

KINETICS AND MECHANISM OF REACTION OF 1,3,5-TRINITROBENZENE WITH 1-NAPHTHOL

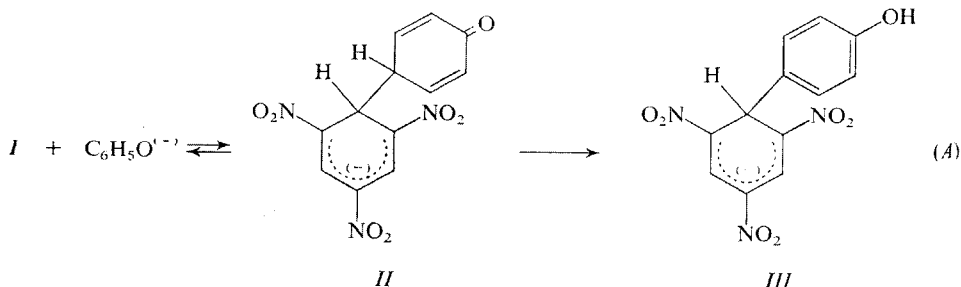
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1,3,5-Trinitrobenzene reacts in methanol–dimethyl sulphoxide mixture with 2-carbon atom of 1-naphtholate ion to form an unstable Meisenheimer complex which splits off the proton from the 2-carbon atom in the rate determining step, the tautomer with rearomatised naphthalene nucleus being formed. 2-Deuterio-1-naphtholate ion reacts 5 times more slowly. The reaction is strongly accelerated by increasing dimethyl sulphoxide content in the solvent. Reaction of the complex with another naphtholate ion produces a di-adduct.

1,3,5-Trinitrobenzene (*I*) reacts with phenolate ion¹ to give the Meisenheimer complexes *II* and *III* (Eq. (A)). The formation of the complex *II* is analogous to reactions of *I* with enolate anions of C-acids such as *e.g.* acetone, acetylacetone *etc.*² The complex *II* is thermodynamically unstable (being derived from a strong C-acid – cyclohexadienone) and isomerizes rapidly into the stable complex *III*. As the overall reaction of phenolate ion with *I* is much too slow for kinetic studies (the reaction half-lives of the order of several days at 25°C), we tried to carry out reactions of *I* with more reactive aromatic hydroxy compounds. Out of them 1-naphthol proved to be most advantageous. The aim of this work was the study of kinetics and mechanism of the reaction of *I* with 1-naphthol in mixture methanol–dimethyl sulphoxide with methoxide ion catalysis and determination of the reaction products.



EXPERIMENTAL

1,3,5-Trinitrobenzene (*I*) was crystallized from acetic acid and ethanol, m.p. 122–123°C (ref.³ 121–122°C); 1-naphthol (commercial reagent) was crystallized twice from tetrachloromethane, m.p. 95–96°C (ref.⁴ 96.1°C). Dimethyl sulphoxide was dried by boiling with calcium oxide and distilled *in vacuo*; the middle runnings were used for the measurements. The other reagents used were commercial *p.a.* chemicals. 4-Bromo-1-naphthol was prepared by bromination of 1-naphthol with BrI in glacial acetic acid⁵. The raw product was crystallized from benzene, chromatographed on a silica gel column (chloroform as the eluent) and again crystallized from benzene; m.p. 128–129°C (ref.⁵ m.p. 121–122°C, ref.⁶ m.p. 127–128°C).

2,4-Dideuterio-1-naphthol. Overall 15 g 1-naphthol was dissolved in 75 ml D₂O (99.8 mol% D) and 50 ml dimethyl formamide, and 1 g NaOH was added thereto. After six days standing at the room temperature the reaction mixture was diluted with 300 ml acidified water and extracted with 300 ml benzene. The benzene layer was shaken with D₂O, dried with sodium sulphate, and benzene was distilled off *in vacuo*. The raw product was crystallized from CCl₄; yield 6.2 g, m.p. 94.5–96.0°C. 5 g of the product thus obtained was subjected to a repeated deuteration under the same conditions to give 1.15 g product melting at 94.0–95.5°C. Integration of NMR spectra gave the hydrogen content at 2 and 4 positions $2 \pm 1\%$ and $5 \pm 5\%$, respectively.

