REACTION OF N-METHYL-N-(2,4-DINITROPHENYL)GLYCINE METHYLAMIDE WITH METHOXIDE

Vladimír MACHÁČEK, Miloslav SEBRÁNEK and Vojeslav ŠTĚRBA

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

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The side reactions of N-methyl-N-(2,4-dinitrophenyl)glycine methylamide with methanolic sodium methoxide reversibly give the spiro adduct (spiro[(1,3-dimethyl-5-imidazolidone)-2,1′-(2′,4′-dinitrobenzenide)]) and irreversibly produce N-methyl-2-nitroso-4-nitroaniline which undergoes subsequent reduction. The diazolidine ring of the spiro adduct is opened by action of methanolic hydrogen chloride, whereby the Smiles rearrangement is completed. The rearrangement product — 2-methylamino-N-methyl-N-(2,4-dinitrophenyl)acetamide hydrochloride — is present in the form of a mixture of *Z* and *E* isomers (ratio 1·9). The equilibrium constant of formation of the spiro adduct from 2-methylamino-N-methyl-N-(2,4-dinitrophenyl)acetamide hydrochloride is by 9 orders of magnitude lower than that found for the analogous trinitrophenyl derivative. The rate-limiting step of the transformation of the *Z*-isomer into the spiro adduct consists in the isomerization $Z \rightleftarrows E$. The *E*-isomer is cyclized with a half-life shorter than 1 ms.

Our earlier papers dealt with the reaction of N-methyl-N-(2,4,6-trinitrophenyl)glycine methylamide[1] and N-(2,4,6-trinitrophenyl)glycine methylamide[2] with methoxide. The former reaction produces spiro[(1,3-dimethyl-5-imidazolidone)-2,1′-(2′,4′,6′-trinitrobenzenide)], the latter one gives only c. 12% of spiro[(1-methyl-5-imidazolidone)-2,1′-(2′,4′,6′-trinitrobenzenide)], the main product being 2-nitroso-4,6-dinitroaniline. This present paper is focused on the reaction of N-methyl-N-(2,4-dinitrophenyl)glycine methylamide (*I*) with the aim of estimation of the proportion of the reactions leading to the nitroso compound and spiro adduct.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured with a JNM FX-100 (Jeol) spectrometer at 99·602 and 25·047 MHz, respectively. The ^{1}H NMR spectrum of the hydrochloride *III* was measured with an AM 400 (Bruker) spectrometer at 400·13 MHz. If not otherwise stated, the samples for the measurements were dissolved in hexadeuteriodimethyl sulfoxide.

The chemical shifts $\delta(^1\text{H})$ are related to hexamethyldisiloxane (δ 0·05), the $\delta(^{13}\text{C})$ values are related to the middle signal of the multiplet of hexadeuteriodimethyl sulfoxide (δ 39·6).

N-Methyl-N-(2,4-dinitrophenyl)glycine Methylamide (I). A mixture of 9·8 g (48 mmol) 1-chloro-2,4-dinitrobenzene, 15·1 g (180 mmol) $NaHCO_3$, 7·1 g (51 mmol) sarcosine methylamide hydrochloride, and 50 ml methanol was stirred at room temperature 5 h. The precipitated solid

was collected by suction and washed with water. After recrystallization from toluene yield 8·45 g (65%),m.p. 169–171°C. For $C_{10}H_{12}N_4O_5$ (268·2) calculated: 44·78% C, 4·51% H, 20·89% N; found: 44·45% C, 4·76% H, 20·87% N. ^{1}H NMR: 8·61 d, 1 H (H-3, J(3, 5) = 2·9 Hz); 8·26 dd, 1 H (H-5, J(5, 6) = 9·5 Hz); 8·09 bq, 1 H (NH); 7·16 d, 1 H (H-6); 4·15 s, 2 H (NCH_2); 2·92 s, 3 H (NCH_3); 2·68 d, 3 H ($NHCH_3$, J = 4·4 Hz). ^{13}C NMR: 167·43 (CO); 148·88, 136·01, 135·43, 127·59, 123·55, 118·64 (Ar); 56·10 (NCH_2); 41·88 (NCH_3); 25·73 ($NHCH_3$).

