Kinetics of Hydrogen Exchange in 1,3-Dinitrobenzene in Sodium Methoxide–Methan$[^2H]$ol Solutions

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Pseudo-first order rate coefficients for protium–deuterium exchange at the 4- and 6-positions of 1,3-dinitrobenzene in methan$[^2H]$ol solution containing 0·2—0·9M-MeO$^-$ have been measured at 75—100 °C by i.r. analysis of the MeOH formed. Second-order rate constants k [log (k/M^{-1} s^{-1}) = 10·8 − 5140/T] were obtained by evaluation of the kinetic activity of the methoxide ions. Comparison with previously determined kinetic parameters relative to the 2-position shows that positional reactivity is determined by the activation energy. The mechanism is discussed in terms of proton removal and internal return.

THE study of catalysed hydrogen exchange in polynitro-compounds has helped to elucidate the mechanisms by which these compounds react with bases.[1] A major problem in such studies is the variety of different types of behaviour exhibited. Thus, nucleophilic addition to the ring,[1d-g,2] hydrogen exchange,[3] nucleophilic substitution of the nitro-group,[4,5] electron transfer,[6] and reduction of the nitro-group to an azoxy-derivative may take place.[7-9] By careful choice of conditions however the kinetics of a single reaction may be studied. Thus addition of base [2] and hydrogen exchange in 1,3,5-trinitrobenzene [3f] have been studied, in the absence of nucleophilic substitution of the nitro-group, the latter being a slower process. Hydrogen exchange at the 2-position in 1,3-dinitrobenzene [3b,f] has also been investigated as a function of base concentration.

It has been generally established that phenyl anions, rather than radical anions or alkoxide addition complexes, are intermediates in the hydrogen exchange of nitroaromatics.

Here we continue an investigation [3e,f] of the effect of methoxide concentration on protium–deuterium exchange at the 4- and 6-positions of 1,3-dinitrobenzene in methan$[^2H]$ol.

EXPERIMENTAL

Materials.—Reagent grade 1,3-dinitrobenzene was recrystallized from methanol (m.p. 90°; lit.,[10] m.p. 90°). Methan$[^2H]$ol (Merck, isotopic purity 99·2%, as indicated by n.m.r. and i.r. analysis) was dried by refluxing it with magnesium turnings (5 mg/ml) and iodine (0·5 mg/ml) followed by fractionation. A stock solution of sodium methoxide (*ca.* 2·5M) in anhydrous methan$[^2H]$ol was prepared by dipping freshly cut pieces of sodium into MeOD for *ca.* 20 s, this operation being repeated twice, each time in fresh solvent; the metal was then dissolved in pure solvent. The solution was filtered (Schleicher and Schull 589 [1] filter papers) and standardized against hydrochloric acid. All manipulations were carried out in a nitrogen-filled glove box; the gas was continuously purged by passage over copper turnings at 550°, phosphorus pentoxide, ascarite, and potassium hydroxide. Glassware was heated at 200° for several hours before use.

Kinetic Procedure.—Solutions of 1,3-dinitrobenzene in anhydrous methan$[^2H]$ol, 0·02—0·1M, were prepared and mixed (1 : 1 volume ratio) with 0·4—2·0M-MeONa in MeOD, obtained by diluting the stock solution of alkoxide. Aliquots of the reaction solution were placed in nitrogen-filled tubes equipped with pressure plugs. The reaction was initiated by immersing the tube in a constant-temperature bath, and was stopped, when desired, by quenching. The ' zero time ' analysis was effected on the quenched mixture, after a time equal to five half-lives for the exchange reaction [3f] at the 2-position of 1,3-dinitrobenzene had elapsed. From that time on, reaction tubes were removed at regular intervals from thermostatted bath for spectrophotometric analysis. The rate of exchange in 1,3-dinitro$[2\text{-}^2H]$benzene at the 4- and 6-positions was followed. ' Infinity time ' absorption was also measured experimentally. As the fraction between initial and final MeOH concentration in MeOD generally exceeded 0·97, this fraction was assumed to equal 1, so that the rate of backward reaction could be neglected and a straightforward pseudo-first order equation was employed [equation (1)], where

$$k_{\mathrm{expt}}t = 2{\cdot}303 \log (A_\infty - A_0)/(A_\infty - A_t) \qquad (1)$$

A_0, A_∞, and A_t represent absorbance at zero, infinity, and t time respectively, at ν 3337 cm^{-1} corresponding to the O–H stretching frequency of MeOH (O–D stretching of MeOD was found at 2485 cm^{-1}). Absorbances of conveniently diluted kinetic samples were measured in i.r. silica cells with optical path lengths of 0·1 or 1 cm, by means of a Beckman DK 2A spectrophotometer.