4-Deuterio-1-naphthol. Overall 5 g 2,4-dideuterio-1-naphthol ($8 \pm 2\%$ H and $10 \pm 5\%$ H in positions 2 and 4, respectively) was dissolved in 4 ml methanol with addition of 1 ml 1M-CH₃ONa. The course of proto-dedeuteration was followed by measurements of NMR spectra of the reaction mixture. After 7 days standing at the room temperature the H content at the positions 2 and 4 was $75 \pm 5\%$ and $25 \pm 10\%$, respectively. The reaction mixture was dissolved in 30 ml 0.1M-HCl and extracted with 30 ml benzene. The benzene extract was shaken twice with distilled water, dried with sodium sulphate, and benzene was distilled off. The yield of the product after crystallization from CCl₄ was 1.3 g; m.p. 93–95°C.

Meisenheimer complex from I and 1-naphthol (VII): 0.47 g (2.2 mmol) *I* and 0.29 g (2 mmol) 1-naphthol were dissolved in 3 ml dimethyl sulphoxide and 0.9 ml 2M methanolic sodium methoxide (1.8 mmol) was added with stirring. After 15 minutes the reaction mixture was poured into c. 200 ml dry ether containing 0.2 ml glacial acetic acid. Ether was decanted, the product was shaken once more with 200 ml ether and dried *in vacuo*. The solution for NMR spectra measurement was obtained by dissolving the product in c. 2 ml dimethyl sulphoxide. The complex of *I* with 4-bromo-1-naphthol was prepared in the same way.

Meisenheimer complex from I and 1-naphthol (IX): 1.2 g (8 mmol) 1-naphthol and 0.43 g (2 mmol) *I* were dissolved in 8 ml dimethyl sulphoxide, and 4 ml 1M sodium methoxide (4 mmol) was added with stirring. After 30 minutes the reaction mixture was poured into 200 ml dry ether containing 0.2 ml glacial acetic acid. Further procedure was the same as in the above case. NMR spectra were measured with a Tesla BS 487 B apparatus at 80 MHz at 50°C in methanol (1-naphthol and deuterated 1-naphthols) and in dimethyl sulphoxide (Meisenheimer complexes).

Kinetic Measurements

Course of the reactions of *I* and complex *VII* with 1-naphthol was followed with the use of a Unicam SP 800 spectrophotometer in the wavelength region 350 to 700 nm. Proper kinetic measurements were carried out with the spectrophotometer Zeiss VSU-2P. When measuring the reaction of *I* with 1-naphthol, 1M 1-naphthol and 1M sodium methoxide mixture in a 1 cm cell was diluted with methanol–dimethyl sulphoxide mixture to 2 ml volume. After temperating at 25°C, $20 \mu\text{l } 5 \cdot 10^{-3}\text{M}$ methanolic *I* was injected into the cell and, at definite time intervals, absorbance

increase was measured in the isobestic point of the complex *VII* and final reaction product *IX* (540 to 549 nm according to the reaction conditions). The rate constants were determined graphically from the relation (1). For determination of the rate constants of the subsequent reaction of

$$k_{\text{obs}}t = -2.303 \log (A_{\infty} - A_t) + \text{const.} \quad (1)$$

the complex *VII* with 1-naphthol the reaction mixtures were prepared in the same way, however, instead of *I* solution 20 μl c. $5 \cdot 10^{-3}\text{M}$ methanolic *VII* was injected at the end, and the reaction was followed at 515 nm (in solution with 30 and 50% by vol. dimethyl sulphoxide) resp. 525 nm (for 70% by vol. dimethyl sulphoxide).

