

KINETICS OF REACTION OF 1-CHLORO-2,4,6-TRINITROBENZENE WITH ENOLATE IONS OF 2,4-PENTANEDIONE AND METHYL 3-OXOBUTANOATE

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Reaction of 1-chloro-2,4,6-trinitrobenzene (*I*) with anions of 2,4-pentanedione (*II*) and methyl 3-oxobutanoate (*III*) produces 3-(2,4,6-trinitrophenyl)-2,4-pentanedione (*IV*) and methyl 2-(2,4,6-trinitrophenyl)-3-oxobutanoate (*V*), respectively, besides 2,4,6-trinitrophenol (*VI*). Amount of 2,4,6-trinitrophenol decreases with increasing amount of dimethyl sulphoxide and 2,4-pentanedione in methanol. A mechanism of formation of 2,4,6-trinitrophenol is suggested. Rate constant of formation of 3-(2,4,6-trinitrophenyl)-2,4-pentanedione in methanol-dimethyl sulphoxide mixtures increases with increasing content of dimethyl sulphoxide and decreases with increasing LiCl concentration. In methanol, 1-chloro-2,4,6-trinitrobenzene reacts with anion of 2,4-pentanedione about $20 \times$ slower than with anion of methyl 3-oxobutanoate.

The study¹ of structure of the Meisenheimer complexes formed by reaction of ambident anions of ketones and diketones only revealed attack by enolate carbon atom in all the cases. Only recently it has been found that reaction of 1-methoxy-2,4,6-trinitrobenzene with phenoxide ion in aqueous dimethyl sulphoxide produces a complex in which phenol is bound by oxygen at 1 position of cyclohexadienide ion². Products of attack by enolate carbon atom were also isolated^{3,4} from reaction mixtures after reactions of 1-halogeno-2,4-dinitrobenzenes or 1-halogeno-2,4,6-trinitrobenzenes with ambident anions. Only small extent of attack by enolate oxygen atom is observed⁵ in substitutions of halogens of aromatic halogenonitro compounds, *e.g.* the reaction of 1-chloro-2,4-dinitrobenzene with potassium salt of ethyl acetoacetate involves 5% and 3% of the O-attack in dimethyl sulphoxide and 1,2-dimethoxyethane, respectively. Moreover, the O-arylation product was unstable and underwent solvolysis during all attempts of isolation⁵. Its formation and structure were proved⁵ by ¹H NMR spectra of the reaction mixtures only.

The aim of the present communication is to study kinetics of reaction of anions of 2,4-pentanedione and methyl 3-oxobutanoate with 1-chloro-2,4,6-trinitrobenzene in methanol and its mixtures with dimethyl sulphoxide and to find the extent to which the attack by enolate oxygen atom makes itself felt besides the attack by carbon atom.

EXPERIMENTAL

The ^1H NMR spectra were measured with a Tesla BS 487 B spectrometer at 80 MHz using hexamethyldisiloxane as internal standard.

1-Chloro-2,4,6-trinitrobenzene (I) was purified by repeated crystallization from methanol. M.p. 82–83°C, ref.⁶ 83°C. Methyl 3-oxobutanoate and 2,4-pentanedione were twice rectified.

3-(2,4,6-Trinitrophenyl)-2,4-pentanedione (IV): Solution of 1 g (4 mmol) 1-chloro-2,4,6-trinitrobenzene in 8 ml (78 mmol) 2,4-pentanedione was treated with mixture of 8 ml (78 mmol) 2,4-pentanedione and 8 ml 1M sodium methoxide (8 mmol). After several minutes, the red solution was acidified with 4 ml 2.5M-HCl and extracted with 2×100 ml benzene. The benzene extract was washed with water and dried with sodium sulphate, and the solvent was distilled off. The excess of 2,4-pentanedione was distilled off *in vacuo* from water bath. The raw product was purified by column chromatography (silica gel; chloroform-ethyl acetate 1 : 1). The evaporation residue was recrystallized from benzene-tetrachloromethane mixture. Yield 1.13 g, m.p. 126 to 127°C. ^1H NMR spectrum and elemental analysis of the product shows that it is a solvate containing 1 molecule CCl_4 per 3 molecules IV. For $3\text{C}_{11}\text{H}_9\text{N}_3\text{O}_8 \cdot \text{CCl}_4$ calculated: 37.39% C, 2.49% H, 11.51% N; found: 37.14% C, 2.41% H, 11.93% N. Drying of the solvate at 100°C at 2 kPa for several hours gave 0.99 g (76%) compound IV, m.p. 133–135°C (decomposition). For $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_8$ (311.2) calculated: 42.45% C, 2.92% H, 13.50% N; found: 42.88% C, 3.06% H, 13.42% N. ^1H NMR spectrum (CDCl_3 , 40°C): $\delta(\text{OH}) = 16.50$ (1 H, broadened singlet), $\delta(\text{Ar}) = 8.85$ (2 H, singlet), $\delta(\text{CH}_3) = 1.89$ (6 H, singlet).

