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

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Reaction rates of 1,3,5-trinitrobenzene (*I*) with anions of acetone, cyclohexanone, methyl aceto-acetate, cyanoacetate and malonate have been measured in methanol. Stability of the Meisen-heimer complexes formed decreases with increasing acidity of the C-acids. In the case of the reaction products of *I* with acetone, cyclohexanone and methyl acetoacetate the rates of the subsequent cyclizations have been measured. The complexes formed in the reactions of *I* with methyl cyanoacetate and malonate react reversibly with a second molecule of the carbanion to give di-adducts, rate of this reaction being lower than that of the reaction of the carbanion with *I* by more than 2 orders of magnitude. The complexes of *I* with methyl cyanoacetate and aceto-acetate anions are stronger acids than the starting C-acids, and they split off the proton from α-carbon atom to form dianions. The rate of C—H bond splitting measured with the aceto-acetate complex is about 100times smaller than with methyl acetoacetate itself.

1,3,5-Trinitrobenzene (*I*) reacts[1,2] with negatively charged bases to give intensively coloured Meisenheimer complexes *II* which, in some cases, form di-adducts *III* with a further molecule of the base (Eq. (*A*)). If the complex of *I* with carbanion has at least one proton at C$_γ$, a base-catalyzed cyclization can take place giving the compound[1,3] *IV* (Eq. (*B*)). The purpose of this work was to study the kinetics and mechanism of reactions of *I* with anions of methyl cyanoacetate (*Va*), malonate (*Vb*) and acetoacetate (*Vc*) in methanol. In contrast to weaker C-acids, in this case it is possible to determine the carbanion concentration in reaction mixture and calculate rate constants of their reactions with *I* resp. with the complex *II*. Reaction kinetics of *I* with acetone (*Vd*) and cyclohexanone (*Ve*) and kinetics of consecutive cyclization of complexes *IId, IIe* were also studied for comparison. In literature preparation and identification of complexes *IId* and *IIe* are described[4,5] as well as consecutive cyclization and isolation of the products *IVd* and *IVe* (ref.[6,7]) and the reaction kinetics of *I* with *Vd* and *Ve* (ref.[8,9]). Cyclization kinetics was studied[10] only for the reaction of *I* with dibenzylketone in dimethyl sulphoxide catalyzed by triethylamine. In the reaction of *I* with ethyl acetoacetate it was possible to prove spectrometrically (electronic spectra) the formation of a complex type *II*, but only the final reaction product (*IV*) could be isolated[6]. Reactions of *I* with *Va* and *Vb* have not yet been studied. Formation of the di-adduct *III* was proved in reactions of *I* with CH$_3$O$^-$ (ref.[11]),

$C_2H_5S^-$ (ref.[12]) and SO_3^{2-} (ref.[13]), and rate of its formation was measured[14,15] in reactions with OH^-, CH_3O^- and SO_3^{2-}. Formation of di-adduct has not yet been observed in reactions of *I* with carbanions.
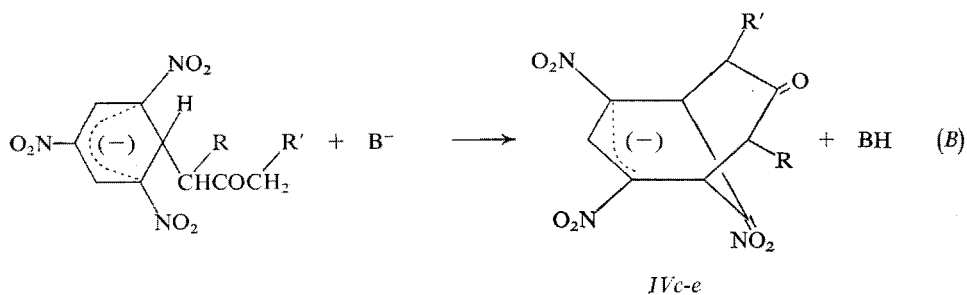