Ratio of concentration of complex of *I* with methoxide ion (*IV*) to that of *I* was determined from the relation (2)

$$[IV]/[I] = (A - A_T)/(A_C - A), \quad (2)$$

where A_T is the absorbance of pure *I*, and A_C is that of the solution in which all *I* was transformed into the complex *IV*. The absorbances were measured at 505 nm in specially prepared mixtures: 0.1 ml 1M sodium methoxide resp. 0.1 ml 0.1M sodium methoxide (in 50 and 70% dimethyl sulphoxide) was added to 1.9 ml methanol-dimethyl sulphoxide mixture containing 0.2 ml $5 \cdot 10^{-4}\text{M}$ *I* and 0.05 to 0.60 ml 1M 1-naphthol (1-naphthol concentration depended on the dimethyl sulphoxide content in the mixture). The reference cell contained the same solution, *I* solution being substituted by the same volume of methanol. The concentration ratio of dianion *VI* and complex *VII* was determined by analogous way: instead of *I* the solution of complex *VII* was added, in all cases 1M sodium methoxide was added. The absorbances were measured at 500 nm.

RESULTS AND DISCUSSION

In the reaction of *I* with naphtholate ion carried out under the same conditions as that with phenoxide ion¹ (*I* : naphthol : naphtholate 1 : 2 : 2; 70% by vol. dimethyl sulphoxide) most *I* reacted within 3 minutes (*cf.* the reaction with phenoxide ion, where 50% *I* reacted within 6 hours). Spectral record of a sample diluted 1 : 10 000 showed 2 intensive absorption bands at 480 and 585 nm (their position and shape being characteristic for complexes of *I* with carbanions²) and one less intensive band with the maximum at 520 nm. In the further samples withdrawn from the reaction mixture the band at 520 nm gradually increased to the detriment of the other 2 bands. After 30 minutes the spectrum contained practically only the band at 520 nm (Fig. 1), and later only slight changes took place due to decomposition and oxidation reactions.

Practically pure complex *VII* (see Fig. 1 for its electronic spectrum) was prepared with molar ratio *I* : naphthol : naphtholate 1 : 0.9 : 0.8. NMR spectrum of this complex contains two sharp signals belonging to sp^2 and sp^3 protons of the cyclohexadienone ring (chemical shifts 1.54 τ and 3.79 τ ; intensity ratio 2 : 1). The other absorptions in the spectrum belong to the protons of naphthalene nucleus and have similar shape and similar chemical shifts as those in 1-naphthol itself; however,

the signals of the 2-proton of the naphthalene nucleus are absent. This fact indicates that *I* attacks the carbon at 2-position of the naphthalene nucleus.

Structure of the product with absorption maximum at 520 nm could not be determined from its NMR spectra. Only signals belonging to protons of naphthalene nucleus were found, whereas the other parts of spectrum could not be interpreted. The structure of di-adduct *IX* was suggested for this compound on the basis of the following findings: the position and shape of absorption maximum in electronic spectrum of the compound are characteristic for di-adducts⁷⁻¹¹; the compound is practically the only reaction product, if two or more mols of naphtholate per one mol *I* are used, whereas if 1 to 2 mol naphtholate per 1 mol *I* are used, then the mixture *VII* + *IX* results; the di-adduct *IX* can also be prepared by reaction of the compound *VII* with naphtholate ion, the rate of formation of *IX* being proportional to the concentration of naphtholate ion.

