

TABLE II

Proton Chemical Shift,  $\delta H$  (Hz), of the  $\text{CH}_3\text{C}(\text{O})$ -Group and the Absorptivity,  $A$  ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ), of the  $\nu(\text{C}=\text{O})$  Band in the Compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OC}(\text{O})\text{CH}_3$

$n$	$\delta H$	$A^a$	$n$	$\delta H$	$A^a$
1	116.84	500	4	116.10	560 <sup>b</sup>
2	115.20	650	5	116.00	575 <sup>b</sup>
3	116.19	650			

<sup>a</sup> Ref.<sup>34</sup>. <sup>b</sup> These lower values can be interpreted similarly as those for  $(\text{C}_2\text{H}_5\text{O})_2\text{CH}_3\text{Si}(\text{CH}_2)_n$ - ( $n = 4, 5$ ) groups (see ref.<sup>35</sup>).

2-Trimethylsilylethyl methyl ether was obtained<sup>49</sup> by reaction of trimethylsilylmethylmagnesium chloride with chloromethyl methyl ether in ether (43% yield, b.p. 80–82°C/168 Torr,  $n_D^{20}$  1.4001,  $d_4^{25}$  0.7682; ref.<sup>51</sup> b.p. 112.5°C,  $n_D^{20}$  1.4037,  $n_D^{20}$  0.7809).

3-Trimethylsilylpropyl methyl ether was prepared by reaction of 3-trimethylsilylpropyl chloride with sodium methylate in methanol (85% yield, b.p. 142°C,  $n_D^{25}$  1.4095; ref.<sup>52</sup> b.p. 140°C/764 Torr,  $n_D^{20}$  1.4102).

Relative basicity of the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCH}_3$  ( $n = 1-3$ ) was determined from the spectra of hydrogen bonds in the region of LiF prism in NaCl cells (0.1 cm thickness) with a double-beam Zeiss, Model UR-20, spectrophotometer. Phenol (0.02M) was used as a proton donor; the concentration of studied compounds in pure  $\text{CCl}_4$  was 0.1–0.2M. Wavenumbers of absorption band maxima were obtained as an average of three measurements. For  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCH}_3$  ( $n$ ,  $\Delta\nu(\text{OH})$  in  $\text{cm}^{-1}$ ): 1,278; 2,274; 3,264.

Absorptivity of the sample at wavenumber of the  $\text{C}=\text{O}$  stretching vibration (around 1700  $\text{cm}^{-1}$ , LiF prism) was measured for 0.1M solutions of the compounds in  $\text{CCl}_4$  (spectrograde) in 0.01 cm-cells. The values presented are the average of six times recorded maxima for twice prepared 0.1M solutions. Relative experimental error did not exceed 3%.

Chemical shifts of the  $\text{CH}_3\text{C}(\text{O})$  group of the acetates  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OC}(\text{O})\text{CH}_3$  in  $\text{CCl}_4$  were recorded on a modified Tesla BS-477 spectrometer (60 MHz), using TMS as internal reference compound; the accuracy was  $\pm 0.2$  Hz. All esters were used in concentrations of 100 mg of the ester per 1 ml of  $\text{CCl}_4$ .

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## KINETICS OF REACTION OF 2,4-DINITROCHLOROBENZENE WITH METHYL MALONATE, CYANOACETATE AND ACETOACETATE

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Kinetics of reaction of 2,4-dinitrochlorobenzene with methoxide ion and anions of methyl esters of malonic, cyanoacetic and acetoacetic acids have been measured in methanol-dimethyl sulphoxide medium. Ratio of the rate constants in methanol is 1 : 4.8 : 5.2 : 0.022. With increasing dimethyl sulphoxide concentration the rate constant values of reaction of dinitrochlorobenzene with carbanions increase more slowly than those with methoxide ions. Dissociation constants of the starting esters and their 2,4-dinitrophenyl derivatives have been measured in methanol. Influence of dimethyl sulphoxide on electronic spectra of anions of the reaction products is discussed.

