

The Influence of the Solvent on Reaction Velocity

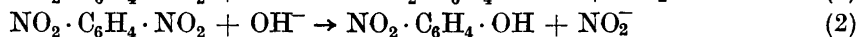
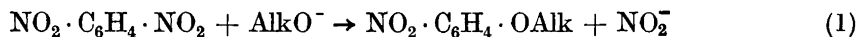
XX. The Reaction of Dinitrobenzenes with Hydroxyl and Alkoxy Ions

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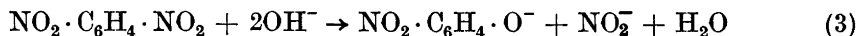
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The bimolecular rate constants of the reactions of *o*- and *p*-dinitrobenzenes with hydroxyl ion in pure water and those of the reaction of *p*-dinitrobenzene in 50 vol-% dioxan-water have been measured at different temperatures. The velocities of the reactions of *o*- and *p*-dinitrobenzenes with ethoxyl ion have been measured in pure ethanol and the velocity of the reaction of *p*-dinitrobenzene with methoxyl ion in pure methanol. The simultaneous reactions of *o*- and *p*-dinitrobenzenes with hydroxyl ion and ethoxyl ion in alkaline ethanol-water mixtures and the corresponding reactions of *p*-dinitrobenzene in alkaline methanol-water mixtures have been studied. Equations for calculating the rate constants of the concurrent reactions were derived by taking into account the equilibrium between hydroxyl and alkoxy ions. Except for the rates in dioxan-water, which were measured at four temperatures, the rates were measured at three temperatures. The parameters of the Arrhenius equation were evaluated. The results are discussed.

The dinitrobenzenes undergo the following reactions with alkoxy and hydroxyl ions:



The nitrophenol formed is converted into the ionic form in the alkaline solution, so that instead of (2) we have the total reaction

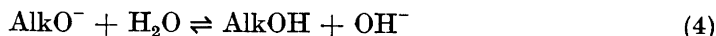


These reactions present an interesting object for kinetic study since it is possible to follow the variation of the concentration of each reactant in the reaction mixture, also in aqueous alcohols where the reactions occur simultaneously. The concentration of the phenol in the reaction mixture can be determined colorimetrically and the concentration of the base by titration. The concentration of the unreacted dinitrocompound can be calculated from these two values. If necessary, also the concentration of the nitrite ion can be determined separately. However, only the reactions of the *ortho*- and *para*-compounds are

appropriate for kinetic study because the reactions of *m*-dinitrobenzene are complicated by the formation of *m*-dinitroazoxybenzene.

The kinetics of the reactions were first studied by Lobry de Bruyn and Steger¹. Steger² investigated the reactions of *o*- and *p*-dinitrobenzenes with methoxyl ion and ethoxyl ion in absolute methanol and ethanol at the temperatures 25°, 35° and 45°C, and Lobry de Bruyn and Steger³ the reactions of *o*-dinitrobenzene in methanol-water and ethanol-water mixtures at 25°C. They found that the *para*-isomeride reacts faster than the *ortho*-isomeride in the absolute alcohols and that the reaction with ethoxyl ion in ethanol is faster than the reaction with methoxyl ion in methanol. In ethanol-water and methanol-water mixtures the over-all reaction velocity is greatly dependent on the composition of the solvent. Lobry de Bruyn and Steger also determined the concentration of the nitrophenol formed and they deduced from their results that the relative concentration of the alcoholate ion in aqueous alcohol is considerable up to a high water content. The reaction between *p*-dinitrobenzene and methoxyl ion in absolute methanol has been studied also by Parijs⁴ and by Bolto and Miller⁵, but these investigations contribute very little to the results of Lobry de Bruyn and Steger.

The work now described was initiated to obtain more detailed information on the kinetics of the reactions in alcohol-water mixtures than was collected by the early workers, and especially to study the equilibrium



The results concerning the latter will be published later by one of us (J.M.) and only the kinetic results are reported in the present communication.

CALCULATIONS

If the initial molar concentration of both reactants is *a*, and if the amount of the dinitrobenzene consumed in the formation of the ether and phenol up to time *t* are *x* and *y* mole/litre, respectively, the total concentration of the unreacted alkali at time *t* is

$$[\text{OH}^-] + [\text{AlkO}^-] = a - x - 2y \quad (5)$$

According to eqn. (4)

$$[\text{OH}^-] = K'[\text{AlkO}^-] \quad (6)$$

where

$$K' = K[\text{H}_2\text{O}]/[\text{AlkOH}] \quad (7)$$

is practically invariable at constant temperature.