The overall reaction course can be represented as in Scheme 1. After injection of *I* (final concentration about $5 \cdot 10^{-5} \text{M}$) into the solution of naphthol and naphtholate anion in methanol-dimethyl sulphoxide mixture, the complex *IV* is formed practically immediately by reaction of *I* with small amount of the methoxide ion present. Free *I* stands in rapid equilibrium with complex *IV* and reacts with naphtholate ion to give complex *VII*. Spectral records show gradual increase of intensity of the bands at 480 and 585 nm. However, gradually the subsequent reaction leading to formation of di-adduct *IX* becomes significant, a new band at 520 nm is increasing. Rate of the both reactions increases with increasing concentration of naphtholate ion. Increasing dimethyl sulphoxide concentration makes the rate of formation of the complex *VII* greater as compared with the rate of the subsequent reaction. In 90% dimethyl sulphoxide the first reaction is faster than the subsequent reaction to such an extent that at the time when almost all *I* was transformed into the complex *VII* the subsequent reaction was practically insignificant.

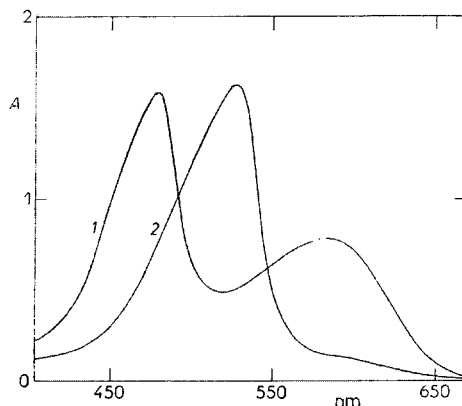
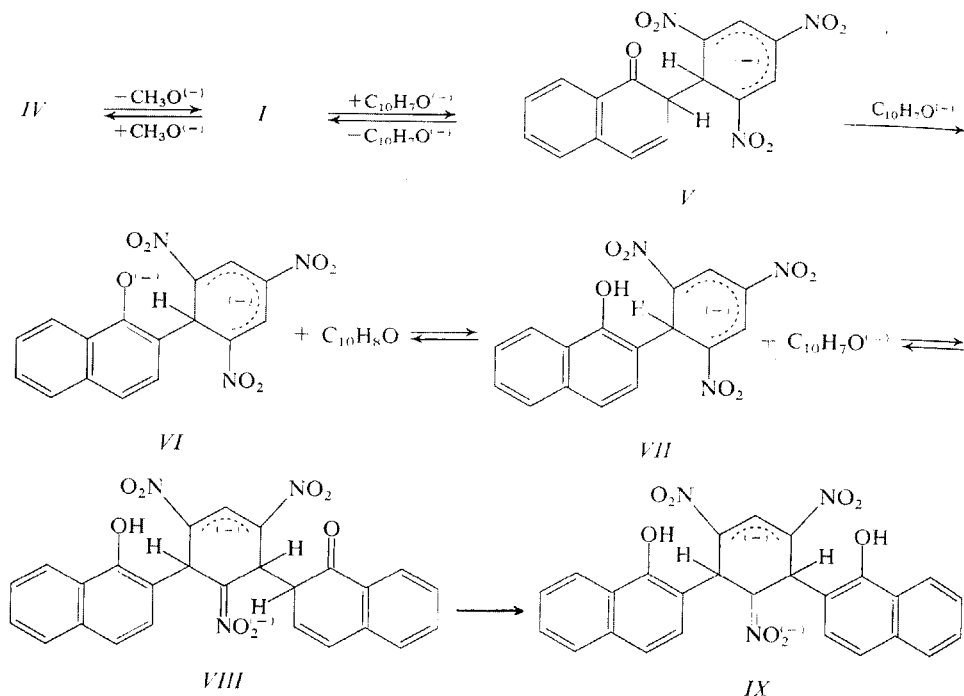


FIG. 1
Electronic Spectra of Complex *VII* 1 and
Complex *IX* 2 in Methanol-Dimethyl Sul-
phoxide Mixture 1 : 1 (by vol.) with Con-
centrations $7 \cdot 10^{-5} \text{M}$



SCHEME 1

Formation of the di-adduct *IX* was followed using the separately prepared complex *VII*. Spectral records crossed isosbestic points up to at least 90% of the reaction, then the decomposition and oxidation reactions became markedly significant.