So far little attention has been paid to reactions of aromatic compounds with carbanions. Out of the published works the majority deal with reactions of carbanions with aromatic polynitro compounds leading to formation of the Meisenheimer complexes<sup>1</sup>. The extensive monograph<sup>2</sup> by Miller gives not a single case of a nucleophilic aromatic substitution with a carbanion in the role of nucleophile. In recent years several papers appeared dealing with the reactions of dinitrofluorobenzene<sup>3,4</sup> resp. substituted chlorobenzenes<sup>5</sup> with sodium salt of ethyl malonate in polar aprotic solvents leading to formation of aryl malonates.

In this work we have studied the reactions of 2,4-dinitrochlorobenzene with the anions of methyl malonate, cyanoacetate and acetoacetate in methanol and mixture of methanol and dimethyl sulphoxide. The reactions with anions of stronger C-acids proceed too slowly, and in reactions with anions of weaker C-acids the reaction of 2,4-dinitrochlorobenzene with methoxide ion giving 2,4-dinitroanisole predominates. The purpose of the present paper was the determination of reactivity of carbanions in nucleophilic aromatic substitution, comparison with the reactivity of methoxide ion, and determination of the influence of dimethyl sulphoxide on the reaction rate constants and composition of the reaction products.

### EXPERIMENTAL

*Reagents.* Methyl malonate (*Ia*), cyanoacetate (*Ib*), and acetoacetate (*Ic*) were prepared by reesterification of the respective ethyl esters. The ethyl ester (1 mol) was treated with 40 mol methanol and 0.05 mol sodium. After 20 hours standing (10 hours boiling in the case of *Ic*) the methyl esters were isolated by vacuum distillation. The reesterification procedure was repeated

twice in the case of the compound *Ia*. Purity of the compounds was checked by NMR spectroscopy and gas-liquid chromatography. The content of ethyl esters was always below 3%. 2,4-Dinitroanisole was prepared by reaction of 2,4-dinitrochlorobenzene with 1M-CH<sub>3</sub>ONa (10% excess), yield 85%, m.p. 92–93°C (ref.<sup>6</sup> 94°C). Dimethyl sulphoxide, commercial reagent, was dried with calcium oxide and distilled. The other reagents used were commercial chemicals of *p.a.* purity grade.

Methyl 2,4-dinitrophenylmalonate (*Ila*) was prepared by slow dropwise addition of 3.6 ml 5.3M-CH<sub>3</sub>ONa into a stirred solution of 1.92 g (0.01 mol) dinitrochlorobenzene and 1.5 g *Ia* in 20 ml dried dimethyl sulphoxide. After 15 minutes the reaction mixture was diluted with 250 ml water containing 3 ml hydrochloric acid. The aqueous solution was extracted 3 × 150 ml benzene. The benzene extracts were washed with water, dried with sodium sulphate, and benzene was distilled off under reduced pressure. The solid residue was crystallized from tetrachloromethane to give 2 g (66%) white needles melting at 93.5–94°C. For C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>8</sub> (298.2) calculated: 44.30% C, 3.36% H, 9.40% N; found: 44.00% C, 3.21% H, 9.56% N.

Methyl 2,4-dinitrophenylcyanoacetate (*Ilb*) was prepared in the same way as *Ila* from dinitrochlorobenzene and *Ib*. The product was isolated as an oil, yield 70%, and it was purified by chromatography on a silica gel column with benzene as eluent. It was identified by NMR spectrum: the aromatic protons 1.03–2.03τ; ν(CH) = 4.23τ; ν(OCH<sub>3</sub>) = 6.15τ. For C<sub>10</sub>H<sub>7</sub>N<sub>3</sub>O<sub>6</sub> (265.4) calculated: 45.30% C, 2.64% H, 15.85% N; found: 45.10% C, 2.78% H, 15.20% N.

Methyl 2-(2,4-dinitrophenyl)acetoacetate (*Ilc*) was prepared by the same procedure as *Ila* from dinitrochlorobenzene and *Ic*. The product was isolated (60%) in the form of yellowish needles (from chloroform), and it melted at 114.5–116°C. For C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>7</sub> (282.2) calculated: 46.80% C, 3.55% H, 9.93% N; found: 47.10% C, 3.58% H, 10.00% N. Structure of the compound was determined from NMR spectrum: ketonic form ν(CH) = 4.58τ; ν(OCH<sub>3</sub>) = 6.19τ; ν(COCH<sub>3</sub>) = 7.51τ and enol form ν(OH) = –2.98τ; ν(OCH<sub>3</sub>) = 6.36τ; ν(=C–CH<sub>3</sub>) = 8.09τ; the aromatic protons 1.15 to –2.45τ. <sup>1</sup>H-NMR spectra of *Ilb* and *Ilc* were measured in deuteriochloroform with the use of a Tesla BS 487 A apparatus at 80 MHz at the room temperature. Hexamethyldisiloxane was used as internal standard (9.95τ). Values of chemical shift were measured with a universal frequency counter.