$$I + A^- \rightleftharpoons IIa\text{-}e \rightleftharpoons IIIa\text{-}e \qquad (A)$$
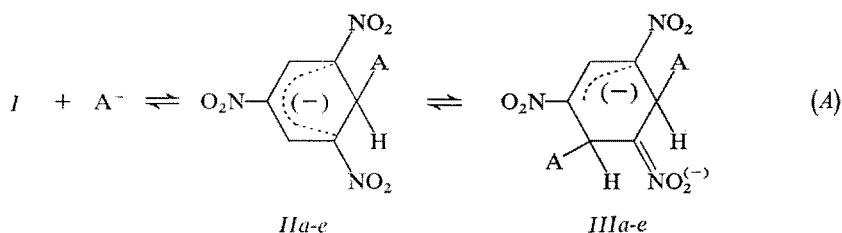
IIa, A = $NCCH_2CO_2CH_3$ *IIc*, A = $CH_3COCH_2CO_2CH_3$
IIb, A = $CH_3CO_2CH_2CO_2CH_3$ *IId*, A = CH_3COCH_3 *IIe*, A = $OC(CH_2)_5$

$$IVc\text{-}e + BH \qquad (B)$$

IVc, R = CO_2CH_3, R′ = H
IVd, R = R′ = H
IVe, R = R′ = $(CH_2)_3$

$$IIc\text{-}e + CH_3O^- \rightleftharpoons VIc\text{-}e \longrightarrow IVc\text{-}e \qquad (C)$$
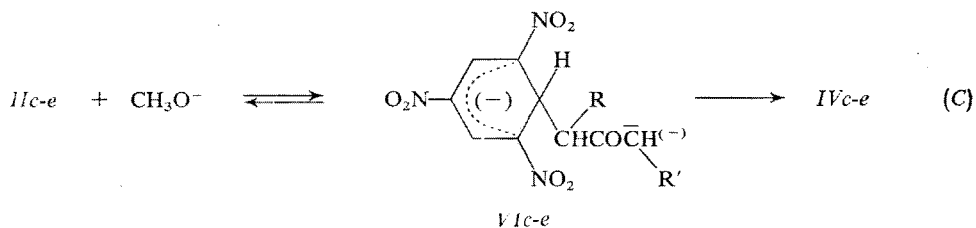
VIc, R = CO_2CH_3, R′ = H
VId, R = R′ = H
VIe, R = R′ = $(CH_2)_3$

EXPERIMENTAL

1,3,5-Trinitrobenzene was prepared by oxidation of trinitrotoluene and decarboxylation of the trinitrobenzoic acid formed[16]. After crystallization from acetic acid and ethanol it melted at 122 to

123°C (ref.[16] 121—122°C). Methyl cyanoacetate (*Va*) and malonate (*Vb*) were prepared by the method described in ref.[17]. Commercial cyclohexanone was rectified, the fraction boiling within 152—154°C was shaken several times with about 10% K_2CO_3, dried with solid K_2CO_3 and redistilled; the middle fraction was used for kinetic measurements. Dimethyl sulphoxide was dried with CaO, distilled *in vacuo*, and kept over molecular sieves. The other reagents used were of *p.a.* purity grade.

Meisenheimer complexes for NMR spectra measurements: Mixture of 0·5 g *I* (2·35 mmol) and 0·25 g (2·5 mmol) methyl cyanoacetate in 10 ml methanol was treated with 2 ml 1M-CH_3ONa (2 mmol), and the reaction mixture was poured immediately into about 200 ml anhydrous ether. The dark red precipitate of the complex *IIa* was collected by suction, washed with ether, dried in a desiccator, and dissolved in dimethyl sulphoxide. The complex *IIb* was prepared in the same way using two mols of *IIb* for one mol of *I*. The di-adduct *IIIa* was prepared by mixing 4 ml 1M-CH_3ONa (4 mmol) with solution of 0·43 g (2 mmol) *I* and 0·8 g (8 mmol) methyl cyanoacetate in 10 ml methanol. By precipitation with ether 0·83 g dark red powder was obtained. The dianion *VIa* was obtained in the same way from 0·43 g (2 mmol) *I*, 0·2 g (2 mmol) methyl cyanoacetate and 4 ml 1M-CH_3ONa (4 mmol); yield 0·73 g of a dark brown powder.

NMR spectra of the prepared complexes *II—IV* were measured with a Tesla BS 487B apparatus at 80 MHz. Solutions of the complexes in dimethyl sulphoxide and dimethyl sulphoxide-d_6 were used for the measurements. Electronic spectra of the products of reaction of *I* with anions of the C-acids in methanol were measured with a Specord UV VIS (Zeiss, Jena) in the wavelength range 400 to 650 nm at the room temperature.