From eqns. (5) and (6) we obtain

$$[\text{AlkO}^-] = (a - x - 2y)/(K' + 1) \quad (8)$$

and

$$[\text{OH}^-] = K'(a - x - 2y)/(K' + 1) \quad (9)$$

Hence, if the reactions (1) and (2) are related only through the equilibrium (4), the rate equations are

$$\frac{dx}{dt} = k_e^{\circ} (a-x-y)(a-x-2y)/(K' + 1) \quad (10)$$

$$\frac{dy}{dt} = k_f^{\circ} (a-x-y)(a-x-2y)K'/(K' + 1) \quad (11)$$

The subscripts e and f refer to the formation of ether and phenol, respectively. Dividing (11) by (10) and taking into account that $dx/dy = x/y$, we find

$$\frac{x}{y} = \frac{k_e^{\circ}}{k_f^{\circ}K'} \quad (12)$$

Substituting the expression for y derived from eqn. (12) in eqn. (10), we have

$$dx/(a-\beta x)(a-\gamma x) = p dt \quad (13)$$

where

$$\alpha = k_e^{\circ}a, \beta = k_e^{\circ} + k_f^{\circ}K', \gamma = k_e^{\circ} + 2k_f^{\circ}K' \text{ and } p = 1/[k_e^{\circ}(K' + 1)].$$

Introduction of the expression for y in eqn. (11) gives the same result. Eqn. (13) can be integrated by the method of partial fractions; the following solutions of eqns. (10) and (11) are obtained:

$$\frac{k_e^{\circ}}{K' + 1} = \frac{x}{y} \frac{1}{at} \ln \frac{(a-x-y)}{(a-x-2y)} \quad (14)$$

$$\frac{k_f^{\circ}K'}{K' + 1} = \frac{1}{at} \ln \frac{(a-x-y)}{(a-x-2y)} \quad (15)$$

The constants

$$\frac{k_e^{\circ}}{K' + 1} = \bar{k}_e \text{ and } \frac{k_f^{\circ}K'}{K' + 1} = k_f \quad (16-17)$$

can be determined experimentally, for $a-x-2y$, the total alkali concentration, can be measured titrimetrically and y , the concentration of the phenol, can be determined colorimetrically. If we write $a-x-2y = b$, or $a-x-y = b + y$, we obtain from (14) and (16) the expression

$$k_e = \frac{x}{y} \frac{1}{at} \ln \left(1 + \frac{y}{b}\right) \quad (18)$$

which is a very convenient one for the practical calculation of k_e from the experiments. If one of the constants k_e and k_f has been determined, the other can be obtained by the equation

$$\frac{k_e}{k_f} = \frac{x}{y} \quad (19)$$

If reaction (1) is much faster than reaction (2), the second order rate constant computed from the total alkali consumptions by the usual formula $dx/dt = k(a-x)^2$ can be taken to be k_e . This formula was used to calculate the rate of reaction of *p*-dinitrobenzene in methanol-water mixtures. Also in this case k_f was computed from formula (19).

EXPERIMENTAL

Materials. The *o*-dinitrobenzene was a product of "purissimum" grade (Fluka); it was used as received. The *p*-dinitrobenzene was a product of the "purum" grade (Fluka) and was recrystallized twice from 96 % ethanol, after which it melted at 174–175°C.

The ethanol used as solvent in the kinetic experiments was commercial absolute ethanol that had been purified by the method of Walden⁶ and finally distilled over anhydrous copper sulphate. The methanol was commercial methanol which was purified by running it through a column of the cation exchange resin Zeo-karb HI, treating it by the method of Lund and Bjerrum⁷ and distilling it over anhydrous copper sulphate. The water was freshly distilled.

Preliminary experiments. All three dinitrobenzenes coloured in solutions containing acetone deep brown. Therefore acetone could not be used as a solvent in the kinetic experiments. *m*-Dinitrobenzene produced brown colour in all solvents used.

The solvolysis of the dinitrobenzenes by alcohols or water is so slow that it can be completely neglected; no detectable ether or phenol formation occurred in the absence of alkali during two weeks at 60°C. The Griess test⁸ for nitrite ion was negative. The hydrolysis of the ether produced to phenol is always so slow that it could be neglected⁹.

