

## The Influence of the Solvent on Reaction Velocity

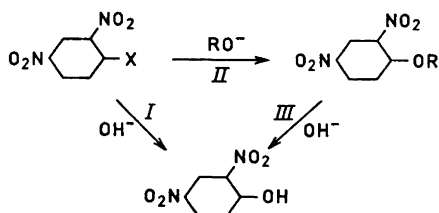
### XXI. The Reaction of 2,4-Dinitrophenyl Alkyl Ethers with Hydroxyl Ion in Water and in Methanol-Water and Ethanol-Water Mixtures

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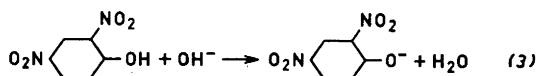
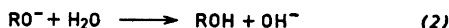
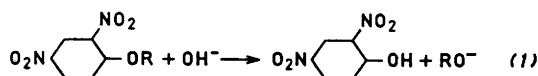
The following reactions have been kinetically investigated: the reaction of 2,4-dinitroanisole with hydroxyl ion in water and in methanol-water mixtures; the reaction of 2,4-dinitrophenetole with hydroxyl ion in water and in ethanol-water mixtures; the reaction of 2,4-dinitrophenyl *n*-propyl ether with hydroxyl ion in water. For the first of these reactions the plot of  $\log k$  against  $\log [H_2O]$  of the medium is linear, whereas the plot for the second reaction passes through a maximum. The curves plotting  $E$  and  $\log A$  as functions of the composition of the solvent resemble closely the corresponding curves for the alkaline hydrolysis of esters in methanol-water and ethanol-water mixtures, but run much higher. The results are discussed.

In a preceding investigation<sup>1</sup> of the reactions of dinitrobenzenes with hydroxyl and alkoxy ions, our attention was drawn to the corresponding reactions of halogenonitrobenzenes. The monohalogenomononitrobenzenes, except the fluoro-derivatives, react considerably slower than the dinitrobenzenes, whereas the 1-halogeno-2,4-dinitrobenzenes react much faster. These reactions have been kinetically investigated in pure methanol and ethanol and also in methanol-water and ethanol-water mixtures<sup>2</sup>. The possible reactions in alcohol-water mixtures are<sup>3</sup> ( $X = \text{halogen}$ ):

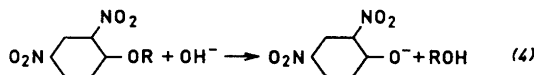


In these previous investigations only the reactions I and II were taken into account. It is, however, possible that phenol is formed by route III, the ether

formed in reaction II reacting with hydroxyl ion. Already the first preliminary experiments showed that under the conditions employed this reaction may proceed at a considerable velocity. The whole process in an alkaline solution is



The over-all reaction is



(R = Me, Et, or *n*-Pr).

The kinetics of reaction (1) which, as far as we are aware, have not been investigated before, formed the subject of the present study. It has been previously known<sup>4</sup> and was also confirmed in our own experiments, that the reactions of *para*- and *ortho*-nitroanisole and phenetole with hydroxyl ion is so slow at the temperatures used<sup>1</sup>, that they can be completely neglected when studying the reactions of the dinitrobenzenes in alkaline alcohol-water mixtures.

## EXPERIMENTAL

**Materials.** The dinitrophenyl methyl and ethyl ethers were prepared by treating 1-chloro-2,4-dinitrobenzene (purissimum, Fluka) with a solution of sodium hydroxide in the alcohol, and dinitrophenyl propyl ether by treating 1-chloro-2,4-dinitrobenzene with a solution obtained by dissolving sodium metal in propanol. The ethers were crystallized twice from the corresponding alcohol; in the case of the propyl ether the solution was cooled in an ice-salt bath. The melting points were: methyl ether 86.6–87.9°, ethyl ether 84.3–85.5°, *n*-propyl ether 30.7–31.2°C.

Methanol and ethanol were purified as in the previous investigation. The *n*-propanol was purified by the same method as ethanol.

**Method.** In the kinetic experiments, the progress of the reaction was followed by determining the concentration of the phenol formed colorimetrically with a Bausch & Lomb Spectronic 20 spectrophotometer. The wave length used was 400 m $\mu$ . In all experiments the initial concentration of the alkali (NaOH) was 0.016 mole/l, and that of the ether, when its solubility permitted, 0.004 mole/l. The reaction mixture was kept in a 50-ml glass-stoppered flask from which 2 ml-samples were taken after suitable intervals and diluted with an appropriate amount of water (to a 2–20-fold volume) for the colorimetric analyses. Since the extinction of 2,4-dinitrophenol proved to be somewhat dependent upon its concentration the readings were compared with a calibration curve recorded with solutions of known dinitrophenol concentrations. Seven to ten samples were taken in each run.

