

KINETICS AND MECHANISM OF FORMATION OF MEISENHEIMER COMPLEXES FROM METHYL MALONATE AND 2,4,6-TRINITROANISOLE

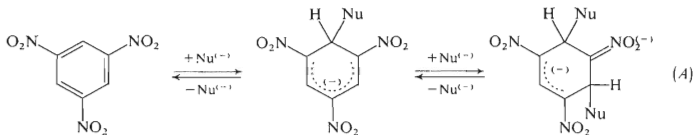
J. KAVÁLEK, V. MACHÁČEK, M. PASTRNEK and V. ŠTĚRBA

*Organic Chemistry Department,
Institute of Chemical Technology, 532 10 Pardubice*

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2,4,6-Trinitroanisole reacts with dimethyl malonate anion to give both the mono-adduct *V* and di-adduct *VI* (addition reaction at 3 and 5 positions) and methyl 2,4,6-trinitrophenylmalonate (*VIII*) (substitution reaction). At the same time methoxide anion is added at 1 position to give the monoadduct *IV*. Methyl 2,4,6-trinitrophenylmalonate (*VIII*) or its anion *IX* are the final reaction products. Rate constant of formation of *IX* is three times smaller than that of the complex *IV*. Rate of formation of the di-adduct *VI* is by several orders of magnitude lower than that of the mono-adduct *V*, the equilibrium constant of formation of *VI* being, however, several times greater (in methanol). Dimethyl sulphoxide causes a lowering of the rate and equilibrium constants of formation of the di-adduct *VI*, a similar effect being exhibited by dimethyl malonate itself.

1,3,5-Trinitrobenzene reacts with nucleophiles to give mono- and di-adducts¹⁻⁹ (*A*). In the case of 2,4,6-trinitroanisole analogous addition reactions of nucleophiles at 3 and 5-positions can be accompanied by an attack at 1 position (refs¹⁰⁻¹⁴). The reaction of 2,4,6-trinitroanisole with methoxide anion was studied in detail^{13,14}. Addition at 1 position is slower by several orders of magnitude than that at 3 posi-



tion, however, the complex formed is more stable (by about 4 orders of magnitude). The present paper deals with the reaction of 2,4,6-trinitroanisole with dimethyl malonate anion in methanol-dimethyl sulphoxide mixture. Besides the attack at 3 and 5 positions of 2,4,6-trinitroanisole giving mono- and di-adduct the 1 position is attacked, too, the respective Meisenheimer complex giving dimethyl 2,4,6-trinitrophenylmalonate or its anion after splitting off methoxide anion.

The aim of this work was comparison of the reactivities of methoxide and dimethyl malonate anions and of 2,4,6-trinitroanisole and 1,3,5-trinitrobenzene, determination of the effect of dimethyl sulphoxide on the rate and equilibrium constants, and suggestion of the reaction mechanism.

EXPERIMENTAL

¹H-NMR spectra were measured with a Tesla BS 487 B apparatus at 80 MHz. Dimethyl sulphoxide was dried by boiling with calcium oxide, distilled *in vacuo* and kept over molecular sieves. 2,4,6-Trinitroanisole, m.p. 57–58°C (ref.¹⁵ 56–57°C). ¹H-NMR spectrum (CDCl₃): 0.05δ (s), 4.05δ (s).

Methyl 2,4,6-trinitrophenylmalonate: 20 ml 2M sodium methoxide (0.04 mol) was added drop by drop to a stirred solution of 4.95 g (0.02 mol) 2,4,6-trinitrochlorobenzene and 2.9 g (0.022 mol) dimethyl malonate in 40 ml dimethyl sulphoxide. After 15 min the solution was diluted with 500 ml water with 6 ml hydrochloric acid, and the mixture was extracted with 3 × 300 ml benzene. The combined extracts were dried with anhydrous sodium sulphate and concentrated to 10 ml volume. The separated crystalline solid was crystallized from tetrachloromethane to give 2.8 g (40%) yellow needles melting at 144–147°C. For C₁₁H₉N₃O₁₀ (343.2) calculated: 38.49% C, 2.62% H, 12.24% N; found: 38.81% C, 2.66% H, 12.43% N. ¹H-NMR spectrum (hexadeuterio-dimethyl sulphoxide): 9.09δ (2 H, s), 5.84δ (1 H, s) and 3.69δ (6 H, s).