Method. The kinetic experiments were carried out in reaction vessels that have been previously described¹⁰. In the experiments with *o*-dinitrobenzene in ethanol-water, 5 ml of a 0.08 N sodium hydroxide solution was introduced into the smaller compartment of the vessel and 20 ml of a 0.02 N solution of the nitrocompound into the larger compartment, so that after thermostating and mixing, the concentration of each reactant was 0.016 M. In the experiments with *p*-dinitrobenzene, owing to its poorer solubility, 10 ml of 0.04 N sodium hydroxide and 40 ml of a 0.01 N solution of the dinitrobenzene were used, so that the initial concentrations of the reactants were 0.008 M. In these experiments the reaction vessels were about twice as large as in the experiments with *o*-dinitrobenzene.

The reaction vessels were taken from the thermostat after suitable times, cooled quickly to room temperature by immersion in cold water, and the mixtures were analysed as quickly as possible. The analytical method was essentially the same as that used by Lobry de Bruyn and Steger. The phenol was determined colorimetrically on a small sample, the sample rinsed back into the reaction vessel and the total alkali in the mixture determined by titration. To avoid decomposition of the nitrite, the titration was carried out with 0.05 N acetic acid. Phenolphthalein was used as indicator.

In most experiments a Bausch & Lomb Spectronic 20 colorimeter was used. In the case of *o*-dinitrobenzene the wave lengths were 475 and 488 $m\mu$; identical results were obtained at both wave lengths. Different wave lengths were tried in the analysis of the reaction mixtures in the case of *p*-dinitrobenzene. The best results were obtained with the wave lengths 400 and 413 $m\mu$. The readings were taken against a blank consisting of the same mixture acidified with acetic acid. However, the accuracy of the analyses was somewhat less in the case of *p*-dinitrobenzene than in the case of *o*-dinitrobenzene. In the experiments with *p*-dinitrobenzene in methanol-water mixtures, where the concentration of the phenol formed was very low, a Beckman DU Spectrophotometer was used instead of the Bausch & Lomb instrument, and the measurements were made at reaction percentages exceeding fifty (*cf.* Table 5).

The temperatures of the electrically controlled thermostats were constant within $\pm 0.02^\circ$. The thermometers were checked against a thermometer calibrated at the U. S. Bureau of Standards.

To study reaction (2) in absence of reaction (1), experiments were performed with pure water as solvent. Owing to the poor solubility, the following method was used. The dinitrocompound was shaken with hot water about half an hour, and the solution was filtered after it had cooled. No phenol formation was observed during this operation. The reaction was carried out in 100-ml glass-stoppered flasks. At suitable times 5-ml samples were taken with a pipette and the phenol contents determined colorimetrically. The wave lengths used were 400 $m\mu$ for the *para* and 425 $m\mu$ for the *ortho* compound. The initial concentration of sodium hydroxide was 0.016 M. To determine the initial concentration of the dinitrobenzene, a measured quantity of the solution was sealed in an ampoule and kept at 100° until the reaction had gone to completion (about 12 h). The ampoule was

Table 1. *o*-Dinitrobenzene in 100 % EtOH, $a = 0.016$, 50°. Formula $dx/dt = k(a-x)^2$.

t min	Tit. ml	p	10^5k l mole ⁻¹ s ⁻¹
0	(8.00)		
168	5.56	30.5	272
265	4.72	41.0	285
281	4.67	41.6	264
383	4.20	47.5	275
350	4.17	47.9	273
478	3.57	55.4	271
485	3.53	55.9	272
Mean			273.1

Table 2. *p*-Dinitrobenzene in 100 % MeOH, $a = 0.008$, 40°. Formula $dx/dt = k(a-x)^2$.

t min	Tit. ml	p	10^5k l mole ⁻¹ s ⁻¹
0	(8.00)		
285	6.27	21.6	202
504	5.41	32.4	196
534	5.31	33.6	198
992	4.07	49.1	203
1 203	3.70	53.8	201
1 208	3.68	54.0	202
1 410	3.39	57.6	202
Mean			200.6

then opened and the phenol determined spectrophotometrically. The rate constant was calculated by the formula

$$\frac{dx}{dt} = k(a-x)(b-2x),$$

which on integration gives

$$k = \frac{2.303}{(2a-b)t} \log \frac{b(a-x)}{a(b-2x)} \quad (20)$$

The constancy of k was satisfactory in all runs.