Spiro[(1,3-dimethyl-5-imidazolidone)-2,1'-(2',4'-dinitrobenzenide)], Sodium Salt (II). A solution of 1·22 g (4·6 mmol) methylamide *I* in 4 ml dimethyl sulfoxide was treated with 3·8 ml 1M sodium methoxide (3·8 mmol). The solid spiro adduct was obtained by a long-term rubbing of the oil (obtained by precipitation with anhydrous ether) with dry ether. The ether saturated with dimethyl sulfoxide was decanted and replaced by the fresh solvent five times. The solid spiro adduct is highly hygroscopic and liquefies immediately on contact with air. ^{1}H NMR: 8·67 d, 1 H (H-3, J(3, 5) = 2·6 Hz); 7·02 dd, 1 H (H-5, J(5, 6) = 10·1 Hz); 4·93 d, 1 H (H-6); 3·42 b, 2 H (CH_2); 2·43 s, 3 H (NCH); 2·10 s, 3 H (NCH). The signal of CH_2 group is broadened due to anisochronism of the protons of this group in the molecule which has no symmetry plane.

2-Methylamino-N-methyl-N-(2,4-dinitrophenyl)acetamide Hydrochloride (III). A solution of 2·7 g (10 mmol) methylamide *I* in 5 ml dimethyl sulfoxide was treated with 14 ml 1M sodium methoxide (14 mmol) with stirring. On standing at room temperature the solution gradually gelatinized. After 15 min, 10 ml 3M methanolic hydrochloric acid (30 mmol) was added, and the precipitate was collected by suction and washed with little methanol (yield 0·65 g after drying in vacuum). The filtrate gradually produced a precipitate of hydrochloride *III*. This solid was collected and recrystallized from ethanol with addition of 1% methanolic HCl (3 mol l^{-1}), yield 1.5 g (47%), m.p. 168–180°C. For $C_{10}H_{13}ClN_4O_5$ (304·5) calculated: 39·42% C, 4·30% H, 18·39% N; found: 39·47% C, 4·62% H, 18·26% N. ^{1}H NMR (tetradeuteriomethanol); *Z*-isomer: 8·77 d, 1 H (H-3, J(3, 5) = 2·6 Hz); 8·58 dd, 1 H (H-5, J(5, 6) = 8·7 Hz); 7·84 d, 1 H (H-6); 4·31 s, 2 H (CH_2); 3·50 s, 3 H (CH_3N); 2·74 s, 3 H ($CH_3NH_2^{(+)}$); *E*-isomer: 8·95 d, 1 H (H-3, J(3, 5) = 2·6 Hz); 8·64 dd, 1 H (H-5, J(5, 6) = 8·6 Hz); 7·97 d, 1 H (H-6); 3·81 and 3·61 AB quartet, 2 H (CH_2, J_{AB} = 16·2 Hz); 3·20 s, 3 H (CH_3N); 2·61 s ($CH_3NH_2^{(+)}$). Ratio (*Z*)-*III*/(*E*)-*III* = 1·9 ± 0·05. The solid precipitated before the hydrochloride *III* (0·65 g) was extracted with 50 ml tetrahydrofurane. The undissolved portion (0·45 g) is sodium chloride. The extract was filtered with charcoal, and the solvent was distilled off in vacuum to give 0·15 g (9%)* 2-amino-2'-methylamino-5,5'-dinitro-ONN-azoxybenzene (*IV*), m.p. 248–253°C, its ^{1}H NMR spectrum was identical with the spectrum of the azoxy compound obtained[3] from N-methyl-N-(2,4-dinitrophenyl)glycine methylester.