Kinetic measurements. Stock solutions of 10⁻²M 2,4,6-trinitroanisole in benzene, 0.9M dimethyl malonate in methanol, and 1M sodium methoxide in methanol were diluted to the required concentration with methanol before each run. The ionic strength was adjusted at 0.02 by addition of 5 · 10⁻²M-NaCl in methanol. The formation of the mono- and di-adduct was followed by the stopped-flow method with a Durrum spectrophotometer Model D 110 at 25°C in methanol or methanol-dimethyl sulphoxide mixture 4 : 1 (by vol.). One syringe contained usually the sodium methoxide solution (concentration 4 · 10⁻³ to 4 · 10⁻²M) and sodium chloride to adjust the ionic strength, and the other syringe contained the 2,4,6-trinitroanisole and dimethyl malonate solution. In several runs the sodium methoxide concentration was kept constant, and dimethyl malonate concentration in the second syringe was varied. The absorbance change at 545 nm was followed. The reaction kinetics of 2,4,6-trinitroanisole with methoxide ion was followed in the same way at 420 nm without addition of dimethyl malonate. The half-lives were read from the screen of the spectrophotometer, and the rate constants k_{obs} were calculated from the relation $k_{\text{obs}} = 0.693/t_{1/2}$. Each measurement was repeated three times at least. At the same time the initial and final absorbance values were read from the screen and used for calculation of the equilibrium constants.

Kinetics of formation of the mono-adduct IV in the presence of dimethyl malonate was followed by measurement of the absorbance increase at 418 nm using a Zeiss spectrophotometer VSU 2P at 25°C in the same media. The rate constant k_{obs} was determined from the time dependence of $\log(A_{\infty} - A_t)$. Kinetics of transformation of the complex IV into dimethyl 2,4,6-trinitrophenylmalonate anion was followed with the spectrophotometer Zeiss VSU 2P. Dimethyl malonate solution was added to the methanolic solution containing the complex IV and sodium methoxide, and the absorbance decrease was followed at 418 nm. The rate constants k_{obs} were determined from the time dependence of $\log(A_t - A_{\infty})$.

Electronic spectra of the complexes V and VI in methanol were obtained by measurement of absorbances of the reaction mixture within 360 to 580 nm (10 nm intervals) using the Durrum spectrophotometer Model D 110 at the time base 200 ms cm⁻¹. One syringe contained 5 · 10⁻⁵M

2,4,6-trinitroanisole solution with 0.9M dimethyl malonate, the other one contained $3.6 \cdot 10^{-2}$ M sodium methoxide. The initial absorbances corresponded to the complex *V*, whereas the absorbances after 2 s were taken for the complex *VI* (6 to 7 half-lives of the reaction $V \rightleftharpoons VI$). The absorbance values measured after 2 s were corrected with respect to the portion corresponding to the complex *V*. The measured spectra of the mono-adduct *V* and di-adduct *VI* along with that of the anion *IX* are given in Fig. 1.

RESULTS AND DISCUSSION

The reactions taking place in the system containing 2,4,6-trinitroanisole, dimethyl malonate and sodium methoxide are described in Scheme 1. Rates of the individual reaction steps differ considerably, which allowed to follow most reactions separately. The equilibrium of the reaction of dimethyl malonate with methoxide anion is established in a time shorter than 1 ms (ref.⁹). The reactions of 2,4,6-trinitroanisole (*II*) with the anion *I* and methoxide ion giving the complexes *V* and *III* proceed with half-lives of 2 to 40 ms. The mono-adduct *V* is transformed into the di-adduct *VI* with a half-life of 0.2 to 3 s. 2,4,6-Trinitroanisole (*II*) is in equilibrium with the complexes *III*, *V* and *VI*, and it is transformed into the complex *IV* on reaction with methoxide anion and, to a smaller extent, into the anion *IX* via the complex *VII*. Half-lives of these reactions are within 30 s to 10 min. When the equilibrium $II \rightleftharpoons IV$ is established, the transformation of the complex *IV* follows with a half-life of 2 to 7 h giving (through the compounds *II*, *VII* and *VIII*) the final reaction product – anion *IX*.