With *p*-dinitrobenzene some experiments were made also in dioxan-water that contained 50 ml of water in 100 ml of the mixture. The initial concentrations of the dinitrobenzene and sodium hydroxide were 0.008 M. Two-millilitre samples of the reaction mixtures were sealed in ampoules of Pyrex glass after deaeration with nitrogen and transferred to the thermostat. After suitable times the ampoules were taken from the thermostat and the phenol determined spectrophotometrically. The rate constant was calculated by formula (20). In the experiments with dioxan-water mixtures it was difficult to obtain a good constancy for k . In these runs k in general gradually decreased as the reaction proceeded. It seemed that the walls of the ampoules were attacked by the alkali during the long reaction periods.

The results of some runs are recorded in Tables 1–5 (p is the per cent conversion).

Table 3. *o*-Dinitrobenzene in 76.6 wt-% EtOH, $a = 0.016$, 40°. Formula 14.

t min	Tit. ml	p	10^4y	10^4x	x/y	10^5k_e l mole ⁻¹ s ⁻¹	
0	(8.00)						
944	5.60	30.0	2.45	43.2	17.6	42.1	
1 240	5.11	36.1	2.92	52.0	17.8	42.2	
1 254	5.12	36.0	2.93	51.9	17.7	41.8	
1 434	4.92	38.5	2.81	56.1	20.0	40.8	
2 227	4.01	49.9	3.51	72.9	20.8	41.6	
2 236	3.99	50.1	3.54	73.2	20.7	41.9	
2 705	3.64	54.5	4.20	19.0	18.8	40.6	
Mean						19.1	41.57

To correct for the thermal expansion of the solvent the above value must be multiplied by 1.020, which gives $k_e = 0.0004241$ l mole⁻¹s⁻¹.

$$k_t = k_e \frac{x}{y} = 0.0004241/19.1 = 0.0000222 \text{ l mole}^{-1}\text{s}^{-1}.$$

Table 4. *p*-Dinitrobenzene in 88.3 wt.-% EtOH, $\alpha = 0.008$, 40°. Formula 14.

<i>t</i> min	Titration, ml	<i>p</i>	10 ⁴ <i>y</i>	10 ⁴ <i>x</i>	<i>x/y</i>	10/ <i>k</i> ⁵ l mole ⁻¹ s ⁻¹	
0	(8.00)						
127	5.46	31.8	0.153	25.1	164	752	
132	5.41	32.4	0.156	25.6	164	744	
201	4.62	42.3	0.198	33.4	169	746	
201	4.60	42.5	0.211	33.5	159	754	
258	4.13	48.4	0.239	38.2	160	744	
330	3.52	56.0	0.273	44.2	162	789	
396	3.24	59.5	0.311	46.9	151	757	
Mean						161	755.3

When corrected for the thermal expansion of the solvent:

$$k_e = 1.021 \times 0.007553 = 0.007710;$$

$$k_f = 0.007710/161 = 0.0000479.$$

RESULTS AND DISCUSSION

The results of our kinetic experiments in alcoholic solutions are summarized in Tables 6 and 7. The values of k_e and k_f have been corrected for the thermal expansion of the solvent. The activation energies and frequency factors were calculated from the variation of $\log k$ with $1/T$ by the method of least squares. The Arrhenius equation was obeyed within the limits of experimental error in all cases. The entropy of activation was calculated from the equation

$$A = e \frac{kT}{h} e^{\Delta S^\ddagger/R}$$

The values of k_e , E and $\log A$ for reaction (1) in pure alcohols (Table 6) represent the true bimolecular rate constant, the true activation energy and the true frequency factor for the reaction. If $[H_2O]/[AlkOH]$ is small, also $K' = K[H_2O]/[AlkOH]$ is small. According to the results of Caldin¹¹, $K \approx 2$ at 25° for ethanol-water mixtures, and according to Koskikallio¹² $K = 0.13$ for methanol-water mixtures. On the basis of the value $K = 2$ we can estimate

Table 5. *p*-Dinitrobenzene in 88.0 wt.-% MeOH, $\alpha = 0.008$, 40°.

