxide ion may be outlined by equations (5)–(8).

$$\text{ArH} + \text{MeO}^- \overset{K_H^*}{\rightleftarrows} [\text{Ar}\cdots\text{H}\cdots\text{OMe}]^{*-} \tag{5}$$

$$[\text{Ar}\cdots\text{H}\cdots\text{OMe}]^{*-} \underset{(k_{-1}^*)_H}{\overset{(k_1^*)_H}{\rightleftarrows}} \text{Ar} + \text{MeOH} \tag{6}$$

$$\text{Ar}^- + \text{MeOD} \underset{(k_1^*)_D}{\overset{(k_{-1}^*)_D}{\rightleftarrows}} [\text{Ar}\cdots\text{D}\cdots\text{OMe}]^{*-} \tag{7}$$

$$[\text{Ar}\cdots\text{D}\cdots\text{OMe}]^{*-} \overset{1/K_D^*}{\rightleftarrows} \text{ArD} + \text{MeO}^-. \tag{8}$$

The rate constant of the forward reaction (7) differs from that of the reverse reaction (6) due to the kinetic isotope effect. For the same reason equilibrium constants of reactions (5) and (8) between non-deuteriated or deuteriated substrate and the methoxide ion on one side and their respective activated complexes (*) on the other are also related by an equilibrium isotope effect.

TABLE II

Kinetic parameters [17–19] *and second order rate constants k at* 90 °C *for the hydrogen-deuterium exchange per position in nitroaromatics* $R_1R_2C_6H_3NO_2$ *in sodium methoxide-methan*$[^2H_1]$*ol solutions.*

R_1	R_2	log (k/l mol^{-1} s^{-1}) at 90 °C	ΔH^*/kcal mol^{-1}	ΔS^*/kcal mol^{-1} °K^{-1}	$\Sigma\sigma$	Position(s) of exchange
$m - NO_2$	$m - NO_2$	0.35	16.4	—12.4	$2\,\sigma_o + \sigma_p$	2, 4, 6
$m - NO_2$	H	—1.28	19.9	—10.1	$2\,\sigma_o$	2
$m - NO_2$	H	—3.37	22.9	—11.5	$\sigma_o + \sigma_p$	4, 6

The positional order of exchange and the relative rates (Table II) give a strong indication that the exchange observed for 1,3-dinitro- and 1,3,5-trinitrobenzene involves proton abstraction by the methoxide ion to give an intermediate carbanion. Further evidence along this line comes from the study of reactivity relationships.

The $\sigma\rho$ Hammett plot for hydrogen exchange kinetics is reported in fig. 1, by employing $\Sigma\sigma$ relative to the reaction centre and making use of σ_0