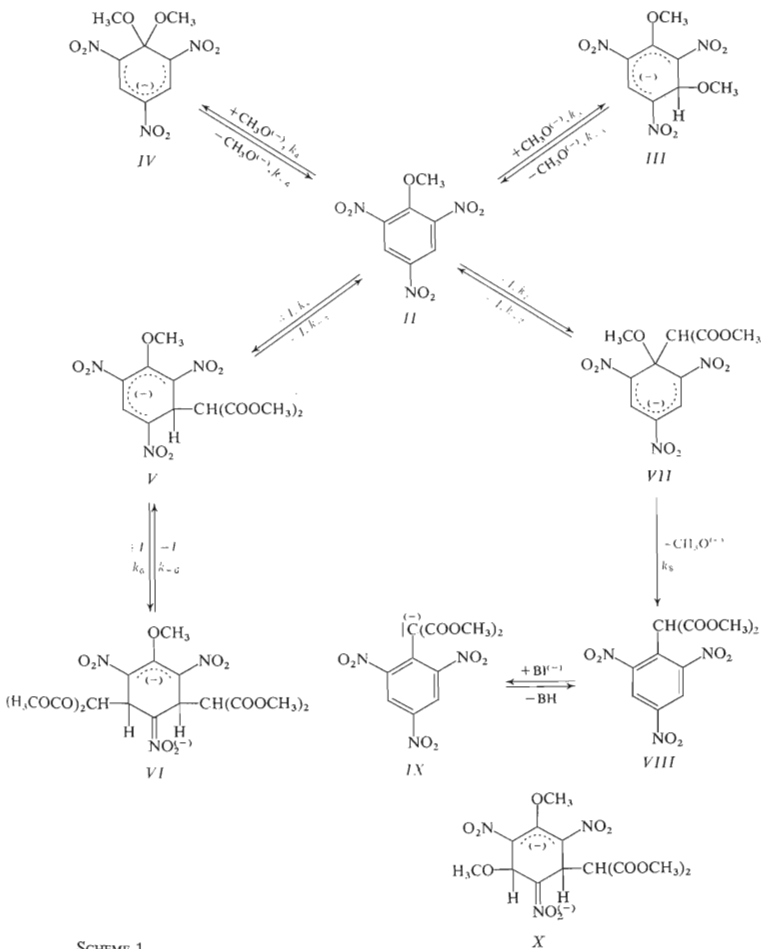
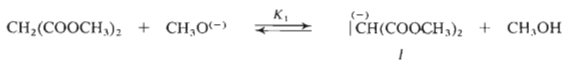
Under the reaction conditions used in methanol the reaction of *II* with methoxide ion giving the complex *III* is insignificant, its equilibrium constant being only $\alpha_3 = 2.71$. (ref.¹³). Thus, in the first phase, only the reaction $I + II \rightleftharpoons V$ takes place. The observed rate constant k_{obs} is given by relation (1).

$$k_{\text{obs}} = k_5[I] + k_{-5} \quad (1)$$

The real concentrations of methoxide ion and anion *I* were calculated from the initial concentrations and the equilibrium constant values $K_1 = 0.5$ (ref.⁶). Dependence of k_{obs} vs concentration of the anion *I* was linear at constant ionic strength. Equilibrium constant of formation of *V* (K_5) is given by Eq. (2)

$$K_5 = [V]/[I][II] = A/(A^T - A), \quad [I] = k_5/k_{-5}, \quad (2)$$

where *A* and *A*^T are the absorbances of the mixtures after reaching the equilibrium and after transformation of all 2,4,6-trinitroanisole into the complex *V*, respectively. In the mixture methanol–dimethyl sulphoxide the formation of the complex *III* is significant, as the equilibrium constant K_3 is far higher in this medium than in methanol (Table I). At the highest methoxide concentrations the ratio $[III]/[II] \sim 0.3$.