*Dissociation constants* of *Ia–c* in methanol were determined by absorbance measurements in sodium methoxide solutions using a Zeiss VSU-2P spectrophotometer at 25°C at the wavelengths 250, 245 and 285 nm. The p*K*<sub>a</sub> values were obtained from Eq. (1)<sup>7</sup> where *J* is the concen-

$$pK_a = pK_s + \log [\text{CH}_3\text{O}^-] + \log J, \quad (1)$$

TABLE I

Dependence of λ<sub>max</sub> (nm) and (log ε) of Compounds *Ila–c* on by Vol. % Dimethyl Sulphoxide in Methanol

% DMSO	<i>Ila</i>	<i>Ilb</i>	<i>Ilc</i>
0	480 (3.93)	474 (4.07)	455 (3.72)
20	488 (4.10)	480 (4.08)	468 (3.79)
40	503 (4.15)	486 (4.09)	481 (3.85)
60	510 (4.21)	490 (4.11)	500 (3.92)
80	518 (4.26)	494 (4.13)	518 (3.99)

tration ratio of non-dissociated and dissociated forms of the compounds *I*.  $pK_S$  (16.916) is the negative logarithm of the ionic product of methanol. The dissociation constants of *Ila*–*c* in methanol were determined in similar way by measurements in acetate and chloroacetate buffers at  $\lambda_{\max}$  of the respective anions *IIla*–*c* (Table I). During the measurement constant concentration of the buffer anion was maintained (0.1M-CH<sub>3</sub>COONa for *Ila* and *Ilc* and 0.02M-ClCH<sub>2</sub>COONa for *Ilb*). Calculation was carried out by the described method<sup>8</sup>; the literature data<sup>9</sup> were used for  $pK_a$ 's of acetic and chloroacetic acids. Influence of medium on spectra of the anions *IIla*–*c* was determined by measuring the spectra with a Unicam SP 800 spectrophotometer in the range 250–650 nm in mixtures methanol–dimethyl sulphoxide, the sodium methoxide concentration being  $5 \cdot 10^{-3}$ M.

*Kinetics of reaction of 2,4-dinitrochlorobenzene with Ia–c and methoxide ion* in mixtures methanol–dimethyl sulphoxide were measured with the Zeiss VSU-2P apparatus at 25°C at  $\lambda_{\max}$  of the anions *IIla*–*c* (Table I) resp. at 300 nm ( $\lambda_{\max}$  of dinitroanisole). 0.2 ml tempered 2,4-dinitrochlorobenzene ( $5 \cdot 10^{-4}$  to  $1 \cdot 10^{-3}$ M) solution was added into 2.3 ml tempered mixture of methanol, dimethyl sulphoxide, *I*, and sodium methoxide in a 1 cm quartz cell. In the kinetic measurements of the reaction of 2,4-dinitrochlorobenzene with sodium methoxide no compound *I* was added. As the other reagents were present in an at least hundredfold excess as compared with dinitrochlorobenzene, the reactions took pseudomonomolecular course, and the rate constants were computed from the relation  $kt = -\log(A_\infty - A_t) + \text{const}$ .

The reaction with *Ia* was followed by the absorbance changes at  $\lambda_{\max}$  of the anion and also at 300 nm (2,4-dinitroanisole). From the found absorbance changes the concentrations of the compounds type *II* and dinitroanisole in the final reaction mixture were computed, and these values were used in determination of the reaction rate constant with malonate anion and equilibrium constant of reaction of malonate anion with methoxide ion in methanol–dimethyl sulphoxide medium.