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The log term in equation (1) was plotted against time. Good straight lines were generally obtained through three half-lives of the exchange reaction at the 4- and 6-positions, with some scatter towards the end, which was not completely random. Pseudo-first order rate coefficients k_{exp} were calculated by a least-squares treatment of data, in the linear region of the plot.

TABLE 1

Rate constants for H–D exchange at 4- and 6-positions of 1,3-dinitrobenzene in MeOD solution containing various concentrations of MeONa

T/°C	c_{MeO^-}/M	a_{MeO^-}/M [equation (11)]	10^5k_{exp}/s^{-1}
75·0	0·198	0·197	1·15
75·0	0·555	0·695	4·48
75·0	0·625	0·842	5·30
75·0	0·698	0·996	6·00
75·0	0·835	1·43	8·90
85·0	0·190	0·190	3·85
85·0	0·420	0·468	7·30
85·0	0·580	0·736	13·6
85·0	0·622	0·838	14·1
85·0	0·898	1·77	30·9
100·0	0·199	0·198	11·8
100·0	0·381	0·430	23·7
100·0	0·451	0·528	29·8
100·0	0·560	0·700	39·1

Values of k_{exp} reported in Table 1 correspond to the exchange of one of the two hydrogen atoms, the second atom being protium or deuterium. If secondary isotope effects are neglected, the second deuterium atom is incorporated at the 4- or 6-position at the same rate as that of the first. The rate coefficient corrected for the statistical factor is thus $2k_{\text{exp}}$.

The base concentrations shown in Table 1 are corrected for solution expansion by multiplying concentrations at room temperature by the ratio of the density of methanol [11] at the reaction temperature to that at room temperature.

The estimated errors determined by straightforward methods are reported as standard deviations for rate coefficients and probable errors for kinetic parameters in Table 2. Activation entropies were calculated from the formula $\Delta S^{\ddagger} = 4{\cdot}576\ (\log A - \log T_m) - 49{\cdot}207$, where A = frequency factor, and $T_m = 360{\cdot}7$ K

TABLE 2

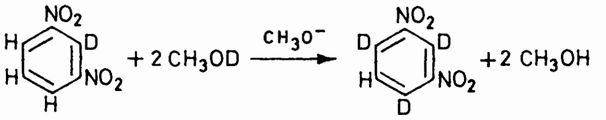
Kinetic parameters and rate constants for H–D exchange per position in 1,3,5-trinitrobenzene and 1,3-dinitrobenzene in MeOD solution containing 0·1—1M-CH$_3$ONa

	Position(s) of exchange	T/°C 75	85	100	$\Delta E^{\ddagger}$ kcal mol^{-1}	log (A/M^{-1} s^{-1})	$\Delta S^{\ddagger}$ cal mol^{-1} K^{-1}
1,3,5-Trinitrobenzene [a,b] k/M^{-1} s^{-1}	2,4,6	0·795	1·62	4·47	17·0 ± 0·4	10·6 ± 0·1	−12·4
1,3-Dinitrobenzene [b] 10^2k/M^{-1} s^{-1}	2	1·55	3·80	12·0	20·5 ± 0·5	11·1 ± 0·1	−10·1
1,3-Dinitrobenzene [a] 10^4k/M^{-1} s^{-1}	4,6	1·24	3·48	11·2	23·5 ± 0·7	10·8 ± 0·1	−11·5

[a] Corrected for statistical factor. [b] Calculated values from kinetic parameters of ref. 3*f*.

RESULTS AND DISCUSSION

The protium–deuterium exchange in 1,3-dinitrobenzene at the equivalent 4- and 6-positions was found to take place at convenient rates in methan[^{2}H]ol containing 0·2—1·0M-sodium methoxide in the temperature range 75—100 °C. Exchange at the 2-position of a non-deuteriated substrate was much faster.[3f] Consequently after a short reaction time the substrate was completely converted into 1,3-dinitro[2-^{2}H]benzene. It was then substantially this latter compound that underwent exchange at the 4- and 6-positions of the ring. Positions of exchange were checked during preliminary runs by recording the n.m.r. spectra of the reaction products: absorption due to the C-2 proton (τ 2·07) was the first to disappear, followed by a slower decrease of absorption of the multiplet at τ 1·3 (corresponding to protons at C-4, -5, and -6) up to *ca.* 2/3 of the integrated area at infinity time. Mass spectrochemical analysis of a partially deuteriated 1,3-dinitrobenzene sample showed that the distribution of deuterium over C-4, -5, and -6 was practically the same as that calculated statistically from total deuterium content and on the assumption that exchange at C-5 was negligible compared with that at C-4 and -6. The stoicheiometry is thus represented by equation (2).