SCHEME 1

The equilibrium $II \rightarrow III$ is established faster by about one order of magnitude than the equilibrium $II \rightleftharpoons V$. After the first reaction phase, in which the formation of the complex III is predominant, a steady state is established, and the ratio $[II]/[III]$ remains constant; then the rate constant k_{obs} is defined by Eq. (3).

$$k_{\text{obs}} = k_5[I] \frac{[II]}{[II] + [III]} + k_{-5} = k_5[I] \frac{I}{I + K_3[\text{CH}_3\text{O}^{(-)}]} + k_{-5}. \quad (3)$$

For the calculations of the anion I concentrations the value $K_1 = 1.5$ was used¹⁶. In an experimental series with constant dimethyl malonate concentration and varying methoxide anion concentration the value of the fraction decreases with increasing methoxide concentration, so that the dependence of k_{obs} vs dimethyl malonate anion concentration is not linear. In these cases the values of the constants k_5 and k_{-5} were found by comparison of the measured values k_{obs} with those calculated according to Eq. (3). In the experimental series with constant methoxide concentration ($2 \cdot 10^{-3}\text{M}$) and varying dimethyl malonate concentration the value of the fraction was almost constant, so that the rate constants k_5 and k_{-5} could be determined from the linear dependence k_{obs} vs concentration of I . The values of rate constants k_5 and k_{-5} from the two experimental series are equal within experimental error. The equilibrium constant K_5 was calculated both from the constants k_5 , k_{-5} and from the absorbances according to Eq. (4)

$$K_5 = A/(A^T - A)[I] - K_3[\text{CH}_3\text{O}^{(-)}]/[I], \quad (4)$$

where A and A^T are the absorbances of the equilibrium mixture of the adducts III and V and of the mixture with all 2,4,6-trinitroanisole transformed into the equilibrium mixture of the adducts III and V , respectively. The found rate and equilibrium constants are given in Table I.

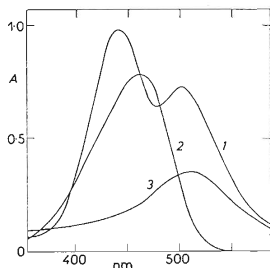


FIG. 1
Electronic Spectra of the Compounds 1 V ,
2 VI and 3 IX (concentrations $5 \cdot 10^{-5}\text{M}$
in methanol)

The rate constant k_{obs} of formation of the di-adduct *VI* from the mono-adduct *V* is defined by Eq. (5).

$$k_{\text{obs}} = k_6 [I] \frac{[V]}{[V] + [II]} + k_{-6} = k_6 [I] \frac{K_5 [I]}{1 + K_5 [I]} + k_{-6}. \quad (5)$$

Out of the constants k_6 , k_{-6} and K_6 the value K_6 was determined first from the absorbance value after reaching the equilibrium. At 540 nm practically only the mono-adduct *V* absorbs, so that the absorbance value corresponds to its concentration (concentration of the complex *III* in the equilibrium mixture is negligible). From the concentration of the mono-adduct *V* and value K_5 the concentration of 2,4,6-trinitroanisole in the reaction mixture was calculated, the rest being the di-adduct *VI*. From the concentrations thus obtained the equilibrium constant K_6 value was calculated ($K_6 = [VI]/[V][I]$). In the reaction solution the equilibrium mixture *II* + *V* is transformed into the di-adduct *VI*. For this case k_{obs} and k_{-6} fulfil the relation (6). The value k_{-6} thus found is introduced into Eq. (5) to give the value k_6 . The obtained values of the rate and equilibrium constants are given in Table I.