  Kinetic measurements. Formation of complexes *IId* and *IIe*, their reverse reactions, and formation of the products *IVd*, *IVe* and *IVc* were measured at 25°C at the wavelength 560 nm with a VSU-2P spectrophotometer (Zeiss, Jena). When following the kinetics of formation of *IId*, *IIe* and *IVc* the reaction was started by injection of 0·1 ml 10^{-3}M *I* into 1·9 ml methanolic solution of the C-acid and sodium methoxide. For following the reverse reaction of the complexes

TABLE I
Rate and Equilibrium Constants of Reactions of *I* with Anions of C-Acids *Va—c*

C-acid K^a, l mol^{-1}	$k_2 \cdot 10^{-3,b}$ $k_{-2} \cdot 10^{-1}$, s^{-1}	K_2, l mol^{-1} λ, nm	$k_3{}^b$ k_{-3}, s^{-1}	K_3, l mol^{-1} λ, nm
Va	103 ± 4	1 660 ± 70	50 ± 3	73 ± 6
54	6·2 ± 0·2	450, 560^c	0·69 ± 0·02	502^d
Vb	250 ± 15	12 200 ± 50	110 ± 11	275 ± 30
0·5	2·05 ± 0·1	455, 555^e	0·40 ± 0·01	505^f
Vc	5·50 ± 0·6	11·7 ± 1·6		
418	47 ± 3	465^g, 565		
CH_3OH	7·05^h	23·0^h	7·5^i	37^i
	30·5^h		0·2^i	

^{a} Ref.[17], ^{b} in (l mol^{-1} s^{-1}), $^{c-g}$ $\varepsilon \cdot 10^{-4}$ for the given wavelengths 2·3, 1·1, 2·6, 2·4, 1·1, 2·55, 1·15, ^{h} ref.[23], ^{i} ref.[14], in the mixture methanol–water 22·5 : 77·5 (by vol.).

IId and *IIe* and their cyclization to *IVd* and *IVe*, solutions of the complexes *IId* and *IIe* were prepared under the conditions of kinetic experiments. The reverse reaction was then followed after neutralization of CH_3O^- with acetic acid, and the cyclization was followed after a further addition of CH_3O^-. The rate constants k_{obs} were calculated from the time dependence of log . $. (A_t - A_\infty)$ resp. $\log(A_\infty - A_t)$. The other reactions were far quicker and, therefore, were followed by the stopped-flow method with a spectrophotometer Durrum Model D 110. In the case of kinetic measurement of formation of *IIa*, *IIb*, *IIIa* and *IIIb* one syringe contained methanolic solution of a mixture of *I* and the C-acid, and the other one contained solutions of CH_3ONa of various concentrations. In measurements of formation of *IIc* and *VIc* one syringe contained methanolic solution of *I*, and the other one contained methanolic solution of methyl acetoacetate and various concentrations of CH_3ONa. In measurements of the reverse reactions of the complexes *IIa* and *IIb* and *IIIa* and *IIIb* one syringe contained freshly mixed solutions of *I*, C-acid, and CH_3ONa, and the other one contained methanolic solution of acetic acid the amount of which was by about 10% higher then that of CH_3ONa in the first syringe. The change of absorbances during the reactions was followed at λ_{max} of the complex *II* (formation and the reverse reaction of complexes *II* and *VI*), at λ_{max} of the complex *III* (formation and the reverse reaction of *III*) (Table I) at 25°C. The reaction half life $t_{1/2}$ was read from the screen of the spectrophotometer, and the rate constants k_{obs} were calculated from the relation $k_{obs} = 0.693/t_{1/2}$. Each measurement was repeated three times at least. The absorbance coefficients were calculated from the found A_∞ values.

RESULTS AND DISCUSSION

Formation of the complexes *IId* and *IIe* by reaction of acetone and cyclohexanone with *I* is a first order reaction with respect to *I*, and its rate constants are directly proportional to the concentrations of CH_3O^- and C-acid (Eq. (*1*)).

$$v = k_{obs}[I] = k_2K[I][V][CH_3O^-] \qquad (1)$$

K is the equilibrium constant of the reaction of C-acid with CH_3O^-, and k_2 is the rate constant of the reaction of *I* with the respective carbanion. The reverse reaction was always pseudomonomolecular, and the found rate constant $k_{obs} = k_{-2}$ was independent of acetic acid concentration. Formation of the products *IVd* and *IVe* is a first order reaction with respect to complex *IId* resp. *IIe*. The reaction rate is directly proportional to concentration of CH_3O^- and independent of concentration of C-acid (Eq. (*2*)); at the highest used acetone concentration (0.75M)

$$v = k_{obs}[II] = k_4[II][CH_3O^-] \qquad (2)$$

the observed acceleration of the reaction was by 15%. The rate determining step consists probably in cyclization of dianion *VI* (Eq. (*C*)). The rate constants k_2K, k_{-2} and k_4 are given in Table II.