a. Rate constants.				b. Ratio <i>x/y</i> .	
Formula $\frac{dx}{dt} = k(a-x)^2$				(Different samples)	
<i>t</i> min	Titration, ml	<i>p</i>	10 ⁴ <i>k</i> l mole ⁻¹ s ⁻¹	<i>p</i>	<i>x/y</i>
0	(8.00)			50.9	2 220
466	5.14	35.8	249	51.1	2 300
473	5.12	36.0	251	51.6	2 160
544	4.87	39.1	246	62.1	2 460
857	3.92	51.0	253		
862	3.90	51.3	254		
870	3.92	51.0	249		
928	3.77	52.9	252		
Mean				250.6	

When corrected for the thermal expansion of the solvent:

$$k = k_e = 1.023 \times 0.002506 = 0.002563;$$

$$k_f = 0.002563/2290 = 0.0000112.$$

Table 6. The reaction $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{AlkO}^- \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OAlk} + \text{NO}_2^-$ in alcohol-water mixtures.

Iso-meride Alcohol	In the solvent			$10^5 k_e \text{ l mole}^{-1} \text{ s}^{-1}$			E cal.	$\log A$	ΔS^* (35°) E.U.
	H_2O ml/l	alcohol wt.-%	x_{alc}	25.00°	40.00°	50.00°			
Ortho EtOH	0	100	1.000	18.5	99.0	283	20 890	11.57	- 7.7
	50	94.2	0.862	13.5	70.2	195	20 450	11.12	- 9.7
	100	88.3	0.743	11.4	57.9	156	20 080	10.77	-11.3
	200	76.6	0.562	9.03	42.4	107	18 960	9.85	-15.5
	300	66.0	0.427	7.12	29.8	74.7	17 980	9.03	-19.2
	400	55.6	0.329	5.51	22.7	53.1	17 370	8.49	-21.8
Para EtOH	0	100	1.000	197 ^a	1 160	3 590	21 960	13.40	+ 0.7
	50	94.2	0.862	171	1 000	2 860	21 600	13.07	- 0.8
	100	88.3	0.743	144	771	2 250	21 060	12.59	- 3.0
	150	82.6	0.645	120					
	200	76.6	0.562	100	498	1 340	19 870	11.56	- 7.7
Para MeOH	0	100	1.000	34.0	206	640	22 450	12.98	- 1.2
	100	88.0	0.804	41.9	256	784	22 430	13.06	- 0.8
	200	76.7	0.650	45.9	280	852	22 370	13.06	- 0.8

^a 15.00° : 56.2.

that if $[\text{H}_2\text{O}]/[\text{AlkOH}] < 0.1$, $K' < 0.2$ and $1 < k_e^0/k_e < 1.2$. Thus in highly alcoholic solvents the values of k_e , E and $\log A$ of Table 6 do not differ much from the true values. By contrast, the values of k_t , E and $\log A$ given in Table 7 for reaction (2) in these solvents differ much from the true values; e.g., if $[\text{H}_2\text{O}]/[\text{AlkOH}] = 0.1$, $k_t^0/k_t > 6$. With increasing water content this ratio becomes smaller; thus if $[\text{H}_2\text{O}]/[\text{AlkOH}] = 1$, $k_t^0/k_t \approx 1.5$. In highly aqueous solvents this latter ratio approaches unity. It seems that if specific

Table 7. The reaction $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{OH}^- \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{NO}_2^-$ in alcohol-water mixtures.

Iso-meride Alcohol	Alcohol wt.-%	x/y			$10^5 k_t \text{ l mole}^{-1} \text{ s}^{-1}$			E cal	$\log A$	ΔS^* (35°) E.U.
		25.00°	40.00°	50.00°	25.00°	40.00°	50.00°			
Ortho EtOH	94.2	62.0	35.7	27.2	0.218	1.97	7.18	26 800	14.0	+ 3.5
	88.3	40.5	24.9	18.5	0.280	2.33	8.41	26 100	13.6	+ 1.6
	76.6	28.3	19.1	13.8	0.319	2.22	7.75	24 400	12.4	- 4.0
	66.0	23.3	13.5	10.1	0.306	2.20	7.43	24 400	12.4	- 4.0
	55.6	18.1	11.9	8.35	0.305	1.91	6.36	23 200	11.5	- 8.3
Para EtOH	94.2	503	316	220	0.340	3.16	13.0	28 300	15.2	+ 9.0
	88.3	254	161	119	0.565	4.79	18.9	27 000	14.5	+ 5.8
	76.6	157	86	65	0.641	5.78	20.8	26 800	14.4	+ 5.3
Para MeOH	88.0	3 760	2 290	1 510	0.0111	0.112	0.519	29 500	14.7	+ 6.7
	76.7	1 570	1 010	850	0.0292	0.277	1.00	27 100	13.3	+ 0.3