Methyl 2-(2,4,6-trinitrophenyl)-3-oxobutanoate (V): Solution of 4.95 g (20 mmol) 1-chloro-2,4,6-trinitrobenzene and 3.5 g (30 mmol) methyl 3-oxobutanoate in 40 ml dimethyl sulphoxide was stirred and treated with 20 ml 2M sodium methoxide (40 mmol) added drop by drop. After 15 min, the solution was diluted with 500 ml water, acidified with 6 ml conc. hydrochloric acid, and extracted with 3×300 ml benzene. The benzene extract was dried with sodium sulphate, and the solvent was distilled off. The raw product was crystallized twice from benzene-tetrachloromethane mixture. Yield 2.95 g (45%), m.p. 137–139°C. For $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_9$ (327.2) calculated: 40.38% C, 2.77% H, 12.84% N; found: 40.17% C, 2.76% H, 12.88% N. ^1H NMR spectrum (CDCl_3 , 25°C): $\delta(\text{OH}) = 12.99$ (1 H, broadened singlet), $\delta(\text{Ar}) = 8.88$ (2 H, singlet), $\delta(\text{OCH}_3) = 3.68$ (3 H, singlet), $\delta(\text{CCH}_3) = 1.81$ (3 H, singlet).

Kinetic measurements: The reactions were followed spectrophotometrically with a Unicam SP 800 apparatus. One drop of benzenic solution of compound I (0.1 mol l^{-1}) was added to 2 ml methanolic solution of 2,4-pentanedione and sodium methoxide in a glass cell, and spectra of the mixture were measured in the region 300–650 nm. In methanolic solutions the compound I undergoes slow methanolysis to 1-methoxy-2,4,6-trinitrobenzene. The kinetic experiments were carried out with a Zeiss VSU 2P apparatus at 25°C: One drop of benzenic solution of the compound I (0.1 mol l^{-1}) was added to 2 ml tempered solution containing $2.5 \cdot 10^{-3}$ to $5 \cdot 10^{-2} \text{ mol l}^{-1}$ sodium methoxide and 0.5 to 1.5 mol l^{-1} 2,4-pentanedione in methanol or its mixture with dimethyl sulphoxide (10, 20 or 30% v/v dimethyl sulphoxide). At definite time intervals absorbance was measured at 540 nm (in methanol and in 10% v/v dimethyl sulphoxide in methanol) and at 550 nm (in the other solutions). The rate constants k_{obs} were calculated from the relation $k_{\text{obs}} = -2.3 \log (A_{\infty} - A_t) + \text{const}$. In the same way the reaction rate was measured in methanol in the presence of LiCl (up to 0.125M-LiCl). The reaction of methyl 3-oxobutanoate with the compound I in methanol was followed in the same way at sodium methoxide concentrations from $5 \cdot 10^{-3}$ to $2.5 \cdot 10^{-2} \text{ mol l}^{-1}$ at concentrations of ester III from 0.5 to 1.5 mol l^{-1} at analytical wavelength 570 nm.

Estimation of amounts of 3-(2,4,6-trinitrophenyl)-2,4-pentanedione (IV) and 2,4,6-trinitrophenol (VI): 20 μ l 0.1M solution of *I* was added to 2 ml tempered solution of *II* and sodium methoxide in methanol or methanol–dimethyl sulphoxide. Absorbance of anion of compound *IV* was measured at 500 nm after at least 10 half-lives of the substitution reaction taking place at the given conditions. Then the solution was acidified with 0.1 ml acetic acid, and absorbance of anion of phenol *VI* was measured at 400 nm. Absorbances of pure compound *IV*, its anion, and anion of phenol *VI* at the mentioned wavelengths were determined with the use of 10^{-2} M solution of compound *IV* and 10^{-3} M solution of phenol *VI*. The same procedure was used for determination of product composition in reactions of methyl 3-cyobutanoate.