When following spectrophotometrically the reaction of *I* with *Va* ([CH_3ONa] $\leq$ $\leq 10^{-3}$M; [$NCCH_2COOCH_3$] < 0.05M) we could observe an instantaneous forma-

TABLE II
Rate Constants of Reactions of *I* with Acetone (*Vd*) and Cyclohexanone (*Ve*)

Ketone	$k_2 K$, l^2 mol^{-2} s^{-1}	$k_{-2} . 10^5$, s^{-1}	$k_4 . 10^3$, l mol^{-1} s^{-1}
Vd	$3 \cdot 30 \pm 0 \cdot 1$	$0 \cdot 82 \pm 0 \cdot 05$	$14 \cdot 20 \pm 0 \cdot 6$
Ve	$16 \cdot 20 \pm 0 \cdot 3$	$17 \cdot 60 \pm 1 \cdot 00$	$7 \cdot 10 \pm 0 \cdot 2$

tion of the product having λ_{max} 450 and 560 nm (Fig. 1, curve *1*). Both the character of the spectrum and the λ_{max} values are typical[1] for complexes of *I* with carbanions type *II*. With increasing concentration of CH$_3$ONa further bands appeared in the spectrum at 470 and 502 nm, the reaction mixture containing still a considerable part of the unreacted *I*. At highly increased concentration of methyl cyanoacetate anion and with the effective concentration of CH$_3$O$^-$ below 10^{-2}M the visible part of the spectrum contained only one absorption band having its maximum at 503 nm (Fig. 1, curve *2*). Shape of the spectrum as well as the λ_{max} value are typical[1,2] for a di-adduct type *III*. On the contrary, with 0·1M-CH$_3$ONa and ten times lower concentration of methyl cyanoacetate anion the dianion type *VI* is practically the only product of the reaction (Fig. 1, curve *3*) (two absorption bands in visible region typical for monoadduct, and a bathochromic shift of the band from 450 to 470 nm due to a further negative charge).

Tendency to formation of complex *II* was far greater in dimethyl sulphoxide than in methanol. Complex *IIa* was transformed into dianion *VIa* both at increased
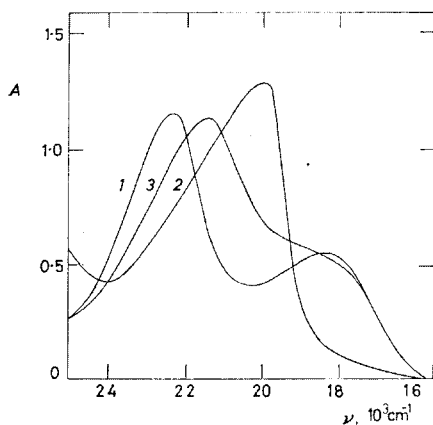

FIG. 1

Electronic Spectra of Complexes *IIa* (*1*), *IIIa* (*2*) and *VIa* (*3*) of Concentrations $5 . 10^{-5}$M in Methanol

methoxide concentration and at increased concentration of anion *Va*. Formation of di-adduct was not observed in dimethyl sulphoxide. On the contrary, if dimethyl sulphoxide was added to methanolic solution of di-adduct *IIIa*, a gradual transformation into complexes *IIa* and *VIa* took place.