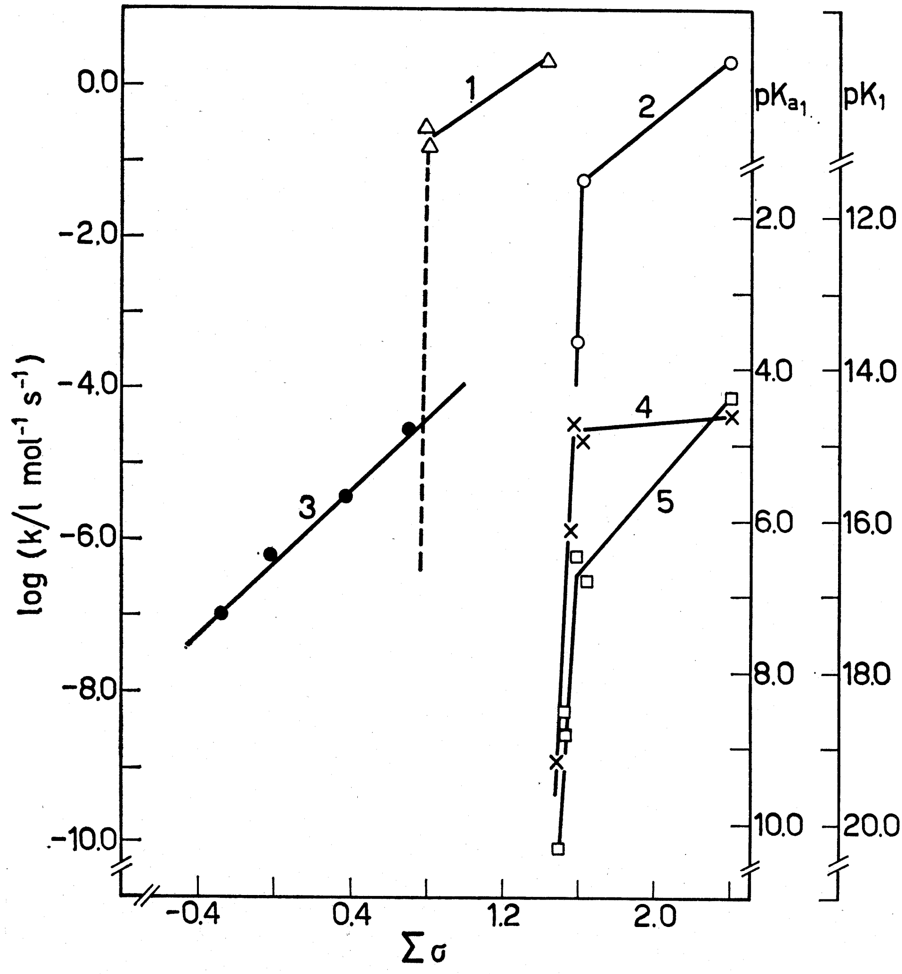


Fig. 1. – Plots, as a function of $\Sigma\sigma$ of R substituents, of: 1) log (k/l mol^{-1} s^{-1}) for the nucleophilic substitution of the nitro-group in nitroaromatics $R_1R_2C_6H_3NO_2$ by the methoxide ion in methanol solution, at 90 °C; 2) log (k/l mol^{-1} s^{-1}) for the hydrogen-deuterium exchange per position in nitroaromatics $R_1R_2C_6H_3NO_2$ in sodium methoxide–methan[$^2H_1$]ol solutions at 90 °C; 3) log (k/l mol^{-1} s^{-1}) for the electron transfer reaction between nitroaromatics $RC_6H_4NO_2$ and the methoxide ion in methanol, at 90 °C; 4) pK_{a1} (K_{a1} in mol l^{-1}) at 25 °C for equilibrium constants of reaction (9 a); 5) pK_1 (K_1 in mol l^{-1}) at 25 °C for equilibrium constants of reaction (10a).

values [41] in order to account for *ortho*-effect in nitroaromatics in the absence of steric hindrance. In the same figure kinetic data of the nucleophilic substitution reaction (Table I), as well as equilibrium data for reactions (9a) and (9b) (acid-base equilibria)

(9a) $$ArH_2 \underset{(H_2O)}{\overset{K_{a_1}}{\rightleftarrows}} ArH^- + H^+$$

(9b) $$ArH^- \underset{(H_2O)}{\overset{K_{a_2}}{\rightleftarrows}} Ar^{2-} + H^+$$

TABLE III

Equilibrium constants and their standard deviations for acid-base equilibria of polynitrobenzenes (reactions (9a) *and* (9b)), *and their addition complex formation (reactions* (10a) *and* (10b)), *at* 25 °C *in aqueous solution*

ArH_2	Substituents	pK_{a1} (K_{a1} in mol l^{-1})	pK_{a2} (K_{a2} in mol l^{-1})	pK_1 (K_1 in mol l^{-1})	pK_2 (K_2 in mol l^{-1})
o—dinitrobenzene	—	4.7 ± 0.4	27.6 ± 0.9	16.75±0.35	36.5 ± 2.8
»	3—CH_3	6.2 ± 0.5	19.6 ± 1.2	18.53±0.31 (a)	29.5 ± 2.1
»	4—CH_3	6.5 ± 0.4	33 ± 3	18.78±0.18 (a)	—
m—dinitrobenzene	—	5.0 ± 0.3	14 ± 2	16.88±0.21 (16.80) (b)	25 ± 3
»	4—CH_3	7.3 ± 0.6	9.7 ± 1.2	17.28±0.14 (17.12) (b)	21.5 ± 2.3
»	2—CH_3	8.4 ± 0.6	10.8 ± 0.8	20.35±0.55 (a)	22.6 ± 1.2
»	2—CH_3, 4—CH_3	20.0 ± 2.6	*ca.* 38	30±3.5 (a)	≥ 45
»	2—CH_3, 4—CH_3, 6—CH_3	21.6 ± 2.8	—	31±4 (a)	—
p—dinitrobenzene	—	6.0 ± 0.3	9.0 ± 0.8	18.58±0.38 (a)	21.5 ± 1.6
»	2—CH_3	9.2 ± 0.2	9.9 ± 1.2	18.75±0.65 (a)	19.6 ± 0.5
s—trinitrobenzene	—	4.6 ± 0.3	6.1 ± 0.6	14.40±0.16 (14.52) (b)	(18.00) (b)
»	2—CH_3	4.8 ± 0.4	6.3 ± 0.7	14.45±0.20 (14.56) (b)	(17.55) (b)