Table 1. Reaction of 2,4-dinitroanisole with hydroxyl ion in 76.7 wt. % methanol. Temperature 40°C,  $a_{\text{base}} = 0.016$ ,  $a_{\text{ether}} = 0.004$  mole/l.  $p$  = percentage of ether that has reacted.

Time min.	$10^4 x$	$p$	$10^5 k$ l mole <sup>-1</sup> s <sup>-1</sup>
699	5.85	15.0	24.6
1383	10.35	26.8	23.9
1960	14.05	36.0	24.8
1980	14.34	36.7	25.3
2854	17.95	46.0	24.0
4949	24.63	63.0	23.0
4953	24.65	63.1	23.0
6000	27.70	70.9	23.9
			Mean 24.06

When corrected for solvent expansion,  $k = 1.021 \times 0.0002406 = 0.0002457$  l mole<sup>-1</sup>s<sup>-1</sup>.

The rate constants were calculated using the formula

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where  $a$  is the initial concentration of the base and  $b$  that of the ether. The reactions were of the second order in all cases. Data from several runs are given in Tables 1–3.

Because the ethers are sparingly soluble in pure water, the experiments in pure water and in solvents of high water content were carried out in the same manner as the determinations of the velocities of hydrolysis of the dinitrobenzenes in water in the earlier investigation<sup>1</sup>.

## RESULTS AND DISCUSSION

The results of the kinetic measurements are summarized in Tables 4, 5 and 6. The rate constants are corrected for the thermal expansion of the solvent. The Arrhenius equation was obeyed in all cases within the limits of

Table 2. Reaction of 2,4-dinitrophenetole with hydroxyl ion in 36.3 wt. % ethanol. Temperature 25°C,  $a_{\text{base}} = 0.016$ ,  $a_{\text{ether}} = 0.004$  mole/l.

Time min.	$10^4 x$	$p$	$10^5 k$ l mole <sup>-1</sup> s <sup>-1</sup>
759	8.45	21.2	33.6
1228	12.52	31.4	33.4
1402	13.79	34.6	33.1
1454	14.10	35.3	32.8
1734	16.30	40.8	33.5
1961	17.85	47.2	33.7
3044	23.32	58.4	32.9
3044	23.44	58.9	33.2
3499	24.78	62.2	31.9
4338	28.00	70.2	32.6
			Mean 33.07

When corrected for solvent expansion,  $k = 1.003 \times 0.0003307 = 0.0003317$  l mole<sup>-1</sup>s<sup>-1</sup>.

Table 3. Reaction of 2,4-dinitrophenyl propylether with hydroxyl ion in water. Temperature 40°C,  $a_{\text{NaOH}} = 0.016$ ,  $a_{\text{ether}} = 1.81 \times 10^{-4}$  mole/l.

Time min.	$10^4 x$	$p$	$10^5 k$ l mole <sup>-1</sup> s <sup>-1</sup>
154	0.245	13.5	98.7
251	0.397	21.9	102.9
354	0.536	29.6	103.6
437	0.641	35.4	104.5
479	0.697	38.6	106.0
597	0.821	45.4	105.8
643	0.859	47.5	104.5
1383	1.326	73.4	99.9
$\infty$	1.81		Mean 103.2

When corrected for solvent expansion,  $k = 1.006 \times 0.001032 = 0.001038$  l mole<sup>-1</sup>s<sup>-1</sup>.

experimental error. The activation energies, frequency factors and activation entropies were calculated as described before.

In pure water the rate constants follow the sequence Me > Et  $\approx$  Pr. Except in highly aqueous media, the specific rates of the reaction of the ethyl ether in ethanol-water mixtures are greater than those of the methyl ether in methanol-water mixtures of equal water content (Fig. 1). The rate constant of the latter reaction increases continuously with the water content of the solvent, whereas the curve plotting  $k$  as a function of the solvent composition for the former reaction passes through a pronounced maximum. From Fig. 2 it is seen that the plot of  $\log k$  against  $\log [\text{H}_2\text{O}]$  for 2,4-dinitroanisole is a straight line whose slope approaches the value 1 as the temperature rises. This can be taken to imply that one water molecule participates in the formation of the transition state, for if the rate equation is written in the form

Table 4. The reaction  $\text{R} \cdot \text{OMe} + \text{OH}^- = \text{R} \cdot \text{O}^- + \text{MeOH}$  in methanol-water.  $a_{\text{base}} = 0.016$  mole/l. ( $\text{R} \cdot \text{OMe} = 2,4$ -dinitroanisole).