$$k_{-6} = k_{\text{obs}} \frac{[V] + [II]}{[V] + [II] + [VI]}, \quad (6)$$

In 20% dimethyl sulphoxide the equilibrium constant of formation of the adduct *V* (K_5) is about five times greater than that in methanol. This increase is caused

TABLE I
Rate and Equilibrium Constants of Formation and Decomposition of the Complexes *V*, *VI* and *III*

$k_5 \cdot 10^{-3}$ l mol ⁻¹ s ⁻¹	k_{-5} s ⁻¹	$K_5 \cdot 10^{-3}$ l mol ⁻¹	$k_6 \cdot 10^{-2}$ l mol ⁻¹ s ⁻¹	$k_{-6} \cdot 10$ s ⁻¹	$K_6 \cdot 10^{-2}$ l mol ⁻¹
A ^a					
29.5 ± 1.0	14.2 ± 0.4	2.09 ± 0.12 ^b 2.10 ± 0.05 ^c	10.0 ± 1.5 ^d 6.5 ± 0.2 ^e	1.1 ± 0.2 ^d 1.1 ± 0.1 ^e	90 ± 10 ^d 57 ± 2 ^e
B ^a					
84 ± 4	7.6 ± 0.2	11.0 ± 0.9 ^b 10.3 ± 0.4 ^c	3.3 ± 0.6 ^d 3.1 ± 0.2 ^e	3.7 ± 0.6 ^d 4.0 ± 0.3 ^e	9.0 ± 1.0 ^d 7.5 ± 0.5 ^e
2.45 ± 0.2 ^g	95 ± 4 ^g	(33 ± 2) · 20 ^{-3g}	2.6 ± 0.1 ^f	4.3 ± 0.2 ^f	6.0 ± 0.3 ^f

^a A methanol, B 20% dimethyl sulphoxide in methanol; ^b calculated from the rate constants k_5 and k_{-5} ; ^c calculated from absorbances; ^d initial methyl malonate concentration 0.09M; ^e 0.18M; ^f 0.36M; ^g for reaction of *II* with CH₃O⁽⁻⁾, k_3 , k_{-3} and K_3 .

by an increase of the constant k_5 and a comparable decrease of the rate constant k_{-5} . Influence of dimethyl sulphoxide on the rate and equilibrium constants is similar to that of the other complexes of aromatic polynitro compounds with negatively charged nucleophiles¹⁷. On the contrary, the equilibrium constant of formation of the di-adduct (K_6) in 20% dimethyl sulphoxide is lower than that in methanol by about one order of magnitude, this decrease being caused by both increase in k_{-6} and decrease in k_6 . Influence of medium on the stability of the di-adduct was studied in the reaction of 1,3,5-trinitrobenzene and sodium ethanthiolate¹⁸, and it was found that the equilibrium constant of formation of the di-adduct in methanol is smaller than that in water by about 3 orders of magnitude. This result was explained by a lower solvation of the negative charge localized at the nitro group between the both sp^3 carbon atoms by methanol. Crampton² supposes dimethyl sulphoxide to be still less favourable for formation of the di-adduct due to a worse solvation of the localized negative charge. This fact was confirmed qualitatively in the case of reaction of 1,3,5-trinitrobenzene with dimethyl malonate anion⁹ and quantitatively in the present paper.

Dimethyl malonate (up to 2% concentration by vol.) has no influence on the rate and equilibrium constants of formation of the mono-adduct *V*. On the other hand, the equilibrium and rate constants of formation of the di-adduct *VI* are affected by dimethyl malonate in the same way as by dimethyl sulphoxide. Influence of medium on the formation of the di-adduct *VI* is, however, quite complicated, as an addition of 5% by vol. benzene in the reaction mixture had no influence on the formation of the di-adduct.