(*a*) Molar absorptivity of the addition complex was measured in lithium 2-ethylamide ethylenediamine solutions [45].
(*b*) Values reported by Schaal [43].

and for reactions (10a) and (10b) (formation of hydroxide addition complex)

$$\text{ArH}_2 + \text{H}_2\text{O} \underset{(\text{H}_2\text{O})}{\overset{\text{K}_1}{\rightleftarrows}} (\text{ArH}_2\text{OH})^- + \text{H}^+ \tag{10a}$$

$$(\text{ArH}_2\text{OH})^- + \text{H}_2\text{O} \underset{(\text{H}_2\text{O})}{\overset{\text{K}_2}{\rightleftarrows}} \text{ArH}_2(\text{OH})^- + \text{H}^+ \tag{10b}$$

are also reported (cfr. Table III). These equilibrium constants have been evaluated as described in the experimental section: their determination and their meaning will be discussed further on.

It may be now observed that the reactivity behaviours for these four reactions show similar features. Since in the transition state the nucleophilic substitution involves some sort of σ-complex, in which there is addition to a position carrying the nitro group, it may be inferred that either a similar σ-complex in which there is addition to a position carrying hydrogen intervenes in hydrogen exchange (in analogy with nucleophilic substitution of the nitro group and with reaction (10)), or the phenyl anion is the intermediate (in analogy with reaction (9)). While the reactivity pattern of fig. 1 suggests that the four reactions being now considered are intrinsically dependent on " acidity " (hydrogen exchange and proton abstraction reaction (9)) or " antibasicity " (nucleophilic substitution and base addition reaction (10)) of polynitrobenzenes, conclusive evidence of the fact that rather than alkoxide addition complexes or other species of phenyl anions are intermediates in the hydrogen exchange of nitroaromatics, may be deduced from kinetic parameters. The entropies of activation (Table II) are about half the value (ca. — 20 cal/mole °K) expected for a normal second-order reaction. If the magnitude af activation entropies is diagnostic of internal return [42] we may argue that the mechanistic scheme of reactions (5)–(8) should be of importance in the hydrogen exchange reactions reported in Table II. The internal return mechanism requires that the " return steps " (reverse reactions (6) and (5)) must be especially fast, a condition which is fulfilled in the case under consideration, in which the conversion of anion to hydrocarbon involves little structural reorganization [19].

Furthermore, the absence of any significant primary isotope effect in this reaction [19] may be indicative of an extensive internal return mechanism, such as that of reactions (5)–(8).

ELECTRON TRANSFER PROCESSES

The mechanism of the reduction of the nitro group in nitroaromatics $\text{RC}_6\text{H}_4\text{NO}_2$ by the methoxide ion to yield the corresponding *trans*-azoxy derivatives has been studied in detail with R = H; *p* —MeO; *m* — Cl; and *m* —NO_2 [27, 28, 30]. The following general scheme has been proposed:

$$\text{RC}_6\text{H}_4\text{NO}_2 + \text{CH}_3\text{O}^- \xrightarrow{k_{11}} \text{RC}_6\text{H}_4\text{N(OH)O}^{\bullet} + {}^{\bullet}\text{CH}_2\text{O}^- \tag{11}$$

(12) $RC_6H_4N(OH)O^{\cdot} + CH_3O^- \xrightleftharpoons{\text{fast}} RC_6H_4NO_2^{\cdot -} + CH_3OH$