The course of reactions of *I* with *Vb* was similar with the only difference that dianion *VIb* was formed to a little extent even at relatively high methoxide concentrations (about 0·5м). Further increasing of methoxide concentration makes the competitive formation of complex *I* with CH_3O^- ion more significant. Methyl malonate is a weaker acid than methyl cyanoacetate by about 3 orders of magnitude[17]. Therefore, also the complex *IIb* shows a far lower tendency to split off the proton as compared to complex *IIa*.
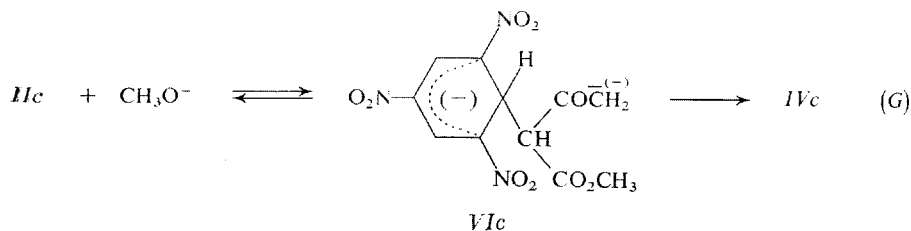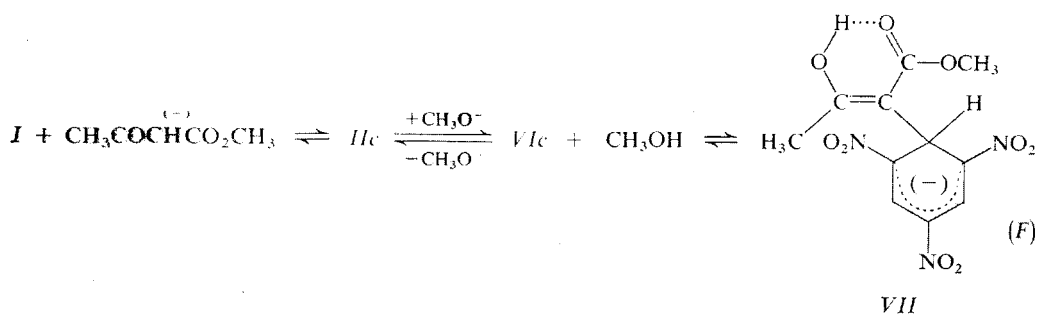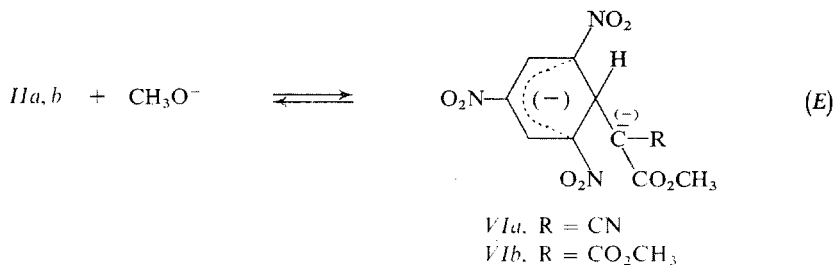
In the range 0 to 6τ of the NMR spectrum of complex *IIa* there are 3 broadened signals with intensities 2 : 1 : 1 and chemical shifts 1·70τ, 4·61τ, and 5·79τ corresponding to the protons at sp^2 and sp^3 carbon atoms of the nucleus and to the proton of cyanoacetate residue. Shape of the signals did not change even after addition of *I* to the sample. At 45°C the signal of sp^2 protons of complex *IIa* coalesced with that of the protons of *I*, the signal of sp^3 protons (ring) strongly broadened, and that at 5·79 quite disappeared. On the contrary, cooling of the sample at 10°C makes all the signals considerably sharper. If methyl cyanoacetate was added to the measured sample (half a mol per one mol of *IIa*) at 10°C, the signal at 5·79τ split into a doublet ($J = 2·5$ Hz), that at 4·61τ was considerably broadened by spin-spin coupling, and the sp^2 protons gave two broadened signals ($\Delta v = 3$ Hz) of a similar shape as those of complexes of *I* with cyclohexanone[5]. The splitting of spectrum of the sp^2 protons is due to their magnetic non-equivalence[5].

In the range 0 to 6τ of NMR spectrum of dianion *VIa* there are two sharp signals with chemical shifts 1·88τ and 4·86 τ and relative intensities about 2 : 1. The spectrum lacks the signal with the chemical shift about 5·8τ belonging to the proton of cyanoacetate residue. The same is the spectrum of *IIIa* in dimethyl sulphoxide. This means that in dimethyl sulphoxide the di-adduct *IIIa* decomposes to dianion *VIa* (Eq. (*D*)), which has already been observed during measurements of electronic spectra. This observation agrees with that of Crampton, that increasing concentration of aprotic solvent decreases the relative stability of the di-adduct with respect to mono-adduct[2,18].