In the solvent			$a_{\text{ether}}$ mole/l	$10^5 k$ l mole <sup>-1</sup> s <sup>-1</sup>				$E$ cal.	log $A$
$\text{H}_2\text{O}$ ml/l	$\text{MeOH}$ wt. %	$x_{\text{MeOH}}$		25.00°	25.10°	40.00°	50.00°		
1000	0	0	$6.60 \times 10^{-4}$	34.5	76.6 <sup>b</sup>	182	499	20 480	11.55
800	16.2	0.097	$4.49 \times 10^{-4}$	24.8		142	406	21 430	12.10
600	36.5	0.244	0.004	(16.2) <sup>a</sup>	16.4	94.4	287	22 010	12.34
500	46.1	0.325	»	(12.7) <sup>a</sup>	12.8	76.7	235	22 360	12.49
400	56.0	0.417	»	(9.32) <sup>a</sup>	9.44	59.1	181	22 730	12.63
300	66.1	0.523	»	(6.40) <sup>a</sup>	6.49	40.7	130	23 020	12.68
200	76.7	0.650	»	(3.67) <sup>a</sup>	3.72	24.6	79.6	23 560	12.83
100	88.0	0.804	»	(1.43) <sup>a</sup>	1.45	11.1	36.0	24 760	13.31

a. By the Arrhenius equation.

b. At 32.00°.

Table 5. The reaction  $R \cdot OEt + OH^- = R \cdot O^- + EtOH$  in ethanol-water.  $\alpha_{base} = 0.016$  mole/l. ( $R \cdot OEt = 2,4$ -dinitrophenetole).

In the solvent			$\alpha_{ether}$ mole/l	$10^5 k$ l mole <sup>-1</sup> s <sup>-1</sup>					$E$ cal	log $A$
H <sub>2</sub> O ml/l	EtOH wt. %	$x_{EtOH}$		15.00°	25.00°	25.10°	40.00°	50.00°		
1000	0	0	$2.66 \times 10^{-4}$		20.9	45.7 <sup>a</sup>	105	283	19 950	10.95
800	16.2	0.070	$3.84 \times 10^{-4}$		30.1	63.0 <sup>a</sup>	142	376	19 350	10.66
600	36.3	0.182	0.004	$b$	(32.8) <sup>d</sup>	33.2	148	384	18 820	10.31
500	45.6 <sup>c</sup>	0.247	»	10.7	(33.0) <sup>d</sup>	33.4	155	402	19 150	10.55
400	55.2 <sup>c</sup>	0.326	»	9.80	(33.0) <sup>d</sup>	33.4	164	432	19 990	11.16
300	65.5 <sup>c</sup>	0.425	»	9.68	(33.8) <sup>d</sup>	34.2	173	483	20 610	11.62
200	76.6	0.562	»	9.68	(33.6) <sup>d</sup>	34.0	187	506	20 970	11.90
100	88.3	0.743	»	7.78	(27.8) <sup>d</sup>	28.1	157	467	21 620	12.29
50	93.3 <sup>c</sup>	0.844	»	5.25	(19.4) <sup>d</sup>	19.7	120	358	22 350	12.70

a. At 32.00°.

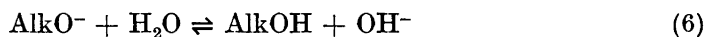
b. A part of the ether crystallized from the solution.

c. The ethanol in these experiments was "ethanol for spectroscopy", which contained a little water; hence the values of the mole fractions differ slightly from these given in the previous paper.

d. Calculated from the Arrhenius equation.

$$\frac{dx}{dt} = k' [H_2O]^n (a - x)(b - x) \quad (5)$$

we see that the experimental bimolecular rate constant  $k = k' [H_2O]^n$  or  $\log k = \log k' + n \log [H_2O]$ . A change in the value of  $n$  may be connected with the shift of the equilibrium



with temperature. Also the form of the curve in Fig. 1 which plots the rate constant of the reaction between 2,4-dinitrophenetole and hydroxyl ion in ethanol-water can probably be explained, at least partly by a shift of the above equilibrium with varying solvent composition. From Table 7 of the previous paper we see that also the curves plotting the rate constants of the reactions between the dinitrobenzenes and hydroxyl ion in ethanol-water mixtures go through a maximum. This shows that the discussion in the previous paper rests on a sound basis.