(13) $RC_6H_4NO_2 + {}^{\cdot}CH_2O^- \xrightarrow{\text{fast}} RC_6H_4NO_2^{\cdot -} + CH_2O$

(14) ${}^{\cdot}CH_2O^- + CH_3OH \xrightleftharpoons{\text{fast}} {}^{\cdot}CH_2OH + CH_3O^-$

(15a) $RC_6H_4NO_2^{\cdot -} + CH_3OH \xrightarrow{k_{15a}} RC_6H_4NO + {}^{\cdot}CH_2O^- + H_2O$

(15b) $RC_6H_4NO_2H^{\cdot} + {}^{\cdot}CH_2O^- \xrightarrow{\text{fast}} RC_6H_4NO_2 + CH_3O^-$

(16) $RC_6H_4NO + CH_3O^- \xrightarrow{k_{16}} RC_6H_4NOH^{\cdot} + {}^{\cdot}CH_2O^-$

(17) $RC_6H_4NO + {}^{\cdot}CH_2OH \xrightarrow{\text{fast}} RC_6H_4NOH^{\cdot} + CH_2O$

(18) $RC_6H_4NOH^{\cdot} + CH_3O^- \xrightarrow{\text{fast}} RC_6H_4NO^{\cdot -} + CH_3OH$

(19) $2\ RC_6H_4NO^{\cdot -} \xrightleftharpoons{\text{fast}} RC_6H_4N(O^-)N(O^-)C_6H_4R$

(20) $RC_6H_4N(O^-)N(O^-)C_6H_4R + CH_3OH \xrightleftharpoons{\text{fast}} RC_6H_4N(OH)N(O^-)C_6H_4R + CH_3O^-$

(21) $RC_6H_4N(OH)N(O^-)C_6H_4R + CH_3OH \xrightleftharpoons{\text{fast}} RC_6H_4N(OH)N(OH)C_6H_4R + CH_3O^-$

(22) $RC_6H_4N(OH)N(OH)C_6H_4R \xrightarrow{k_{22}} RC_6H_4N{=}N(O)C_6H_4R + H_2O.$

In the redox reaction of $(m - NO_2)C_6H_4NO_2$ with CH_3O^- to give *trans*-3,3′-dinitroazoxybenzene, the role of the radical anion $(m - NO_2)C_6H_4NO_2^{\cdot -}$ as first reaction intermediate [27] was established by electron paramagnetic resonance and electronic spectroscopy. Accumulation of $(m - NO_2)C_6H_4NO_2^{\cdot -}$ and change in the rate determining step from (11) to (15a) occurred in this case when concentration of CH_3O^- was increased to 3–5 M. With $(m - NO_2)C_6H_4NO_2$ as substrate [28] as well as with some substituted nitrosobenzenes RC_6H_4NO ($R = m -$ and $p - NO_2$) [28, 29], another intermediate species was observed, the kinetic coefficients of formation of which were the same as those of reaction (11), and depended linearly on the kinetic activity of the methoxide ion. The kinetic coefficients for the decomposition of this intermediate, on the contrary, showed a simple linear dependence on methoxide ion concentration [27–29]. Since this intermediate species could be produced both from reaction of $(m - NO_2)C_6H_4NO_2$ and of $(m - NO_2)C_6H_4NO$ with CH_3O^-, it was possible to check that kinetic coefficients relative to base catalyzed decomposition of this species were the same, thus confirming the part played by the nitroso derivative as precursor of this intermediate. The structure suggested for this species was that of N,N-dihydroxy, N,N-diphenylhydrazine, the transformation of which (reaction (22)) was interpreted in terms of proton transfer from an oxygen atom and water elimination.