$$VIa \; \rightleftharpoons \; IIa + \overset{(-)}{NCCHCOOCH_3} \; \rightleftharpoons \; IIIa + Va \, . \qquad (D)$$
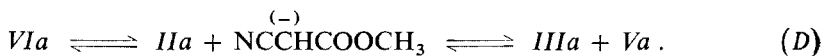
The above explanation was confirmed by the following experiments: *a*) Addition of *I* to the measured solution of *IIIa* in dimethyl sulphoxide brings about a change of the original spectrum of dianion *VIc* into that of mono-adduct *IIa*, intensity of signals being doubled. *b*) Molar ratio of *I* to *Va* in the prepared sample of *IIIa*

was determined by comparison of electronic spectrum of c. 10^{-4}M *IIIa* in methanol with the artificially prepared mixtures of *I* and *Va* (*I* was determined after its conversion into complex *IIe*, *Va* was determined as anion). The molar ratio *Va/I* was found to be 1.85 ± 0.20. In the same way value of this ratio was determined for the isolated product *VIa*; *Va/I* was 1.35 ± 0.20. *c*) If *I* was added to solution of *VIa*

$$IIa, b \ + \ CH_3O^- \ \rightleftharpoons \qquad (E)$$

VIa. R = CN
VIb. R = CO$_2$CH$_3$

$$I + CH_3COCHCO_2CH_3 \ \rightleftharpoons \ IIc \ \underset{-CH_3O^-}{\overset{+CH_3O^-}{\rightleftharpoons}} \ VIc \ + \ CH_3OH \ \rightleftharpoons \qquad (F)$$

VII

$$IIc \ + \ CH_3O^- \ \rightleftharpoons \qquad \longrightarrow \ IVc \qquad (G)$$

VIc

in dimethyl sulphoxide, the signal of the sp^2 protons shifted from 1.88τ to 1.82τ. This means that the ratio of the mixture of *IIa* and *VIa* in the solution was about 1 : 2. Due to rapid chemical exchange, the both compounds give one common signal of sp^2 protons. From these results it follows that the prepared di-adduct was practically pure, whereas the dianion *VIa* contained about 20% of di-adduct *IIIa*.

NMR spectrum of the prepared samples of *IIb* contained a singlet and two doublets $(1\cdot68\tau, 4\cdot50\tau, 6\cdot29\tau;\ J = 3\cdot4$ Hz; intensity ratio 2 : 1 : 1), corresponding to the protons of the complex *IIb*, and two singlets $(1\cdot99\tau, 4\cdot20\tau;$ intensities 2 : 1), corresponding to the dianion *VIb*. Amount of the dianion in the prepared samples of *VIb* was within 10 to 30% mol. After addition of *I* the dianion *VIa* was transformed quantitatively into *IIb*. This suggests that the prepared products contain various amounts of the di-adduct which is transformed into dianion in dimethyl sulphoxide solution.

When following the reaction kinetics of *I* with *Va*, 3 relaxation times can be observed: two of them are comparable (about 1 to 5 ms) and correspond to formation of mono-adduct *IIa* and dianion *VIa*, and the third one is longer by more than 2 orders of magnitude and corresponds to formation of *IIIa*. The relaxation time of the reaction of *Va* with CH_3O^- is substantially shorter than 0·5 ms (when this reaction was followed, only the absorption of equilibrium mixture was recorded even if the time constant of the spectrophotometer was 1 ms). As the first two relaxation times are comparable and very short, it was impossible to determine the rate constant of formation of *VIa*, and only the equilibrium constant value of the reaction (E) was calculated $(K_6 = 110 \pm 30\ \text{l/mol})$. The rate constants of formation of *IIa* and *IIIa* were measured at the effective CH_3O^- concentration below 10^{-3}M when the formation of dianion *VIa* was practically insignificant. Formation of *IIa* and *IIIa* is reversible, and the rate constants k_{obs} are defined by relations (3) and (4). Formation of *IIIa* was followed at such

$$k_{obs} = k_2[\overset{(-)}{\text{NCCHCOOCH}_3}] + k_{-2}\,, \tag{3}$$

$$k_{obs} = k_3[\overset{(-)}{\text{NCCHCOOCH}_3}] + k_{-3} \tag{4}$$

high concentrations of anion *Va* when practically all *I* was transformed into *IIa*. Values of the rate constants k_{-2} and k_{-3} were checked also by direct measurements of the reverse reaction rates of *IIa* and *IIIa*. The values of rate and equilibrium constants along with λ_{max} and absorbance coefficient values are given in Table I.

Reactions of *I* with *Vb* had a similar course. The rate constants of formation of *IIb* and *IIIb* were measured under similar conditions, only the used concentrations of *Vb* being far higher. Values of the equilibrium constants K of reaction of the C-acids with CH_3O^- used for calculation of concentration of anion *Va* are given in Table I.