Table 8. The reaction $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{OH}^- \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{NO}_2^-$ in pure water

Com- pound	Initial conc.		$10^5 k \text{ l mole}^{-1}\text{s}^{-1}$				<i>E</i> cal	log <i>A</i>	ΔS^* (35°) E.U.
	[NaOH]	[Dinitro- benzene]	25.00°	40.00°	50.00°	60.00°			
<i>Ortho</i>	0.016	4.73×10^{-4}	(0.260)	1.68	5.18	15.4	23 010	11.28	-9.0
<i>Para</i>	0.016	1.64×10^{-4}	(0.0968)	0.758	2.70	8.93	25 560	12.72	-2.4

The values for 25° given in brackets were calculated from the Arrhenius equation.

solvent influences are taken into account the values of Table 7 gradually change with increasing water content towards values found for reaction (2) in pure water (Table 8; in this table $k = k_t^0$).

The results obtained for *p*-dinitrobenzene in dioxan-water containing 50 ml of water in 100 ml of the mixture are:

	25.00°	40.00°	50.00°	60.00°
$10^5 k \text{ l mole}^{-1}\text{s}^{-1}$	1.45	9.20	25.0	67.0
$E = 21\,600 \text{ cal}, \log A = 11.0.$				

The rate constants are considerably larger and the activation energy lower than for the reaction in pure water. The frequency factor is of the same order of magnitude as in water. Evidently the addition of dioxan to the water accelerates the reaction by lowering the energy of activation.

Lobry de Bruyn and Steger used for the calculation of the rate constants the formula

$$k = \frac{100 (T_1 - T_t)}{t T_1 T_t \Theta}$$

where *t* is the time, Θ the normality of the acid used as titrant, T_1 the consumption of the acid at the start of the reaction and T_t the consumption at time *t*. The volume of the sample does not occur in this formula, and therefore their values of *k* are twice as great as the true values¹³. The rate constants recalculated from the data of Lobry de Bruyn and Steger for pure alcohols and corrected for the thermal expansion of the solvent and the activation energies,

Table 9. Reaction (1) of dinitrobenzenes in absolute ethanol and methanol. (Based on data of Lobry de Bruyn and Steger.)

	Tempera- ture	Ethanol		Methanol	
		<i>Ortho</i>	<i>Para</i>	<i>Ortho</i>	<i>Para</i>
$10^5 k$ $\text{l mole}^{-1}\text{s}^{-1}$	25°	21.8	177	14.3	37.1
	35°	66.6	599	41.1	121
	45°	200	1 890	119	407
<i>E</i> cal		20 800	22 300	20 000	22 600
log <i>A</i>		11.6	13.6	10.8	13.1
ΔS^* (35°), E.U.		-7.5	+1.6	-11.3	-0.6

frequency factors and activation entropies obtained from these values are given in Table 9. The values are in good agreement with the values of Table 6 for the reactions in absolute alcohols.

The rate constants of Lobry de Bruyn and Steger for *o*-dinitrobenzene in aqueous ethanol and methanol at 25° are, when corrected as above:

Alcohol, wt.-%	100	98	96	94	92	90	80	70	60	50
10 ⁶ k, { EtOH	21.7	20.0	18.8	17.6	16.5	15.8	12.8	10.3	9.3	8.7
l mole ⁻¹ s ⁻¹ { MeOH	14.1	14.3				15.2	16.3	17.4	18.8	20.8

To compare our results for *o*-dinitrobenzene in ethanol-water with these values the rate constant for the total reaction at 25° was calculated from the simple second-order formula. The following results were obtained:

EtOH, wt.-%	100	94.2	88.3	76.6	66.0	55.6
10 ⁶ k l mole ⁻¹ s ⁻¹	18.5	14.4	12.0	9.79	7.84	6.23

It is seen that our values are considerably lower than those of Lobry de Bruyn and Steger.