The values k_{obs} of the reaction $VII \rightarrow IX$ increase linearly with increasing concentration of naphtholate ions (Table I) and are directly proportional to the concentration of *VII*. The rate constants k_2 (Table I) were calculated from the kinetic

$$v = k_{\text{obs}}([VI] + [VII]) = k_2[VII][C_{10}H_7O^{(-)}], \quad (3)$$

$$k_2 = k_{\text{obs}}(K_6 + x)/x[C_{10}H_7O^{(-)}] \quad (4)$$

equation (3) and relation (4). K_6 is the acid-base equilibrium constant of the reaction of *VII* with naphtholate ion (Scheme 1, Table II), and x stands for the ratio $[C_{10}H_8O]/[C_{10}H_7O^{(-)}]$. The rate constant values depend but slightly on dimethyl sulphoxide concentration. It is caused by two antagonistic effects: increasing dimethyl sulphoxide concentration increases the activity of naphtholate ion, but, at the same time, stability of the complex *VII* increases, too¹² (as compared with that of the complex *IX*).

Values of rate constants k_{obs} of formation of the complex *VII* (Table III) are directly proportional to concentration of free *I*, and their value increases roughly linearly with the square of naphtholate ion concentration. The constants k_3 were computed on the basis of kinetic equation (5) from relation (6).

$$v = k_{\text{obs}}([I] + [IV]) = k_3[I][C_{10}H_7O^{(-)}]^2, \quad (5)$$

$$k_3 = k_{\text{obs}}(K + x)/x[C_{10}H_7O^{(-)}]^2. \quad (6)$$

TABLE I

Rate Constant Values k_{obs} (s^{-1}) and k_2 ($l \text{ mol}^{-1} s^{-1}$) of Formation of Complex *IX* in Methanol-Dimethyl Sulphoxide Mixtures at 25°C

% CH ₃ OH (by vol.)	[C ₁₀ H ₇ O ⁽⁻⁾]	[C ₁₀ H ₈ O]	$k_{\text{obs}} \cdot 10^3$	$k_2, 10^{2a}$
70	0.10	0.50	1.56	1.78
	0.10	0.10	1.27	2.13
	0.05	0.25	0.68	1.54
50	0.05	0.15	0.61	1.59
	0.10	0.30	1.20	1.57
30	0.05	0.15	0.75	2.01
	0.10	0.10	0.96	2.02
	0.05	0.05	0.56	2.37
	0.10	0.05	0.86	2.73

^a ± 10%.

TABLE II

Equilibrium Constants Values K_C ($l \text{ mol}^{-1}$), K and K_6 in Methanol-Dimethyl Sulphoxide Mixtures at 25°C

Constant	% CH ₃ OH (by vol.)			
	70	50	40	30
$K_C \cdot 10^{-3, a}$	2.25	6.80	14.0	35.0
K^b	0.69	7.40	29.0	112
K_6^c	0.68	0.92	—	1.10

^a ± 10%; ^b ± 5%; ^c ± 2%.

The equilibrium constant K (Table II) is defined by Eq. (7).

$$K = \frac{[IV]}{[I]} x = \frac{[IV]}{[I] [\text{CH}_3\text{O}^{(-)}]} \cdot \frac{[\text{C}_{10}\text{H}_8\text{O}] [\text{CH}_3\text{O}^{(-)}]}{[\text{C}_{10}\text{H}_7\text{O}^{(-)}]} = K_B K_C^{-1}. \quad (7)$$

The determination of naphtholate ion concentration was based on the presumption that almost all methoxide ion reacts with naphthol to give naphtholate ion. This presumption is reasonable as it follows from the magnitude of the constant K_C (Table II) calculated from the found values K and the values K_B calculated from literature data¹³ for the same mixtures of methanol and dimethyl sulphoxide.