Reactions of methyl acetoacetate (Vc) with *I* proceed in three steps differing considerably in their velocities. The first step has the half-life about 1 ms and produces reversibly the product *IIc*.*

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*   Rate constant of formation of anion *Vc* $k = (1\cdot8 \pm 0\cdot6) \cdot 10^4$ 1/mol s and the rate of the reverse reaction $k = (40 \pm 10)\ \text{s}^{-1}$. That is why in the study of reaction of *Vc* with *I* the solution of *Vc* was mixed first with CH_3ONa.

The rate constants k_2 and k_{-2} were determined in the same way as in the previous cases. The reverse reaction could not be followed separately, because the complex *IIc* is transformed into other substances within a half-life of several seconds. The found values of rate and equilibrium constants are given in Table I. The second subsequent reaction step has the half-life 16 to 1·7 seconds* and involves splitting off of the proton from *IIc* to form dianion *VIc* which is partially transformed into the enol *VII* (Eq. (*F*)).

At low methoxide concentrations predominantly enol *VII* is formed, whereas higher $[\text{CH}_3\text{O}^-]$ is favoured for dianion *VIc*. Reaction *IIc* $\rightleftharpoons$ *VIc* is rate limiting. Rate of formation of *VIc* + *VII* is given by kinetic equation (5), that of the reverse reaction is given by Eq. (6).

$$\vec{v} = k_6[IIc][\text{CH}_3\text{O}^-] = \vec{k}([I] + [IIc]), \tag{5}$$

$$\overleftarrow{v} = k_{-6}[VIc] = \overleftarrow{k}([VIc] + [VII]), \tag{6}$$

$$k_{\text{obs}} = \vec{k} + \overleftarrow{k} = \left(\frac{k_6 K_2[\text{CH}_3\overset{(-)}{\text{C}}\text{OCHCOOCH}_3]}{1 + K_2[\text{CH}_3\overset{(-)}{\text{C}}\text{OCHCOOCH}_3]} + \right.$$

$$\left. + \frac{k_{-6}K_7}{1 + K_7[\text{CH}_3\text{O}^-]} \right)[\text{CH}_3\text{O}^-]. \tag{7}$$

A good agreement between the rate constants k_6 and k_{-6} in various kinetic experiments was reached for $K_7 = [VIc]/[VII][\text{CH}_3\text{O}^-] = 2 . 10^3$ l/mol, $([IIc]/[VII] = 3)$ (Table III).

The last and slowest reaction step (half-lives above 15 to 30 minutes) produces the cyclic substance *IVc*. Two mechanisms were suggested for its formation[6]. According to the first one the rate-limiting step consists in the reaction of methoxide ions with *IIc* or in cyclization of the formed dianion *IVc* (Eq. (*G*)). According to the second mechanism (Scheme 1) steady state is established after a certain time, and the reaction rate is given by kinetic equation (8). The concentration values of *I*, *Vc* and

$$v = k_8[I][\overset{(-)}{\text{C}}\text{H}_2\text{COCH}_2\text{COOCH}_3] = k_8 K_1[\text{CH}_3\text{O}^-][I][Vc] \tag{8}$$

CH_3O^- can be obtained from the previous constants, so that the value $k_8 K_1$ can be determined from kinetic experiments. From the experiments it followed that the

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* The considerable difference in the relaxation times of formation of *IIc* and *VIc* is due to two factors: the reverse reaction of *IIc* is substantially faster than those of *IIa* and *IIb*, and, on the contrary, protonation of *VIc* is slower.