## RESULTS AND DISCUSSION

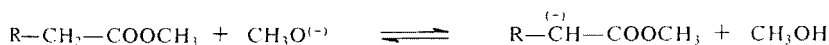
The methoxide-catalyzed reactions of 2,4-dinitrochlorobenzene with C-acids in methanol resp. methanol–dimethyl sulphoxide mixtures are described in Scheme 1. Simultaneously substitution of chlorine by methoxyl group takes place (especially in the reaction with *Ia*), 2,4-dinitroanisole being formed. The neutral primary products *II* are much stronger C-acids than the starting compounds *I* (Table II) and react quickly<sup>3</sup> and practically quantitatively with methoxide ion eventually with anion of *I* to give the carbanion *III*. Structures of *IIa*–*c* were confirmed by NMR spectra measurements of the separately prepared compounds.

Linear dependence (with the slope 1) of logarithm of the ratio carbanion to C-acid ( $\log [C^-]/[CH]$ ) on  $\log [CH_3O^-]$  resp. logarithm of the ratio of the both buffer components (for *IIa*–*c*) was found in the case of determination of the dissociation constants of C-acids *Ib* and *Ic* and *IIa*–*c*; with the malonate *Ia* the measured dependence was linear but up to 0.1M CH<sub>3</sub>O<sup>-</sup>, whereafter the value of its angular coefficient rapidly increased, the ratio of carbanion to C-acid being more than 100 times greater at 1M-CH<sub>3</sub>O<sup>-</sup> than that at 0.1M-CH<sub>3</sub>O<sup>-</sup>. The increase in the slope was far greater than that of other acids measured in this concentration range<sup>10,11</sup>. In other words, value of the ratio carbanion to C-acid increased much more rapidly than it would

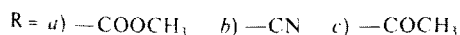
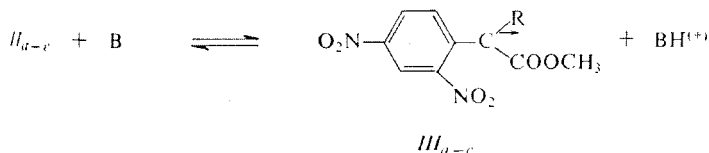
correspond to any of the acidity functions  $H_M$  known by now. This course is due to formation of a complex of the anion *Ia* with sodium ions. We presume that, in this case, structurally similar chelates are formed to those in the reactions of  $\beta$ -dicarbonyl compounds with polyvalent metal cations<sup>12</sup> for the following reasons. The complexes are formed with the anion *Ic* and not with the anion *Ib*. Lithium chloride is more efficient than sodium chloride, the difference being greater than one order of magnitude. The complex formed from magnesium methoxide has practically the same spectrum ( $\lambda$  and absorbance) as those from cations  $Li^+$  resp.  $Na^+$ . The complex of anion *Ic* and  $Na^+$  has the same maximum absorbance as the free anion, but the  $\lambda_{max}$  is shifted towards shorter wavelengths by 2–3 nm. Presuming that the same is true for the compound *Ia*, we calculated  $\log([C^-]/[CH])$  for  $[CH_3O^-] < 0.1M$ , and therefrom we determined the dissociation constant.

Substitution of one hydrogen atom by dinitrophenyl group causes a great increase in acidity of the second hydrogen. The highest and lowest acidity increases are encountered with *Iib* and *Iic*, respectively (Table II). (In methanol about 90% of the compound *Iib* is present in enol form\* so that the real  $pK_a$  of the ketonic form is lower by about unity). The main reason of the different  $\Delta pK_a$  values probably consists in steric hindrance to conjugation which is smallest in the derivative<sup>14</sup> *Iib*.

Shape of spectra of the carbanions *IIIa–c* depends on the content of dimethyl sulphoxide in methanol. Decreasing dimethyl sulphoxide content brings about a hypsochromic shift and lowering of absorbance coefficient (Table I). The found



*Ia–c*



SCHEME 1

\* In deuteriochloroform the content of enol form is 95% (according to NMR spectra), in methanol the enol content is usually slightly lower<sup>13</sup>.