The ratio $[IV]/[I]$ depends only on the ratio of the buffer components ($[\text{C}_{15}\text{H}_8\text{O}] : [\text{C}_{10}\text{H}_7\text{O}^{(-)}]$) and not on the overall buffer concentration. It means that practically no complex of I with naphtholate ion, analogous to the complex IV (with C—O—C bond), was formed. In 50 to 70% dimethyl sulphoxide a decrease in K was observed at the highest used naphthol concentrations. At these highest naphthol concentrations the non-dissociated naphthol affects considerably the basicity of medium.

Quadratic dependence of k_{obs} on naphtholate ion concentration suggests that splitting off of the proton from the complex V is the rate-determining step, naphtholate anion playing predominantly the role of the base.

In 30% dimethyl sulphoxide an increase of k_3 with increasing naphtholate ion concentration can be seen. This is due first of all to the effect of increasing ionic strength on the reaction rate of the complex V and naphtholate ion. In 70% dimethyl sulphoxide at a given ratio naphthol: naphtholate the constants k_3 do not practically change with increasing naphtholate concentration (experiments 9, 13, 14; Table III). This fact is caused by two antagonistic effects. Increasing naphtholate ion concentration results in increase of ionic strength, which makes the reaction faster (experiments No 12, 11, 10, 9), on the other hand, increasing naphthol concentration makes the reaction slower, as it can be seen from experiments No 13, 15, 11, where the naphtholate ion concentration was constant, but the naphthol concentration increased. This retardation is probably again caused by the lowered basicity of medium due to increased naphthol concentration.

In 50 and 70% dimethyl sulphoxide the rate constant k_3 is $10 \times$ resp. 300 times higher than that in 30% dimethyl sulphoxide. This acceleration is much greater than that found with formation of the Meisenheimer complexes from methoxide ion and 1-trifluoromethyl-3,5-dinitrobenzene¹⁴ resp. 3,5-dinitro-4-methoxypyridine¹⁵ in the same media. This fact is due to that two naphtholate ions take part kinetically in formation of the compound VI , and the influence of medium will make itself felt within a much broader extent of the reaction: in the establishing of the equilibrium concentration of the complex V by reaction of I with naphtholate ion, and by affecting the reaction rate constant of the complex V with naphtholate ion.

The rate-determining splitting off of the proton in the complex *V* was confirmed by measuring the reaction rate of *I* with 2,4-dideuterio-1-naphthol in 70% dimethyl sulphoxide (Table III). The found value of the isotopic effect $k_H/k_D = 5.1 \pm 0.4$ is similar to the values found for the reactions of substituted naphtholate ions with substituted benzenediazonium ions¹⁶. Measurements of the isotopic effect of the reaction of *VII* with dideuterionaphthol in 70% dimethyl sulphoxide gave the k_H/k_D values 1.4 and 1.6 for 0.1M and 0.05M naphtholate concentrations, respectively. Assuming that splitting of C—D bond in formation of *IX* is 5 times slower than that of C—H bond (as it is the case with reaction $V \rightarrow VI$), in the first case about 65% *VIII* is transformed into *IX*, and 35% *VIII* is decomposed into *VII*, whereas in the second case 50% goes into *IX*, and 50% goes into *VII*. In the reaction of non-deuterated naphthol the decomposition into *VII* makes 10% and 20% in the first and the

TABLE III

Rate Constants Values k_{obs} (s^{-1}) and k_3 ($1^2 \text{ mol}^{-2} \text{ s}^{-1}$) of Formation of Complex *VII* in Methanol-Dimethyl Sulphoxide Mixtures at 25°C