Information concerning equations (15) and (16) was obtained from the kinetic study [29] of the reaction of RC_6H_4NO ($R = H$; $p-NMe_2$; $p-MeO$; and $p-Cl$) witn CH_3O^- to yield the corresponding *trans*-azoxy derivative (eq. (23)) and of the corresponding reaction of RC_6H_4NO ($R = H$; $p-MeO$; and $p-Cl$) with CH_3O^- to yield the nitro derivative $RC_6H_4NO_2$ in the presence of oxygen (eq. (24)):

$$(23)\quad 4\,RC_6H_4NO + CH_3O^- \rightarrow 2\,RC_6H_4N = N(O)C_6H_4R + HCOO^- + H_2O$$

$$(24)\quad 2\,RC_6H_4NO + CH_3O^- + 2O_2 \rightarrow 2\,RC_6H_4NO_2 + HCOO^- + H_2O.$$

Reaction (24) was explained substantially in terms of elementary steps (15 a) and (15 b) preceded by the fast reaction of $RC_6H_4NOH^{\cdot}$ with oxygen to give $RC_6H_4N(OH)O^{\cdot}$. The ρ value for reaction (24) and the low entropy of activation [29] support equation (15 a) as being the rate determining step, since it is evident from ESR data that the radical anion of nitroaromatics is strongly solvated in methanol solutions.

The validity of the mechanistic scheme given by reactions (11)-(22) is finally corroborated if the Hammett $\sigma\rho$ relationship for reaction (11) is examined, in comparison with the reactivity behaviour of nucleophilic substitution, hydrogen exchange and acid-base equilibria of polynitroaromatics. The log k *vs.* σ plot for reaction (11) at 90 °C is represented in fig. 1. Besides the fact that ρ value [30] for this reaction affords a satisfactory qualitative and quantitative interpretation of the rate determining step involving electron transfer from methoxide to nitro compound, it is important to assess the reason for which the reduction of the nitro group by methoxide is solely confined to mononitro and *m*-dinitrobenzene, whereas nucleophilic aromatic substitution, for instance, is kinetically preferred by other dinitrobenzenes.

If the curve log k *vs.* σ for nucleophilic substitution of the nitro group is extrapolated, owing to the analogy of this reaction with base addition equilibrium, the point representative of $(m-NO_2)C_6H_4NO_2$ should lie below the corresponding point of this substrate in the line log k *vs.* σ for electron transfer. It should be consequently easier, as it is, for *m*-dinitrobenzene to accept an electron from CH_3O^- than to add this nucleophile on a position carrying a nitro group.

ACID–BASE BEHAVIOUR OF POLYNITROBENZENES

Equilibrium constants of reactions such as (9) and (10) cannot be determined directly in aqueous solutions, mainly because the kinetic control of proton transfer processes in polynitroaromatics requires a strong nucleophile and hyperbasic media. It may be possible, however, to " extrapolate " the acid-base behaviour of polynitrocompounds in water by carrying out spectrophotometric measurements in mixtures of water and ethylenediamine or by potentiometric titration, *e.g.* in ethylenediamine solution, with a suitable titrant such as lithium-2-aminoethylamide, making use of a calibration curve with some reference $pK_a(H_2O)$ values relative to water. The first of these techniques was employed for some of the polynitroaromatics by Schaal [43], who determined the values of the acidity function in the mixed solvent. It has also been used to study qualitatively the equilibria corresponding to reactions (10) with a systematic series of polynitrobenzenes [44, 45] and quantitatively these same equilibria in anhydrous ethylenediamine. The spectrophotometric technique allows the evaluation of equilibria (10) because absorbance measurements refer to the presence of addition complexes which prevail in dilute solutions of amine solvents. The potentiometric technique has been described by various Authors [46–49] but no potentiometric $pK_a(H_2O)$ values of polynitrobenzenes have as yet been reported. By the latter method equilibria (9) between substrates and their carbanions in the anhydrous solvent can be investigated [48], and, by a suitable calibration, $pK_a(H_2O)$ values in water can be obtained [46, 48].

By application of these two techniques to a series of polynitrobenzenes (cfr. Table III) the first and in many cases also the second equilibrium constant of reactions (9) and (10) were evaluated. In order to be able to evaluate equilibrium constants for the second dissociation (reactions (9b) and (10b)) measurements must be carried out on the second inflection point of the titration curve or on the addition complex resulting from the reaction with two nucleophile ions.

The data of Table III quantitatively confirm the earlier qualitative observations [44, 45] on the "acidity" and "antibasicity" of polynitrocompounds. The effect of progressively substituting hydrogens with methyl groups, which decreases both pK_1, pK_2 and pK_{a1}, pK_{a2} up to limit of "unmeasurable" equilibrium constants, is particularly evident in *m*-dinitrobenzene. The approximate equivalency of positions is *p*-dinitrobenzene in shown by the similarity of pK_1 and pK_2 as well as of pK_{a1} and pK_{a2}, both for the unsubstituted nitrocompound and for its methyl derivative.