Measurements of Kinetics and Equilibria

The constants of the equilibria established between the ammonium salt *III*, its conjugated base, and spiro adduct *II* were determined in methanolic acetate buffers ([CH_3COONa]/[CH_3COOH] = = 8 to 1) and triethylamine buffers ([$(C_2H_5)_3N$]/[$(C_2H_5)_3N$.HCl] = 1 to 8) at the ionic strength of 0·04 mol l^{-1} (due to the ionic buffer component) in the following way: A solution of 0·4 ml triethylamine buffer (I = 0·2 mol l^{-1}) and 1·2 ml methanol was placed in a 1 cm cell and treated with 0·4 ml 2 . 10^{-4}M methanolic solution of compound *III*, and the absorbance–time dependence was followed at 510 nm. The equilibrium constants were calculated from the absorbance values

* In a repeated experiment the hydrochloric acid was not added until after 1 h; the yield of the azoxy compound was increased up to 31% and that of the ammonium salt *III* was decreased to c. 10%.

extrapolated to the time $t = 0$. In acetate buffers the measurements were carried out similarly after mixing 0·4 ml buffer ($I = 0{\cdot}2$ mol l^{-1}), 0·8 ml methanol, and 0·8 ml $2 . 10^{-4}$M solution of compound *III*. The absorbance of pure spiro adduct *II* at 510 nm was measured after an addition of 20 μl 1M sodium methoxide to a solution composed of 0·4 ml $2 . 10^{-4}$M compound *III* and 1·6 ml methanol. The absorbance of pure compound *III* was measured after addition of 20 μl 0·1M methanolic HCl to a mixture of 1·6 ml methanol and 0·4 ml $2 . 10^{-4}$M compound *III*. The methanolic stock solution of compound *III* (c $2 . 10^{-4}$ mol l^{-1}) contained $5 . 10^{-4}$ mol . $. l^{-1}$ HCl.

The reaction kinetics of amide I *with methoxide ion.* A 1 cm cell was charged with 2 ml methoxide solution (0·1 to 0·9 mol l^{-1}), and 50 μl $6 . 10^{-3}$M amide *I* solution was injected therein, whereupon the absorbance–time dependence was followed at 510 nm. The way of calculation of the rate constants is described in Discussion.

Kinetics of the reverse reaction II → I. The absorbance decrease at 510 nm was followed after injection of 20 μl 0·1M methoxide solution into 2 ml methanolic solution of compound *III* ($5 . . 10^{-5}$ mol l^{-1}) in $1 . 10^{-4}$M-HCl. The rate constants were calculated from the equation $kt = -2{\cdot}3 \log (A_t - A_\infty) + \text{const}$.

The kinetics of the reaction *III* → *II* was measured by the stopped-flow method using a Durrum Gibson D-110 spectrophotometer. The reaction was accomplished by mixing equal amounts of methanolic solutions of $5 . 10^{-5}$M compound *III* and $4 . 10^{-3}$ to 10^{-2}M methoxide. The absorbance increase was followed at 510 nm. The absorbance–time dependence was transferred from the memory of a PM 3 311 oscilloscope (Philips) to a BAK 5T recorder (ZPA Čakovice), and the rate constants were calculated in the standard way used for pseudo-first-order reactions.