Dissociation constant of the compound IV was determined by measurement of absorbances of its anion at 460 nm in a series of 11 methanolic acetate buffers (25°C, ionic strength 0.1) and in $2 \cdot 10^{-2}$ M sodium methoxide; absorbance of the non-dissociated compound *IV* was measured in methanolic 0.25M-HCl. The pH values were calculated from composition of the buffers and pK_a of acetic acid in methanol ($pK_a = 9.52$, ref.⁷). The pK_a value of compound *V* was determined in the same way at the wavelength 485 nm.

RESULTS AND DISCUSSION

The main product of the substitution reaction of 1-chloro-2,4,6-trinitrobenzene (*I*) with anion of 2,4-pentanedione (*II*) is 3-(2,4,6-trinitrophenyl)-2,4-pentanedione (*IV*). The ¹H NMR spectra showed that the compound *IV* in dimethyl sulphoxide solutions exists exclusively as enol form. The side product, 2,4,6-trinitrophenol (*VI*),

TABLE I

Rate constants k_2 ($1 \text{ mol}^{-1} \text{ s}^{-1}$) of reaction of 1-chloro-2,4,6-trinitrobenzene with anion of 2,4-pentanedione (*II*) and content of 3-(2,4,6-trinitrophenyl)-2,4-pentanedione (*IV*) in the reaction products after reaction in methanol and methanol–dimethyl sulphoxide mixtures at 25°C

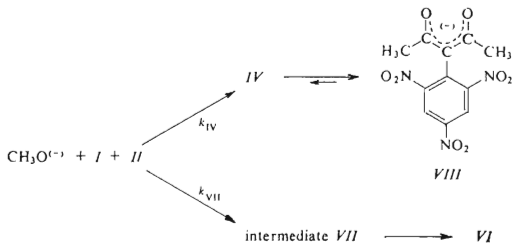
Medium ^a	[<i>II</i>]	[CH ₃ ONa] · 10 ³	% <i>IV</i>	$k_2 \cdot 10^2$ ^b
A	0.5	2.5–50	56 ± 3	6.9 ± 0.1
	1.0	10–35	65 ± 2	7.1 ± 0.2
	1.5	15–45	73 ± 2	7.4 ± 0.1
B	0.5	5–40	86 ± 5	14.6 ± 0.6
	1.0	15–30	82 ± 4	15.3 ± 0.5
	1.5	12.5–30	85 ± 3	18.0 ± 0.5
C	0.5	7.5–30	95 ± 2	26.4 ± 0.9
	1.5	3.5–23.5	96 ± 3	33.0 ± 1.8
D	0.5	5–27.5	94 ± 2	52.8 ± 2.1
	1.0	5–20	95 ± 2	73.1 ± 5.8

^a Methanol (A), 10% v/v dimethyl sulphoxide in methanol (B), 20% v/v dimethyl sulphoxide (C), 30% v/v dimethyl sulphoxide (D); ^b $k_2 = k_{\text{obs}} \cdot \% IV / [\text{CH}_3\text{ONa}] \cdot 100$.

was determined spectrophotometrically in washing water from preparation of compound *IV*, and it was found that less than 1% of compound *I* is converted to the phenol *VI* under the conditions of preparation. Also the amount of 1-methoxy-2,4,6-trinitrobenzene (formed by reaction of the substrate *I* with methoxide ion) in raw compound *IV* was less than 1% (1-methoxy-2,4,6-trinitrobenzene was determined spectrophotometrically after transformation to the respective Meisenheimer complex by action of methoxide ion).

The kinetic experiments were carried out with molar ratios of the substrate *I* to 2,4-pentanedione 1 : 500 to 1 : 1 500 in $2.5 \cdot 10^{-3} \text{ M}$ to $5 \cdot 10^{-2} \text{ M}$ sodium methoxide. Under these conditions the amount of 1-methoxy-2,4,6-trinitrobenzene formed was below 1% again, but the amount of phenol *VI* produced in methanol was 27 to 44% (Table I). Proportion of phenol *VI* in reaction products decreased with increasing content of 2,4-pentanedione in the reaction mixtures. In methanol-dimethyl sulphoxide mixtures the proportion of phenol *VI* decreased as low as to 5% (30% v/v dimethyl sulphoxide).

The course of the reactions studied in the wavelength region $\lambda > 450 \text{ nm}$ showed exponential absorbance increase,* which corresponds kinetically to a one-step pseudomonomolecular reaction. In the wavelength region 360–420 nm the absorbance increase showed a mildly S-shaped course characteristic for consecutive reactions. This finding is explained by Scheme 1.