% CH ₃ OH (by vol.)	Experiment No	[C ₁₀ H ₇ O ⁽⁻⁾]	[C ₁₀ H ₈ O]	$k_{\text{obs}} \cdot 10^3$	k_3^a
70	1	0.20	0.20	3.73	0.16
	2	0.15	0.15	1.93	0.15
	3	0.10	0.10	0.80	0.14
50	4	0.10	0.20	2.41	1.13
	5	0.075	0.15	1.58	1.32
	6	0.10	0.10	1.57	1.32
	7	0.05	0.10	0.63	1.18
	8	0.05	0.05	0.38	1.28
	30	9	0.10	0.10	3.58
10		0.075	0.125	2.80	33.9
11		0.05	0.15	2.06	31.5
12		0.025	0.175	0.90	24.6
13		0.05	0.05	0.89	40.2
14		0.075	0.075	1.90	38.0
15		0.05	0.10	1.64	37.3
16 ^b		0.10	0.10	6.58	—
17 ^b		0.05	0.05	1.71	—
18 ^c		0.10	0.10	3.08	—
19 ^d		0.10	0.10	0.76	—

^a $\pm 10\%$ (in 70% CH₃OH); $\pm 5\%$ (in 50 and 30% CH₃OH); ^b for 4-bromo-1-naphthol; ^c for 4-deuterio-1-naphthol; ^d for 2,4-dideuterio-1-naphthol.

second case, respectively. Hence the rate-determining step consists predominantly in formation of *VIII*.

Different kinetic behaviour during the formation of the mono- and di-adducts (reaction order with respect to naphtholate ion, isotopic effect) can be explained as follows. The reverse reaction of di-adducts (type *VIII*) is slower than that of mono-adducts (type *V*) by several orders of magnitude¹¹, whereas the rates of the reactions *V* → *VI* and *VIII* → *IX* are, perhaps, not very different. Therefore, splitting of C—H bond is the rate-determining step of formation of *VII*, whereas addition of naphtholate ion to the monoadduct *VII* is rate-limiting in the case of formation of *IX*.

Structure of the complex *VII* was confirmed also by the results of reactions of *I* with 4-bromo-1-naphthol and 4-deuterio-1-naphthol. NMR spectrum of the reaction product of *I* with 4-bromo-1-naphthol is similar to that of the complex *VII*; again the signals of protons at 2-position of the naphthalene nucleus are lacking. 4-Bromo substituent increases the acidity of naphthol and, hence, the concentration of free *I* in the reaction mixture (methoxide ion concentration is decreasing), at the same time, however, it decreases the reactivity of 2-position. The two factors are antagonistic, their effects are partially compensated, so that the reaction rate of *I* with 4-bromo-1-naphthol should be comparable with the same reaction of 1-naphthol at 2-position. The found values of k_{obs} in 70% dimethyl sulphoxide are, in average, 1.85 times higher than the corresponding values of reaction with 1-naphthol. The equilibrium constant K for 4-bromo-1-naphthol is 10.45 ± 2.75 , and k_3 is $7.5 \pm 1.5 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$. Thus 4-bromo-1-naphthol is about 10 times more acidic than 1-naphthol, and bromonaphtholate ion is 5 times less reactive than naphtholate ion (in 70% dimethyl sulphoxide).

Deuteration of 1-naphthol proceeds faster at 2-position than at 4-position by about one order of magnitude. Similarly proto-dedeuteration of 2,4-dideuterio-1-naphthol is fundamentally faster at 2-position than at 4-position. After one-week standing the sample of deuterated naphthol contained 75 and 25% H at 2-position and 4-position, respectively, and it was used for measurement of the reaction rate with *I* in 70% dimethyl sulphoxide. The found rate constant is a sum of the rate constants of the reactions of *I* with naphtholate ions containing H resp. D in the reactive position multiplied by the molar fractions of the respective naphtholate ions. For the reaction at 2-position the calculation gave the value of this constant $2.85 \pm 0.20 \text{ s}^{-1}$. Assuming that the reaction takes place at 4-position the calculated rate constant has the value $1.3 \pm 0.3 \text{ s}^{-1}$. The constant measured has the value $3.08 \pm 0.10 \text{ s}^{-1}$, i.e. equal (within experimental error) to that calculated under assumption that the reaction takes place at 2-position.

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