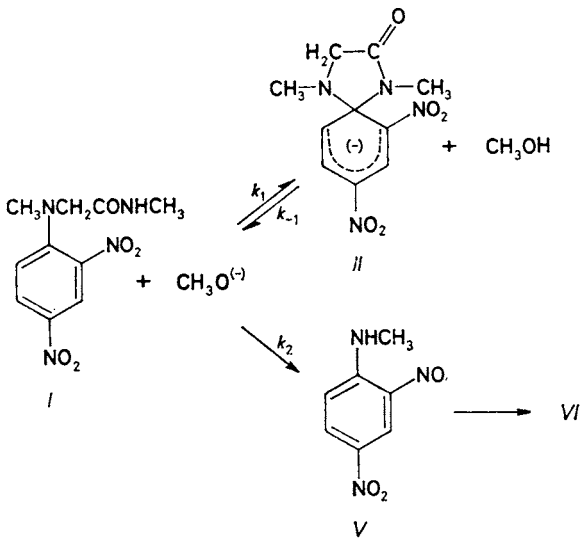
RESULTS AND DISCUSSION

Reaction of N-*Methyl*-N-(2,4-*dinitrophenyl*)*glycine Methylamide* (I) *with Methoxide*

The reactions taking place are represented in Scheme 1. The spectral changes accompanying the reaction of amide *I* ($6 . 10^{-5}$ mol l^{-1}) with methoxide (0·8 mol l^{-1}) are recorded in Fig. 1. The reaction takes place in two steps of considerably different rates. The first step, which is finished after c. 10 min at a methoxide concentration of 0·8 mol l^{-1}, produces – in its side reactions – a mixture of spiro adduct *II* with $\lambda_{max} = 510$ nm and the product of subsequent reaction of N-methyl-2-nitroso-4--nitroaniline *V* ($\lambda_{max} = 395$ nm). The second, slower step (the half-life above 1 h) consists in transformation of spiro adduct *II* into final reaction product *VI*.

The spiro adduct *II* was prepared on preparative scale by the reaction of amide *I* with methoxide in a mixture of methanol and dimethyl sulfoxide in which the formation of nitroso compound *V* is strongly suppressed as compared with purely methanolic solutions. Both the chemical shifts and coupling constants found are close to those given for other Meisenheimer adducts with 2,4-dinitrocyclohexadienide systems[4,5]. The azoxy compound formed in the side reaction during preparation of the ammonium salt *III* was identified as 2-amino-2′-methylamino-5,5′-dinitro--ONN-azoxybenzene (*IV*), hence it is identical with the predominant final product

of the reaction of N-methyl-N-(2,4-dinitrophenyl)glycine methylester* with methoxide[3].



SCHEME 1

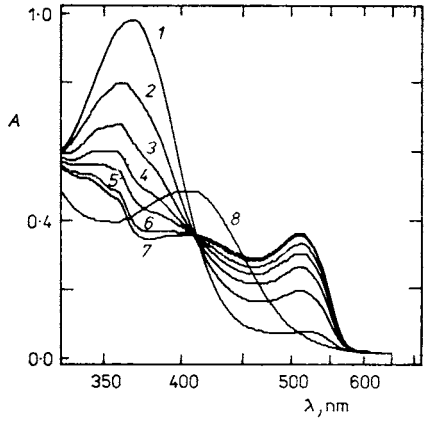


FIG. 1

The spectral records of the reaction course of N-methyl-N-(2,4-dinitrophenyl)glycine methylamide (*I*) ($5{\cdot}85 \cdot 10^{-5}$ mol l^{-1}) with methoxide (0·75 mol l^{-1}). The time intervals $\Delta t = 15$, 100, 190, 270, 350, 540, 730 s and 16 h after the addition of methoxide (the records *1* to *8*, respectively)

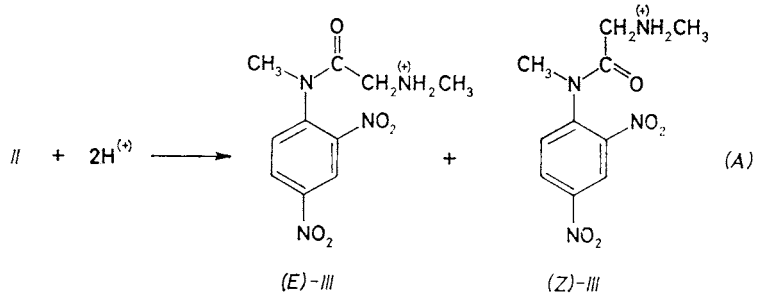
* The compound formed from N-methyl-2-nitroso-4-nitroaniline (*V*) at concentrations below 10^{-4} mol l^{-1} was not identified. At higher concentrations (c. 0·1 mol l^{-1}) a mixture of 2-amino-2'-methylamino-5,5'-dinitro-ONN-azoxybenzene (*IV*) and 2,2'-bis(methylamino)-5,5'-dinitroazoxybenzene (*VII*) is formed[3].