SCHEME 1

* At $\lambda > 450 \text{ nm}$ practically the only absorbing species is anion of compound *IV*, because sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide is present in negligible amount. At the lowest used concentration of dione *II* (0.5 mol l^{-1}) a small amount of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide is formed. As absorbance coefficient of this Meisenheimer complex (formed in a consecutive reaction) is about 15 times greater than that of compound *IV*, the kinetic measurements were carried out at 540 nm where the Meisenheimer complex does not absorb practically.

The rate constant k_{obs} measured at 540 nm is a sum of rate constants of formation of product *IV* (k_{IV}) and formation of the intermediate *VII* (k_{VII}) (Eq. (1)). The both side reactions are of the same order (*i.e.* first order in substrate *I* and first order in anion of 2,4-pentanedione), and hence also the summary reaction is first order in each component and shows pseudomonomolecular course under the used experimental conditions.

$$k_{\text{obs}} = k_{\text{IV}} + k_{\text{VII}} \quad (1)$$

2,4-Pentanedione is a relatively strong acid ($\text{p}K_{\text{a}} = 13.25$ in 1 mol l^{-1} methanolic solution⁸), hence concentration of its anion in the reaction mixture is practically equal to concentration of added sodium methoxide. The dependence k_{obs} vs concentration of anion of compound *II* and proportion of compounds *IV* and *VI* in products were used for calculation of the rate constants k_2 of formation of product *IV* (Table I).

Increasing dimethyl sulphoxide content in the reaction mixtures results in rapid increase of k_2 values (Table I). The k_2 values also increase with 2,4-pentanedione concentration, which is probably connected with decrease of concentration of methanol which is able to solvate the anion of compound *II*. This effect is the more distinct the higher is concentration of dimethyl sulphoxide. Above 30% v/v dimethyl sulphoxide concentration, formation of the Meisenheimer complex of compound *I* with enolate anion of dione *II* begins to make itself felt markedly, so the kinetic measurements were not carried out in these media.

The results are described in Scheme 2. In the first step the substrate *I* reacts with anion of compound *II* to give the product *IV*. The latter splits off the proton practically immediately ($\text{p}K_{\text{a}} = 9.74$) to give the anion *VIII* — the final reaction product. At the same time the substrate *I* reacts with anion of *II* to give the intermediate *VII* which, on reaction with methoxide ion or other nucleophiles,

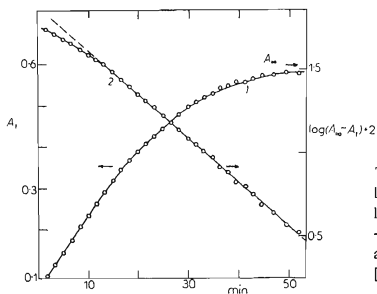
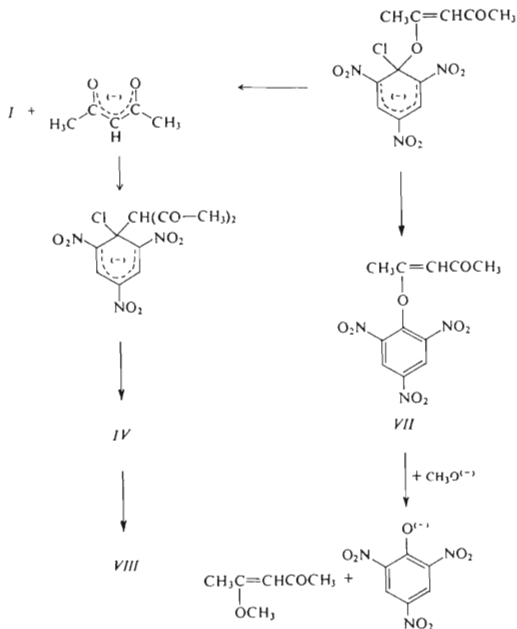


FIG. 1

Time dependence of absorbance A_t 1 or $\log(A_{\infty} - A_t) \cdot 2$ measured at the wavelength 390 nm in the reaction of 1-chloro-2,4,6-trinitrobenzene ($10^{-3} \text{ mol l}^{-1}$) with anion of 2,4-pentanedione ($10^{-2} \text{ mol l}^{-1}$), $[II] = 0.5 \text{ mol l}^{-1}$ in methanol at 25°C