(2)

The kinetics of reaction (2) were followed by i.r. analysis of MeOH formed. Experimentally, because the concentration of excess methoxide ion remained constant, the rate was pseudo-first order within a given run. Pseudo-first order rate coefficients k_{exp} are collected in Table 1.

It may be observed that no linear correlation exists between the pseudo-first order rate coefficients and concentration of sodium methoxide. A similar situation was reported for the nucleophilic substitution of nitro-groups by methoxide ions in polynitro-compounds.[5] Hydrogen exchange, involving the formation of a phenyl anion as intermediate, can be treated analogously. The generalized mechanism for this reaction may be outlined by equations (3)—(6). The rate constant of forward reaction (5) differs from that of the reverse reaction (4) due to the kinetic isotope effect. For the

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[11] (*a*) 'International Critical Tables,' McGraw-Hill, New York, 1928, **3**, 27; (*b*) J. Timmermans, 'Physico-Chemical Constants of Pure Organic Compounds,' Elsevier, Amsterdam, 1950, vol. 1, p. 303.

same reason, equilibrium constants of reactions (3) and (6) between deuteriated or non-deuteriated substrate

$$\mathrm{RH} + \mathrm{MeO}^- \xrightleftharpoons{K_\mathrm{H}^*} [\mathrm{R}\cdots\mathrm{H}\cdots\mathrm{OMe}]^- \quad (3)$$

$$[\mathrm{R}\cdots\mathrm{H}\cdots\mathrm{OMe}]^- \xrightleftharpoons[(k^*_{-1})_\mathrm{H}]{(k_1^*)_\mathrm{H}} \mathrm{R}^- + \mathrm{MeOH} \quad (4)$$

$$\mathrm{R}^- + \mathrm{MeOD} \xrightleftharpoons[(k_1^*)_\mathrm{D}]{(k^*_{-1})_\mathrm{D}} [\mathrm{R}\cdots\mathrm{D}\cdots\mathrm{OMe}]^- \quad (5)$$

$$[\mathrm{R}\cdots\mathrm{D}\cdots\mathrm{OMe}]^- \xrightleftharpoons{1/K_\mathrm{D}^*} \mathrm{RD} + \mathrm{MeO}^- \quad (6)$$

and methoxide ion on one side and their respective activated complexes on the other are also related by an equilibrium isotope effect.

If forward reaction (4) is assumed to be rate-determining, as for protium–deuterium exchange the concentration of MeOD greatly exceeds that of MeOH, its rate r can be expressed as (7), where c are concentrations,

$$r = (k_1^*)_\mathrm{H} K_\mathrm{H}^*\, c_\mathrm{RH}\, c_{\mathrm{MeO}^-} f_\mathrm{RH}\, f_{\mathrm{MeO}^-}/f_* \quad (7)$$

f are activity coefficients of RH, MeO^-, and activated complex (f_*) respectively, and K_H^* is the equilibrium constant of pre-equilibrium (3).

Equation (7) reduces to (8), if the activity coefficient of uncharged species RH is considered close to unity.

$$r = (k_1^*)_\mathrm{H} K_\mathrm{H}^*\, c_\mathrm{RH}\, c_{\mathrm{MeO}^-} f_{\mathrm{MeO}^-}/f_* \quad (8)$$

Alternatively, in terms of a second-order exchange reaction which accounts for base catalysis, the rate equation may be written as (9), where a_{MeO^-} is the

$$r = k\, c_\mathrm{RH}\, a_{\mathrm{MeO}^-} \quad (9)$$

activity of methoxide ion. Comparison of equation (8) with equation (9) gives equations (10) and (11).

$$k = (k_1^*)_\mathrm{H} K_\mathrm{H}^* \quad (10)$$

$$a_{\mathrm{MeO}^-} = c_{\mathrm{MeO}^-} f_{\mathrm{MeO}^-}/f_* \quad (11)$$

The second-order rate constant k is related to methoxide concentration and to pseudo-first order rate constant k_exp, determined experimentally in excess of base, by equation (12). Consistent values of k can be ob-