Figs. 3 and 4 in which the activation energy and frequency factor are plotted as functions of the composition of the solvent show that both  $E$  and  $A$  are greater for anisole than for phenetole. Except in pure water and in the highly aqueous solutions where the frequency factor governs the situation,

Table 6. The reaction  $R \cdot OPr + OH^- = R \cdot O^- + PrOH$  in water. ( $R \cdot OPr = 2,4$ -dinitrophenyl  $n$ -propylether).  $\alpha_{NaOH} = 0.016$ ,  $\alpha_{ether} = 1.81 \times 10^{-4}$  mole/l.

Temp.	25.00°	40.00°	50.00°	$E = 20\ 480$ cal
$10^5 k$ (l mole <sup>-1</sup> s <sup>-1</sup> )	20.1	104	293	log $A = 11.32$

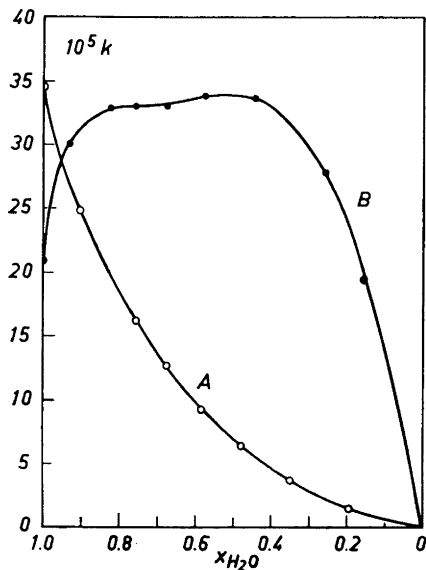


Fig. 1. Plot of  $k$  against the mole fraction of water. A the methyl ether in methanol-water, B the ethyl ether in ethanol-water. Temperature 25°C.

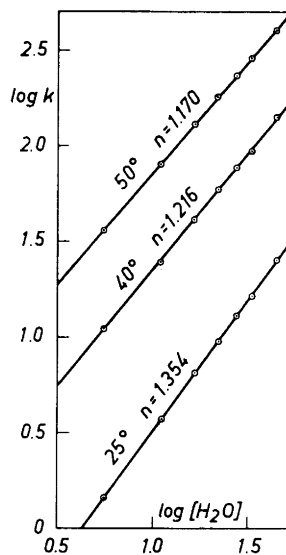


Fig. 2. 2,4-Dinitroanisole, methanol-water. Plot of  $\log k$  against  $\log [H_2O]$ .

the order of the rate constants of both reactions is due to differences in the activation energies. The plots of  $E$  and  $\log A$  for 2,4-dinitroanisole in methanol-water mixtures rise continuously with decreasing water content, whereas the curves for the reaction of 2,4-dinitrophenetole in ethanol-water pass through a pronounced minimum. It is interesting that  $E$  and  $\log A$  for these reactions vary similarly as  $E$  and  $\log A$  for the alkaline hydrolysis of esters in alcohol-water mixtures. The curves for the reaction of 2,4-dinitroanisole in methanol-water mixtures have the same form as the curves for the hydrolysis of methyl acetate or ethyl acetate in methanol-water mixtures<sup>5,6</sup>, and the curves for reaction of 2,4-dinitrophenetole in ethanol-water mixtures have the same form as the curves for the hydrolysis of ethyl acetate or ethyl benzoate in ethanol-water mixtures<sup>6,7</sup>. The reactions are similar in that the reagent which attacks the substrate is the hydroxyl ion and that the hydroxyl ion concentration is determined by equilibrium (6).