cyclization proceeds according to the second mechanism, because a) the time dependence of logarithm of the absorbance change was non-linear at the beginning of the reaction (up to 5 to 10% conversion), b) the rate constant values calculated for the first mechanism decreased rapidly with increasing concentration of CH_3O^-, whereas a practically constant value $10.3 \pm 0.6 \, l^2 \, mol^{-2} \, s^{-1}$ was found for $k_8 K_1$.
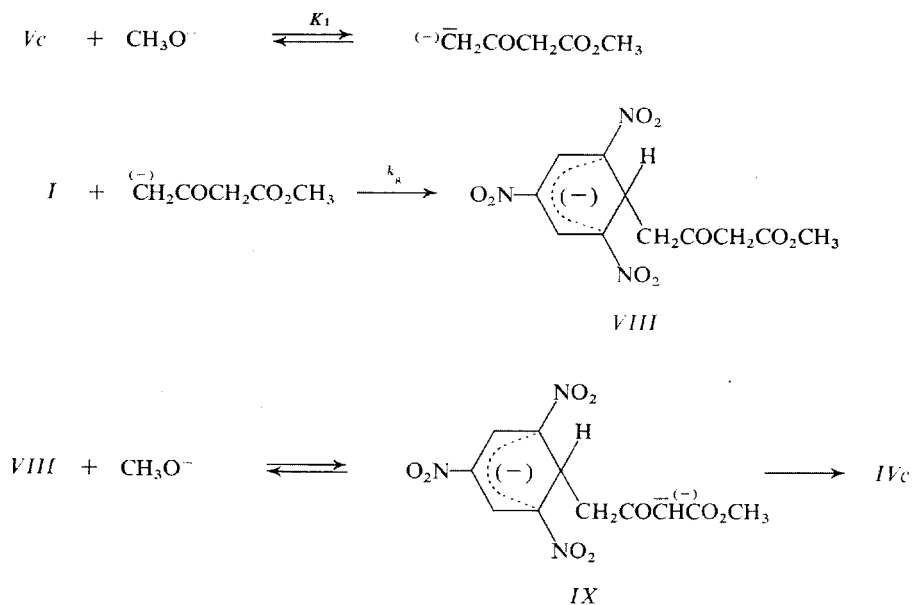
SCHEME 1

TABLE III
Values of Rate Constants k_6 ($l \, mol^{-1} \, s^{-1}$) and k_{-6} (s^{-1}) of Reversible Reaction of IIc with CH_3O^-

$[CH_3COCHCO_2CH_3]^{(-)} \cdot 10^2$	$[CH_3O^-] \cdot 10^4$	$k_{obs}/[CH_3O^-]$	$k_6{}^a$	$k_{-6}{}^b$	A_∞ found	A_∞ calc.
1·93	2·1	206	94	0·14	0·48	0·44
3·22	3·7	181	91	0·14	0·62	0·64
5·15	6·5	178	105	0·16	0·88	0·87
7·72	11·0	158	111	0·17	1·05	1·08
10·30	17·5	138	113	0·17	1·22	1·23
15·45	40·9	101	103	0·15	1·40	1·38

$^a \overline{k}_6 = 103 \pm 9$, $^b \overline{k}_{-6} = 0.155 \pm 0.014$.

The found value of $k_8 K_1$ lies between the rate constant values of reaction of I with acetone and cyclohexanone (Table II).

Dependence of $\log K_2$ on $\log K$ is roughly linear with the slope $-1\cdot2$; $\log k_2$ (slope about $-0\cdot4$) and $\log k_{-2}$ (slope about $+0\cdot8$) correlate much worse. This is due first to that in the two cases rate constants are being correlated with an equilibrium constant and next to the error in estimation of K for acetone and cyclohexanone.*

The K_2 value of the reaction of I with CH_3O^- is smaller than that following from correlation by more than 4 orders of magnitude; methoxide ion reacts about 40 times more slowly, and the decomposition of the complex formed is about $400 \times$ faster than with a hypothetical C-acid having the same K value.

The k_3 values of formation of the di-adducts $IIIa$ and $IIIb$ are smaller than the k_2 values by more than 2 orders of magnitude, which is similar to the reaction of I with CH_3O^- (ref.[14]). In the reaction of I with Vc the di-adduct is not formed, because the anion is a weak nucleophile and, on the contrary, IIc has a strong tendency to form little reactive VIc (opposite to the reactions of Vb).

In the reactions of I with carbanions the formation of di-adducts has not yet been observed, which is due first to that the di-adducts are formed far more slowly than the complexes type II and next to that most of the complexes II prepared so far had one or more hydrogen atoms at γ carbon. These compounds prefer cyclization to formation of di-adducts, and the products IV formed have similar electronic spectra as di-adducts (the same chromophore).

Splitting off of the proton from IIc to form VIc is slower than that from VIc by more than 2 orders of magnitude, and a similar retardation is encountered also with the complexes IIa and IIb, sterical effect being probably the main reason. The complex IIc is almost twice as acidic as VIc (the equilibrium constant value of the reaction of IIc with CH_3O^- is 670), and similar situation is also that of the complex IIa, in spite of the both complexes carrying negative charges; trinitrocyclohexadienyl group is electron-withdraving compared to hydrogen[21,22].

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* Log K for acetone (-6 to -7) and cyclohexanone (about -4) were estimated from the dissociation constants in water[19] and from the observation[20] that K values in methanol are smaller than in water by 1 to 2 orders of magnitude for this type of equilibrium.

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