$$k = k_\mathrm{exp}/a_{\mathrm{MeO}^-} \quad (12)$$

tained only by suitable evaluation of the ratio $a_{\mathrm{MeO}^-}/c_{\mathrm{MeO}^-}$,[5b,*] such as considering the activity coefficient of the activated complex f_* equal to $f_\pm$, the mean ionic activity coefficient of the acid–base couple of indicators used for the determination of the acidity function H_M [12,13] in methanolic solution of sodium methoxide. Strictly speaking, the computation of the activity coefficient ratio is possible only at temperatures of *ca.* 20°, 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 methanolysis of chloroform, for instance, was found to be apparently negligible in the range 20—80°.[14,15] Satisfactory results were obtained in previous work on nucleophilic substitution of a nitro-group [5] by partly accounting for the temperature variation of activity coefficients and employing for f_{MeO^-} the same temperature coefficient as that of sodium hydroxide in aqueous solution, while the temperature variation of f_* was neglected. In this paper, as well as in a previous one,[3f] a further approximation has been necessary: as there are no experimental values of H_M in MeOD, the same activity coefficients ratio used for MeONa in MeOH [5b] was adopted for the deuteriated solvent.

Even if this treatment is far from rigorous, it appears to be the only one accessible at present. In fact, despite the numerous approximations, values of k_exp for hydrogen exchange show a good linearity with a_{MeO^-} evaluated by equation (11).

The second-order rate constants k are reported in Table 2 together with kinetic parameters calculated from Arrhenius plots, and values for other exchange reactions of 1,3-dinitrobenzene and 1,3,5-trinitrobenzene, taken from previous work,[3f] for comparison.

The positional order of exchange and the relative rates give strong indication that the exchange observed for dinitro- and trinitro-benzene with nitro-groups *meta* relative to one another does involve proton abstraction by methoxide ion to give an intermediate carbanion. More importantly, in the light of the proposed mechanism, the reactivity pattern confirms, as has been suggested,[3g] that the nitro-group stabilizes the negative charge of the carbanion by an electrical effect. This may operate either through the bonds, owing to the fact that σ and π systems may not be completely insulated, or as a predominantly ' through space ' interaction with the charge. Since electrical effects fall off rapidly as the distance between the activating group and the reaction site is increased, the 4- and 6-positions of 1,3-dinitrobenzene are less reactive than the 2-position. The reactivity differences between the various positions of 1,3-dinitrobenzene and those of 1,3,5-trinitrobenzene seem to be wholly due to differences in activation energies.

The entropies of activation are about half the value (*ca.* -20 cal mol^{-1} K^{-1}) expected for a normal second-order reaction. Also from this fact, if the magnitude of activation entropies are diagnostic of internal return,[16] we may argue that the mechanism described by reactions (3)—(6) should be of importance in the exchange

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* The ratio $a_{\mathrm{MeO}^-}/c_{\mathrm{MeO}^-}$, which is equal to the activity coefficient ratio f_{MeO^-}/f_*[equation (11)], is reported in Figure 1 of ref. 5*b* for various concentrations of MeO^- in the range 0·15—1·5M. It turns out to be: $\log c_{\mathrm{MeO}^-} f_{\mathrm{MeO}^-} = H_\mathrm{M} - \mathrm{p}K_\mathrm{S} + \log f_\pm$ where K_S is the autoprotolysis contant of methanol.

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reactions reported in Table 2. The internal return mechanism requires that the 'return steps' [reverse reactions (4) and (3)] must be especially fast, a condition which is fulfilled in the present case, in which the conversion of anion to hydrocarbon involves little structural reorganization.

Furthermore, the absence of any significant primary isotope effect has been shown to be indicative of an extensive internal return mechanism.[17-19] The tritium exchange at the 2-position of 1,3-dinitrobenzene has been studied in alkaline methanol solution at 25° by Crampton and Gold.[3b] If experimental data of these authors are treated in terms of kinetic activities of methoxide ion, in order to compare their values with ours, a second-order rate constant k_T of *ca.* $2{\cdot}8 \times 10^{-5}\text{M}^{-1}\,\text{s}^{-1}$ is obtained, which gives a ratio $k_D/k_T = 3{\cdot}8$ (with our k_D value of $1{\cdot}07 \times 10^{-4}\text{M}^{-1}\,\text{s}^{-1}$ at 25°).[3f] This ratio, however, includes a solvent effect, as our study was done in MeOD, while Crampton and Gold's results were in MeOH solution. The primary isotope effect must, therefore, be much smaller, in keeping with the requisites of the internal return mechanism, if the isotope effect criterion is adequate to demonstrate this phenomenon.

In summary, polynitrobenzenes undergo hydrogen exchange by simple proton removal. Consistent second-order rate constants can be obtained by the use of the kinetic activity of methoxide ion. Positional reactivity is determined by the activation energy. Entropies of activation support the suggestion that internal return plays a role in the exchange mechanism.

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