According to previous discussions<sup>6</sup>, the minima observed for the activation energies and entropies arise because of changes in the solvation of the reaction system, *i.e.* the reactants and the activated complex, the water molecules having a specific attraction for the hydrophilic part and the organic solvent molecules for the alkyl groups. It is interesting that the rules found valid for ester hydrolysis are valid also for the reactions between the dinitrophenyl

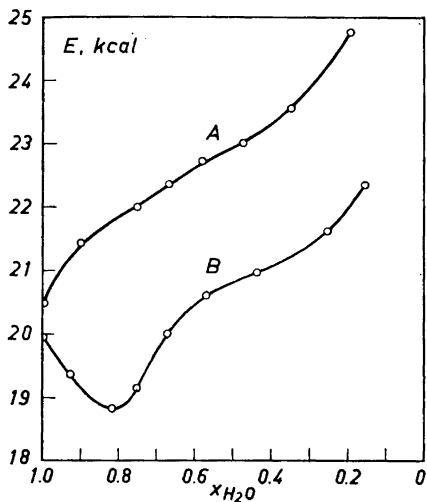


Fig. 3.  $E$  as a function of  $x_{\text{water}}$ . *A* 2,4-dinitroanisole in methanol-water, *B* 2,4-dinitrophenetole in ethanol-water.

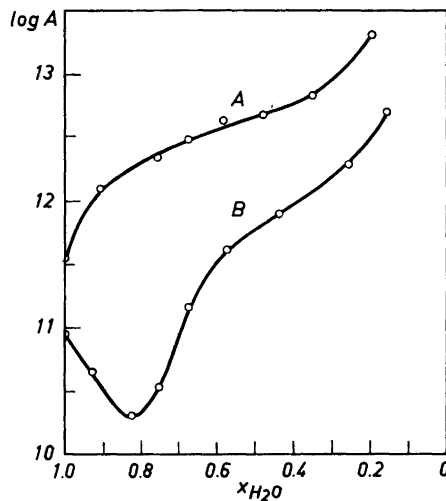


Fig. 4.  $\log A$  as a function of  $x_{\text{water}}$ . *A* 2,4-dinitroanisole in methanol-water, *B* 2,4-dinitrophenetole in ethanol-water.

ethers and the hydroxyl ion. The shift of the equilibrium (6) with varying solvent composition plays a minor part in the formation of the minimum in the plots of  $E$  and  $\log A$ , since the plots for ester hydrolysis have the same form

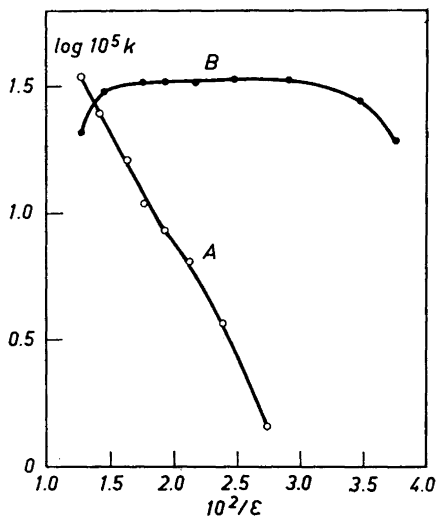


Fig. 5. Plot of  $\log k$  against  $1/\varepsilon$ . *A* 2,4-dinitroanisole in methanol-water, *B* 2,4-dinitrophenetole in ethanol-water.

also in other mixed solvents, *e.g.*, in acetone-water and in dioxan-water mixtures<sup>6</sup>. When suitable concentrations of both water and the organic solvent are present, the solvation of the transition complex is greater than in either solvent alone, with the result that  $E$  and  $A$  go through a minimum. It appears, however, that when methanol is the organic component of the solvent, changes in solvation do not lead to minimum values of  $E$  and  $A$ . The non-appearance of the minimum is specific for methanol and not for the reactant since the minimum is observed also when the alkaline hydrolysis of methyl acetate is carried out in acetone-water mixtures. Furthermore, it has been found for ester hydrolysis that the minimum is deeper the larger the hydrocarbon part of the solvent alcohol molecule.

The activation energies and frequency factors are much higher for the reactions of the dinitrophenyl ethers than for ester hydrolysis in the same solvents. This and especially the fact that the frequency factor is "normal", *i.e.*  $\log A$  is about 11–13, for the dinitrophenyl ethers whereas the value of  $\log A$  for ester hydrolysis is only 7–9, indicate a difference in reaction mechanism.

The relationship between rate constant and dielectric constant of the medium is shown in Fig. 5. The plots of  $\log k$  against  $1/\epsilon$  are seen to be nearly linear for the reaction of the methyl ether in methanol-water mixtures. For the reaction of the ethyl ether in ethanol-water mixtures  $\log k$  is practically constant in the solvent range from 20 wt. % to 75 wt. % ethanol.

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