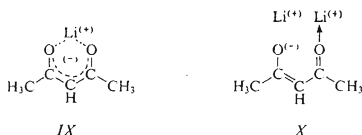


SCHEME 2

produces 2,4,6-trinitrophenoxide ion and 4-substituted 3-penten-2-one. The reaction of intermediate VII with methoxide anion should give 4-methoxy-3-penten-2-one. The reaction of the intermediate VII with nucleophiles is faster than formation of VII, because time dependence of the absorbance at 390 nm (Fig. 1) has only slightly S-shaped character, and it changes soon to exponential dependence. The rate constant k_{obs} determined from this exponential dependence is the same as k_{obs} found for the summary reaction of the substrate I with anion of compound II by the measurement at 540 nm. However, the suggested mechanism could not be confirmed by isolation of 4-methoxy-3-penten-2-one (or, at least, its identification by ^1H NMR), because this compound is formed in the amount less than 1% under the conditions of preparation.

The content of phenol *VI* in products decreases with increasing concentration of aprotic solvent (dimethyl sulphoxide, 2,4-pentanedione) in the mixtures with methanol, the effect of dimethyl sulphoxide being larger. This fact is obviously due to a combined effect of solvent on proportion of conformers of 2,4-pentanedione anion and their solvation and/or on formation of ion pairs.

We also studied the reaction of 1-chloro-2,4,6-trinitrobenzene with 2,4-pentanedione in the presence of lithium chloride. The cation Li^+ forms two types of complexes with anion of *II*. At lower Li^+ concentrations in methanolic solutions the predominant complex *IX* contains one Li^+ cation per one anion of *II*, the respective equilibrium constant of formation being $K_1 = 630 \text{ l mol}^{-1}$ (ref.⁹), whereas at higher Li^+ concentrations the predominant complex *X* contains two Li^+ cations per one anion of *II* ($K_2 = 1.1 \cdot 10^3 \text{ l}^2 \text{ mol}^{-2}$; ref.¹⁰).



The presence of Li^+ in the reaction mixture should affect both the reactivity of enolate ion of compound *II* and proportion of reaction products of this ion with the substrate *I*. Table II gives the results obtained. Against expectation (*i.e.* preference of attack by carbon atom of the enolate ion as a consequence of the oxygen atoms

TABLE II

Effect of LiCl on the product composition and rate of reaction of 1-chloro-2,4,6-trinitrobenzene with anion of 2,4-pentanedione ($\text{C}_5\text{H}_7\text{O}_2\text{Na}$) in methanol at 25°C , $[\text{II}] = 0.5$, $[\text{CH}_3\text{O}^-] = 4 \cdot 10^{-2}$

$[\text{LiCl}] \cdot 10^2$ ^a	$[\text{C}_5\text{H}_7\text{O}_2\text{Na}] \cdot 10^2$ ^b	% <i>IV</i>	$[\text{IX}] \cdot 10^2$	$k_{\text{obs}} \cdot 10^3, \text{s}^{-1}$	$k_{\text{cal}} \cdot 10^3, \text{s}^{-1c}$
2.5	17.0	57	2.05	1.30	1.12
5.0	7.0	51	3.15	0.54	0.55
7.5	3.2	46	3.30	0.31	0.31
10.0	1.9	44	3.20	0.23	0.22
12.5	1.3	46	3.05	0.19	0.18

^a Analytical concentration of LiCl ; ^b effective concentration of free anion of compound *II*; ^c the calculated rate constant.

being bonded to Li^+ ion)¹¹, the proportion of phenol *VI* among the reaction products increased in the presence of Li^+ . With increasing Li^+ concentration the substitution reaction rate decreases. The found dependence k_{obs} vs $[\text{Li}^+]$ can be explained by the substrate *I* reacting with free enolate ion and with complex *IX*. The best agreement between the measured (k_{obs}) and calculated (k_{cal}) values of the rate constants was reached, when we used for the reaction of substrate *I* with free enolate ion of *II* the rate constant value $k = 6.5 \cdot 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$, and for that with complex *IX* the rate constant value $k = 3 \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ and the value $K_1 = 300 \text{ l mol}^{-1}$ instead of the value $K_1 = 630 \text{ l mol}^{-1}$ given in ref.⁹. Table II gives the measured values of rate constants along with the calculated ones.