The difference between $pK_1^{H_2O}$ and $pK_{a1}^{H_2O}$ represents pK_1' for equilibrium (25), which relates reaction (9a) to reaction (10a) and consequently the "acid" to the "anti-base" characteristics

$$(25) \qquad ArH^- + H_2O \overset{K_1'}{\rightleftarrows} (ArH_2OH)^-.$$

The values of Table III indicate that this equilibrium is thermodynamically shifted to the left in aqueous solutions. This, however, may not be equally true in amphiprotic protophilic solvents or in sodium methoxide methanol solutions.

As a concluding remark, we may observe that the scale of "acidity" ($pK_a^{H_2O}$) and "antibasicity" (pK^{H_2O}) represented by the values of Table III for polynitrocompounds, though "extrapolated" in water by measurements made in other solvents and thus liable to incur in some incongruities if not manipulated with care, is of a certain usefulness in rationalising and interpreting the behaviour of polynitroaromatics and their reactivity relationships, as is shown by the discussion of proton transfer processes and nucleophilic substitution of the nitro group in comparison to the electron transfer.

EXPERIMENTAL

$pH_{a_1}^{H_2O}$ *and* $pK_{a_2}^{H_2O}$ *Determinations.*

The potentiometric technique was used in anhydrous ethylenediamine solution, with lithium 2-aminoethylamide as titrant, by employing both a Pt/Pt and a Sb/Sb electrode assembly, as described by Heumann *et al.* [46, 47] and in a previous paper [49], respectively. The data obtained by these two electrode assemblies are quite similar, even if the absolute potential values are not the same: they were mediated in Table III. The calibration was effected both on an $E_{1/2}$ *vs.* $(pK_a^{H_2O})^2$ plot, as suggested by Heumann *et al.* [46], where $E_{1/2}$ represents the potential difference value at the half-neutralization point of the first or second " acidity " for the measurement of pK_{a_1} or pK_{a_2} respectively, and on an $(E_{1/2} - E_0)$ *vs.* pK: plot, where E_0 represents the potential difference value at the beginning of titration. While the first kind of graph was approximatively linear, the second one showed a marked curvature: by means of many calibration points, however, it could be read without difficulty. Besides the reference substances used by Heumann *et al.* [46], 9-phenylfluorene ($pK_a^{H_2O} = 18.49$), fluorene ($pK_a^{H_2O} = 22.83$) and 1,1,3-triphenylpropene ($pK_a^{H_2O} = 26.4$) [48] were employed to construct the calibration curves. In order to obtain reproducible results, calibration was repeated with every batch of solvent and titrant solution.

$pK_1^{H_2O}$ *Determinations.*

When in anhydrous ethylenediamine solutions equilibrium was " completely " shifted towards the addition complex at the concentrations used for the absorbance measurements, the method devised by Schaal [43] could be employed straightforwardly for $pK_1^{H_2O}$ determinations. When this was not the case, $pK_1^{H_2O}$ was obtained from absorbance measurements in the anhydrous solvent by employing for the molar absorptivity of the addition complex a value determined in the anhydrous solution to which a suitable amount of lithium-2-aminoethylamide was added to quantitatively convert the substrate into its addition complex, following the technique of " spectrophotometric titration " already described [45].

$pK_2^{H_2O}$ *Determinations.*

In preceding work [44, 45] the ratio K_1/K_2 was evaluated in ethylenediamine solutions relatively to some standards, such as benzoic acid, phenol, and *m*-hydroxybenzoic acid. With reference to the water scale, and if the behaviour in ethylenediamine can be "extrapolated" in water (this is the basis of the potentiometric technique of calibration), from the pK^{H_2O} values of the standards in water and those of $pK_1^{H_2O}$ (equilibrium (10a)) of polynitrocompounds, the $pK_2^{H_2O}$ of these latter may be calculated.

The values of $pK_2^{H_2O}$ cannot be very accurate, chiefly because the determination of the ratio K_1/K_2 is subject to considerable uncertainty.

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