The decrease in the K_6 constant caused by increasing dimethyl malonate concentration was explained by influence of the change of medium. There can be, however, another explanation that a mixed adduct *X* is formed besides the complex *VI*. Its formation in greater amounts is, however, not likely, as nucleophilicity of methoxide ion (towards 3 or 5 position in 2,4,6-trinitroanisole) is lower by several orders of magnitude than that of the anion *I*. We measured the kinetics of formation of di-adduct *VI* at 0.045 and 0.09M dimethyl malonate concentrations and 0.05 and 0.1M methoxide ion concentrations. The changes in dimethyl malonate concentrations are so small that they cannot influence the character of the medium. Roughly it holds that $k_{\text{obs}} = k_6[\text{nucleophile}]$ (almost all trinitroanisole is transformed to the mono-adduct *V*, and the reverse reaction is practically insignificant). The obtained k_{obs} was directly proportional to the anion *I* concentration and independent of $\text{CH}_3\text{O}^{(-)}$ concentration.

Differences in the rate and equilibrium constants of formation of the mono-adducts *III* and *V* are almost the same as those found with the analogous reactions of 1,3,5-trinitrobenzene with methyl malonate anion⁹ and methoxide ion¹³. Although the equilibrium constant K_5 is 6 times smaller than the corresponding equilibrium constant of reaction of 1,3,5-trinitrobenzene with the anion *I*, the equilibrium constant K_6 of formation of the di-adduct is 20 times greater (in methanol) than the corresponding one of the reaction with 1,3,5-trinitrobenzene. (The difference in equilibrium constants of formation of the di-adducts, found at equal concentrations

of methyl malonate, would be smaller, since the equilibrium constant of 1,3,5-trinitrobenzene was measured at 0.7M methyl malonate concentration, its value being decreased with increasing malonate concentration in the reaction mixture.) A similar difference was observed also with the reactions of 1,3,5-trinitrobenzene and 2,4,6-trinitroanisole with sulphite ion¹⁹ and was explained by a decreased sterical interaction between methoxy group and nitro group during formation of the di-adduct¹⁹.

As only small quantities of the anion *IX* are formed in the side reaction (maximum 3% in methanol under the used conditions), the kinetics of transformation of trinitroanisole to the anion *IX* was followed separately starting from a prepared solution of the complex *IV*. The anion *IX* is most stable out of all the substances given in Scheme 1 and represents the final reaction product. The reaction *IV* → *IX* proceeds as pseudomonomolecular, and the observed rate constant k_{obs} is always smaller than k_{-4} by at least one order of magnitude ($k_{-4} = 1.04 \cdot 10^{-3} \text{ s}^{-1}$ and $2.6 \cdot 10^{-4} \text{ s}^{-1}$ in methanol and in 20% dimethyl sulphoxide, respectively²⁰) (Table II). That means that the rate-limiting step must consist either in formation of the mono-adduct *VII* or its decomposition to methyl 2,4,6-trinitrophenylmalonate (*VIII*). In the initial reaction phase (within several minutes) the equilibrium is established between the substances *II*, *IV*, *V* and *VI*, and the experimental rate constant k_{obs} is (after reaching the steady state) defined by Eq. (7). The value $1.7 \text{ m } 10^4 \text{ l mol}^{-1}$ from ref.²⁰ was used for K_4 .

$$k_{\text{obs}} = \frac{1}{1 + K_5[I] + K_5K_6[I]^2 + K_4[\text{CH}_3\text{O}^{(-)}]} \frac{k_7k_8[I]}{k_{-7} + k_8} \quad (7)$$

TABLE II
Rate Constants of Transformation of the Complex *IV* into Product *IX* in Methanol

$[I] \cdot 10^3$	$[\text{CH}_3\text{O}^{(-)}] \cdot 10^3$	$k_{\text{obs}} \cdot 10^5$ s^{-1}	$k_7k_8/(k_{-7} + k_8)^a$ s^{-1}
0.95	11.05	2.8	5.8
0.65	7.35	3.1	6.3
0.30	3.70	3.4	6.8
1.80	10.20	5.2	6.0
1.20	6.80	5.6	6.1
0.60	3.40	6.1	6.2
2.50	9.50	8.1	5.5
1.70	6.30	8.1	5.9
0.80	3.20	8.1	6.3

^a Average value $6.10 \pm 0.12 \text{ s}^{-1}$.