The reaction of 1-chloro-2,4,6-trinitrobenzene with anion of methyl 3-oxobutanoate (*III*) was studied in methanol only. The reactions are too fast in mixtures methanol-dimethyl sulphoxide, and formation of the Meisenheimer complexes becomes significant at lower concentrations of dimethyl sulphoxide as compared with the reactions of 2,4-pentanedione. The main reaction product is enol form of methyl 2-(2,4,6-trinitrophenyl)-3-oxobutanoate (*V*). Besides, 2,4,6-trinitrophenol is formed, its amount being, however, less than that from 2,4-pentanedione reaction. The smaller amount of phenol *VI* in products can be connected with smaller tendency of methyl 3-oxobutanoate to form enol. The reaction of substrate *I* with dimethyl malonate (which produces almost no enol form) was found⁴ to give no phenol *VI*.

The amount of phenol *VI* formed in reaction of substrate *I* with anion of *III* decreases with increasing concentration of *III* in reaction mixture (Table III). Dependence of rate of formation of product *V* on $[\text{CH}_3\text{O}^-]$ (and, hence, on concentration of anion of compound *III*) is linear in the whole range investigated (Table III). The average bimolecular rate constant $k_2 = 1.26 \text{ l mol}^{-1} \text{ s}^{-1}$ is almost 20 times greater than that of analogous reaction of anion of compound *II* ($k_2 = 6.9 \cdot 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$), although methyl 3-oxobutanoate is a 10 times stronger acid than 2,4-pentanedione (Table IV). It would be more correct to consider only the acidity of keto forms in the calculation. The keto form of 2,4-pentanedione is about 40 times more acidic than that of methyl 3-oxobutanoate (the keto form content of *II* and *III* in methanol is 26% and 94%, respectively¹²), hence $\Delta \log k_2$ is smaller than $\Delta \text{p}K_{\text{a}}$ of the keto forms, which agrees with general relations between basicity and reactivity of nucleophiles.

Table IV gives $\text{p}K_{\text{a}}$ values of the C-acids whose $\text{S}_{\text{N}}\text{Ar}$ reactions were studied and $\text{p}K_{\text{a}}$ values of products of the respective substitution reactions with 1-chloro-2,4-dinitrobenzene³ and 1-chloro-2,4,6-trinitrobenzene⁴. The substitution causes the greatest and the smallest acidity increases in methyl cyanoacetate and 2,4-pentane-

* The value $K_1 = 630 \text{ l mol}^{-1}$ given in ref.⁹ seems to be too high also for the reason that in its calculation the used value of $\text{p}K_{\text{a}}$ of 2,4-pentanedione was 11.78, whereas the $\text{p}K_{\text{a}}$ value found by us⁸ is 13.25 ± 0.1 .

dione, respectively. Obviously the decisive factor affecting acidity is steric hindrance to resonance which is most significant in the reaction product from 2,4-pentanedione. This explanation is supported by electronic spectra of the substitution products of the substrate *I* with carbanions. The absorption coefficient of long-wave band of anion of compound *IV* is small ($\epsilon \sim 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$), which is usual in systems suffering from steric hindrance of resonance¹³. The same bands are 2 and 6 times more intensive in spectra of anion of compound *V* and anion of dimethyl (2,4,6-trinitrophenyl) malonate, respectively. The ΔpK_a values of the C-acids and their α -(2,4,6-trinitrophenyl) derivatives increase in the same order.

TABLE III

Rate constants k_2 ($\text{l mol}^{-1} \text{ s}^{-1}$) of reaction of 1-chloro-2,4,6-trinitrobenzene and anion of methyl 3-oxobutanoate (*III*) and content of methyl 2-(2,4,6-trinitrophenyl)-3-oxobutanoate (*V*) in methanol at 25°C

[<i>III</i>]	[CH ₃ ONa] · 10 ³	% <i>V</i>	k_2^a
0.5	5–25	87 ± 4	1.23 ± 0.12
1.0	5–20	91 ± 5	1.17 ± 0.10
1.5	5–20	94 ± 5	1.36 ± 0.10

$$^a k_2 = k_{\text{obs}} \cdot \% V / [\text{CH}_3\text{ONa}] \cdot 100.$$

TABLE IV

pK_a values of C-acids (A) and of products of their substitution reactions with 1-chloro-2,4-dinitrobenzene (B) and 1-chloro-2,4,6-trinitrobenzene (C) in methanol at 25°C

C-acid	A ^a	B ^a	C
Dimethyl malonate	17.22	11.50	8.50 ^b
Methyl cyanoacetate	15.19	6.80	—
<i>III</i>	14.20	10.95	9.26
<i>II</i>	13.25	—	9.74

^a Ref.³; ^b ref.⁴.

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