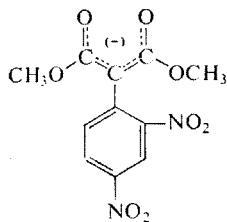
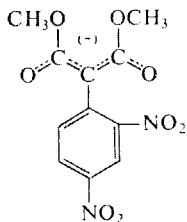
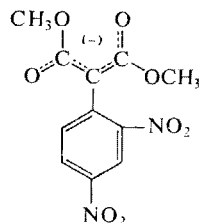
spectral changes of the carbanion *IIIa* are the same as those given<sup>3</sup> for the reaction product of dinitrofluorobenzene with ethyl malonate. In the case of the carbanion *IIIb* influence of solvent on spectrum is similar to that of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienyl anion<sup>15</sup>, and it is probably caused, also in this case, by mutual interaction of dimethyl sulphoxide with the bulky strongly polarized anion. In the case of the carbanions *IIIa* and *IIIc* both the hypsochromic shift and the absorbance decrease are much greater. Gradual addition of lithium chloride has a similar effect on the spectra of *IIIa* and *IIIc* to that of methanol. Lithium cation forms chelates with carbanions *IIIa* and *IIIc*. Carbanion *IIIb* cannot form any chelate and, consequently, addition of lithium chloride has no effect on the spectrum. However, we presume that the big spectral changes observed with *IIIa* and *IIIc* are not caused by gradual transformation of the carbanions into chelates with sodium cations (the reaction mixtures measured contained only the sodium ions added in the form of sodium methoxide), the reasons being as it follows. Concentrations of sodium cations were low ( $5 \cdot 10^{-3}M$ ), and sodium cation was less effective than lithium cation in the formation of chelates, the difference being greater than one order of magnitude. The same changes were observed with *IIIc* when concentration of sodium cations was 10 times higher. The solution of carbanions used for measurements of influence of solvent fulfilled the Lambert-Beer law. Therefore, we take the following explanation for more probable: anions *IIIa* and *IIIc* can exist<sup>16</sup> in three conformations ZZ, EE and EZ. In media containing high dimethyl sulphoxide content negatively charged oxygen atoms of carbonyl groups are slightly solvated and the ZZ conformation is (due to considerable electrostatic repulsion) less advantageous energetically than the other two conformations<sup>17</sup> which absorb at higher wavelength and have greater absorbance coefficient. On the contrary, in chelate the conformation ZZ is stabilized by positively charged metal ion. Increasing methanol concentration brings about gradual solvation of negatively charged oxygen atoms of carbonyl groups by methanol molecules. Thus their mutual repulsion is diminished<sup>16</sup>, and conformation ZZ of the carbanion becomes more populated in the solution<sup>18</sup>. Spectrum of the carbanion in this conformation (with solvated carbonyl groups) resembles that of the chelate.

TABLE II

Dissociation Constants of Compounds *Ia-c* and *IIa-c* in Methanol at 25°C

Compound	$pK_a$	Compound	$pK_a$	$\Delta pK_a$
<i>Ia</i>	$17.22 \pm 0.04$	<i>IIa</i>	$11.5 \pm 0.2$	5.72
<i>Ib</i>	$15.19 \pm 0.02$	<i>IIb</i>	$6.8 \pm 0.1$	8.39
<i>Ic</i>	$14.20 \pm 0.03$	<i>IIc</i>	$10.95 \pm 0.10$	3.35

Formation of the carbanions *III* is a reaction of overall second order, being first order in each dinitrochlorobenzene and anion of C-acid. Formation of the neutral compound *II* is rate limiting. In reaction with the malonate *Ia* considerable substitution of chlorine by methoxyl takes place simultaneously giving dinitroanisole. Spectrum of the reaction mixture contains absorption bands belonging to the both products, and the experimental rate constant is a sum of rate constants of formation of *IIIa* and that of dinitroanisole.

*z,z-IIIa**E,E-IIIa**E,z-IIIa*

Comparison of rate constants of anions of the C-acids *Ia-c* (Table III) with their dissociation constants (Table II) shows a remarkably high reactivity of cyanoacetate *Ib*. A similar increase in reactivity (about 2 orders of magnitude) was observed in correlation of  $\text{p}K_a$  of C-acids with logarithms of rate constants of their reaction with water<sup>19</sup> in the case of the C-acids activated by nitrile groups. Although anions of the C-acids *Ia-c* are weaker bases than methoxide ion, two of them react with dinitro-