For the molar ratios of the ether (*x*) and phenol (*y*) formed in the reaction of *o*-dinitrobenzene Lobry de Bruyn and Steger obtained the following values:

AlkOH, wt.-%	90	80	70	60	50
EtOH, <i>x/y</i>	51	35	27	24.5	21
MeOH, <i>x/y</i>		209	176	170	146

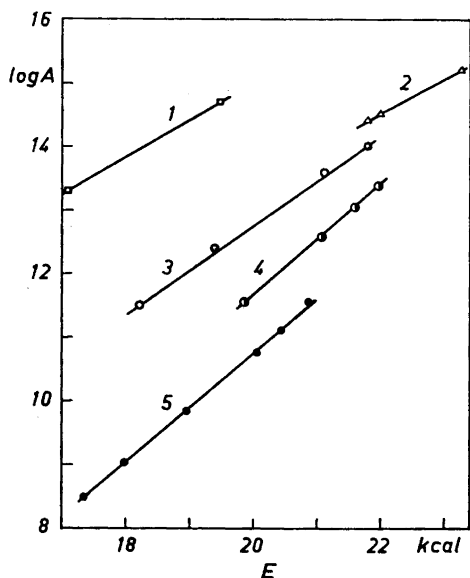


Fig. 1. Plot of $\log A$ against E . 1. *p*-dinitro + OH⁻ (MeOH, E - 10 kcal) 2. *p*-dinitro + OH⁻ (EtOH, E - 5 kcal), 3. *o*-dinitro + OH⁻ (EtOH, E - 5 kcal), 4. *p*-dinitro + OH⁻ (EtOH, E - 5 kcal), 5. *o*-dinitro + EtO⁻.

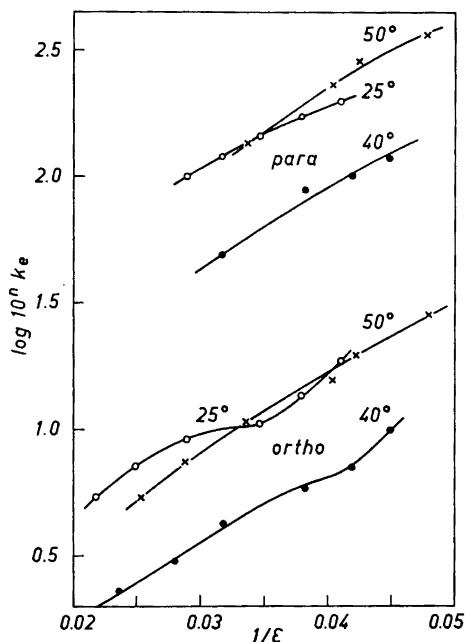


Fig. 2. Plot of $\log 10^n k$ against $1/\epsilon$ in ethanol-water. *o*-dinitro: for 40° and 50° $n = 5$, for 25° $n = 6$. *p*-dinitro: For 40° and 50° $n = 4$, for 25° $n = 5$.

Thus 6—7 times more phenol is formed in ethanol than in methanol. This is in good agreement with our results that were obtained by a more refined technique and more accurate calculations.

Lobry de Bruyn and Steger also stated that the ratio x/y remains constant as the reaction proceeds. This is in accordance with our observations. The derivations of eqns. (14) and (15) are based on the constancy of the ratio x/y .

It is remarkable that k_e and k_f show many regularities. First and foremost they obey the Arrhenius equation. Also is there a simple relation between E and $\log A$ when the composition of the binary solvent mixture is varied. From Fig. 1 we see that straight lines are obtained when $\log A$ is plotted against E . The linear relationship can, of course, be only incidental and be based on the shift of the equilibrium (4) as the composition of the solvent changes. However, one must bear in mind that a linear relationship between $\log A$ and E has often been observed as the composition of a mixed solvent is varied, also in cases where no equilibrium (4) exists. This relationship has been extensively discussed^{14,15}.

The relation between the rate constant and the dielectric constant ϵ of the medium has often been considered. According to theory, a roughly linear relationship between $\log k$ and $1/\epsilon$ should be expected. Plots based on the data of the present study are shown in Fig. 2.

On the basis of our experimental results the following general statements can be made. Reaction (1) is about ten times as fast for *p*-dinitrobenzene as for *o*-dinitrobenzene in ethanol and ethanol-water. This reaction is much slower in methanol and methanol-water than in ethanol and ethanol-water. The velocity of reaction (2) is much smaller than that of (1), and, at least in water, for *p*-dinitrobenzene clearly smaller than for *o*-dinitrobenzene. The activation energy of reaction (2) is always much higher than that of reaction (1).

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