The calculated value of the ratio of the rate constants $k_7k_8/(k_{-7} + k_8)$ is $6 \cdot 10 \pm 0 \cdot 12$ and is about 3 times smaller than the value of the rate constant k_4 .

Transformation of 2,4,6-trinitroanisole (in equilibrium with the complexes *V* and *VI*) to the mono-adduct *IV* is an equilibrium reaction, and the observed reaction constant k_{obs} is defined by Eq. (8). As the complex *IV* is more stable than the complexes *V* and *VI*, it predominates in the reaction mixture after establishing the equilibrium.

$$k_{\text{obs}} = \frac{k_4[\text{CH}_3\text{O}^{(-)}]}{1 + K_5[I] + K_5K_6[I]^2} + k_{-4} \quad (8)$$

Therefore, the rate constant k_{-4} represented maximum 10 to 15% of k_{obs} . The measured values of k_{obs} were compared with the k_{obs} values calculated from Eq. (8). The values from Table I were used for K_5 and K_6 in the calculation, the k_4 values being determined by direct measurement of the reaction of 2,4,6-trinitroanisole with methoxide ion in the absence of malonate ($k_4 = 16 \cdot 5 \pm 0 \cdot 5$ and $44 \pm \pm 21 \text{ mol}^{-1} \text{ s}^{-1}$ in methanol and in 20% dimethyl sulphoxide, respectively). Fendler²⁰ gives the corresponding k_4 values $17 \cdot 3$ and $48 \cdot 0 \text{ l mol}^{-1} \text{ s}^{-1}$. The values of ref.²⁰ were used for k_{-4} . In methanol the agreement between the measured and the calculated k_{obs} values is quite good, however, in 20% dimethyl sulphoxide the found values are in average higher than the calculated ones. This is obviously caused by that the side reaction leading to the anion *IX* was not taken into account in the calculation of k_{obs} . Whereas concentration of the anion *IX* is only 1–3% after the equilibrium $\text{II} \rightleftharpoons \text{IV}$ is established in methanol, in 20% dimethyl sulphoxide the concentration is 5 to 15%, which affects the k_{obs} value considerably.

A good agreement between the measured and the calculated k_{obs} values was obtained only in the experiments having such concentrations of the anion *I* that $[\text{IV}]/[\text{II}] < 0 \cdot 5$ or $[\text{VI}]/[\text{V}] > 3$. Under these conditions the time dependence of $\log(A_\infty - A_t)$ was linear except for the beginning of the reaction (maximum 10%). In the concentration range between the two limits the absorbance change was faster than it should be according to the calculated k_{obs} , the linearity of the time dependence of $\log(A_\infty - A_t)$ being reached at later phases of the reaction. This trend was especially marked in the experiments in 20% dimethyl sulphoxide at the concentration of $[\text{I}] \sim 10^{-3} \text{ M}$ where the time dependence of $\log(A_\infty - A_t)$ was non-linear almost in the whole reaction course. This non-linearity is probably due to accumulation of the complex *VII* in the reaction mixture. The complexes *VII* and *IV* have similar spectra, because they both are complexes of 1 : 1 type. The rate constant k_7 of formation of the complex *VII* is about five times greater than k_4 (ref.²¹). Under the presumption that the equilibrium constant K_7 of formation of *VII* is comparable with K_5 , the experiments having the anion *I* concentration within the two limits exhibit a rapid initial increase of concentration of *VII* and, consequently, a rapid absorbance increase. After reaching steady state ($[\text{VII}]/[\text{II}]$ is not further changed) the logarithmic dependence becomes linear. At low concentrations of the anion *I* the concentration of the compound *VII* is small during the whole reaction course, i.e. it does not affect the absorbance of the reaction mixture. At high concentrations of the anion, on the contrary, most of 2,4,6-trinitroanisole is

transformed into the di-adduct within few seconds, so that concentration of the compound VII is small again and does not affect the absorbance fundamentally.

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