TABLE III

Dependence of Rate Constants (1/mol s) of Reaction of 2,4-Dinitrochlorobenzene with Methoxide Ion ( $k$ ) and Anions of *Ia-c* and Dependence of Equilibrium Constant  $K$  (1/mol) of Reaction of Dimethyl Malonate with Methoxide Ion on by Vol. % Dimethyl Sulphoxide in Methanol

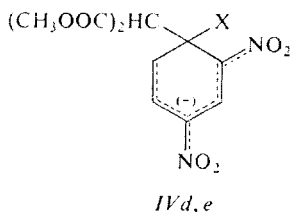
% DMSO	$k^a$	$k_{Ia}$	$K^a$	$k_{Ib}^a$	$k_{Ic} \cdot 10^3$
0	0.023	0.11 ± 0.01	0.5	0.12	0.5 + 0.1
10	0.050	—	—	0.19	—
20	0.114	0.45 ± 0.10	1.5 ± 0.10	0.36	3.1 ± 0.2
40	0.606	0.97 ± 0.15	8.0 ± 2.0	1.00	9.6 ± 0.2
50	1.11	1.70 ± 0.20	22 ± 4	1.49	—
60	3.21	2.60 ± 0.20	130 ± 35	3.61	42.6 + 1.0
70	9.63	—	—	6.70	102 + 3

<sup>a</sup> Where error is not specified it was less than 5%.



chlorobenzene in methanol faster than methoxide ion. Only the anion of acetoacetate *Ic*, which is a weaker base than methoxide ion by 4 orders of magnitude, reacts about 40 times more slowly. Methoxide ion in methanol is strongly bound to three molecules of the solvent<sup>20</sup>. At least one of these solvating methanol molecules must be split off in order that a bond may be formed to C-atom of dinitrochlorobenzene. In the case of the anions of C-acids *Ia-c* negatively charged oxygen atoms event. nitrogen atom are solvated, but the reacting carbon atom is "free". This fact represents obviously the main reason of the higher reactivity of carbanions. With proceeding reaction a new C—C resp. O—C bond is formed, and the negative charge is transferred to the aromatic nucleus. As a consequence the reacting nucleophile is gradually desolvated.

Reaction of the anion *Ia* with dinitroanisole is, according to preliminary experiments, slower than that with dinitrochlorobenzene almost by 3 orders of magnitude. As the methoxyl group activates the nuclear carbon atom to which it is bound, the activation being the same as or even slightly stronger than that by chlorine<sup>21,22</sup>, the rate of formation of the intermediate *IVd* ( $X = \text{OCH}_3$ ) is the same as or somewhat higher than that of *IVe* ( $X = \text{Cl}$ ). It means that decomposition of the intermediate *IVd* is rate limiting, and splitting off of the carbanion is faster than that of methoxide ion by about 3 orders of magnitude.



A partial desolvation of methoxide ion in the activated complex of its reaction with dinitrochlorobenzene is the main reason of the acceleration of this reaction observed when methanol is gradually substituted by dimethyl sulphoxide<sup>23</sup>. In 70% (by vol.) dimethyl sulphoxide the reaction is about 400 times faster than that in methanol. Dependence of  $\log k$  on the acidity function  $H_-$  (ref.<sup>24</sup>) (determined by measurements of dissociation constants of aromatic amines) is linear with the slope 0.72. Also the rate constants of reaction of dinitrochlorobenzene with anions of the C-acids *Ia-c* increase with increasing dimethyl sulphoxide concentration though somewhat more slowly (slope of the dependence  $\log k$  vs  $H_-$  is about 0.5 for *Ia* and *Ib* and about 0.6 for *Ic*). Therefrom it can be deduced that, also in these reactions, formation of the activated complex is accompanied by considerable desolvation of the carbanion.

Although the reactivity of carbanions increases more slowly than that of methoxide ion, the ratio (dinitroanisole)/(III) decreases with increasing dimethyl sulphoxide

concentration, because the equilibrium constant of the reaction of C-acid *I* with methoxide ion considerably increases (Table III). This is obviously true also for weaker C-acids as acetone and cyclohexanone. Therefore, e.g. the observed rate constant of the reaction of arylpyridinium salt with cyclohexanone<sup>25</sup> increases with increasing dimethyl sulphoxide concentration faster than that with methoxide ion.

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