In the reaction of N-methyl-N-(2,4-dinitrophenyl)glycine methyl ester with methoxide the formation of compound *V* is substantially faster than its subsequent transformation[3], hence the reaction takes place in two kinetically separated steps. The nitroso compound *V* can be isolated in good yields.

The formation of nitroso compound *V* from amide *I* is several orders slower than that from N-methyl-N-(2,4-dinitrophenyl)glycine methyl ester (similarly, 2-nitroso--4,6-dinitroaniline is formed c. 100× faster from methyl N-(2,4,6-trinitrophenyl)-glycinate than from N-(2,4,6-trinitrophenyl)glycine methylamide)[2], hence the primary nitroso compound *V* is not accumulated in the reaction mixture but undergoes fast consecutive reactions (Scheme 1). The spectral records of the course of the first, fast reaction phase therefore show a well developed isosbestic point (Fig. 1).

Investigation of Reaction II ⇄ III

In methanolic hydrogen chloride media, the spiro adduct *II* is transformed into the product of Smiles rearrangement – hydrochloride of 2-methylamino-N-methyl-N--(2,4-dinitrophenyl)acetamide (*III*) – see Eq. (*A*). Compound *III* was prepared on preparative scale from methylamide *I* in methanol–dimethyl sulfoxide medium, a small amount of azoxy compound *IV* being isolated as a by-product.



The hydrochloride of 2-methylamino-N-methyl-N-(2,4-dinitrophenyl)acetamide (*III*) represents – according to its ^{1}H NMR spectrum – a mixture of the *E*- and *Z*-isomers, which is analogous to the formerly studied hydrochlorides of 2-methyl-amino-N-methyl-N-(2,4,6-trinitrophenyl)acetamide[1] and 2-amino-N-methyl-N-(2,4,6--trinitrophenyl)propanamide[6]. In contrast to these hydrochlorides, the compounds (*E*)-*III* and (*Z*)-*III* have no symmetry plane which would halve the H—C—H angle of the methylene group, hence the two protons are potentially anisochronous. The anisochronism was really observed in the protons of CH_2 group of compound (*E*)-*III* (the AB quartet, ^2J = 16·2 Hz, $\Delta\delta$ = 0·2 ppm). The methylene group of compound (*Z*)-*III* only gives a slightly broadened singlet. The difference in spectral behaviour of the two CH_2 groups is obviously caused by the fact that in compound

(*E*)-*III* the CH_2 group is nearer to the 2,4-dinitrophenyl group. The relative populations of the two isomers found from the ^1H NMR spectrum is (*Z*)-*III*/(*E*)-*III* = $= 1{\cdot}90 \pm 0{\cdot}05$.

On addition of methoxide to the solution of ammonium salt *III*, the spiro adduct *II* is formed practically instantaneously and quantitatively, and at $[CH_3O^{(-)}] < < 10^{-3}$ mol l^{-1} this spiro adduct is transformed again quantitatively into the starting methylamide *I* (Fig. 2). These reactions were utilized for a measurement of the spectrum of pure spiro adduct *II* and of the rate of its reverse reaction to the methylamide *I*.

In mildly basic methanolic media (pH 9–11) a system of equilibria is established (Scheme 2)*.

$$\begin{array}{ccccccc} 2\,H^+ + II(A) & \rightleftarrows & (E)\text{-}III(O) + H^+ & \rightleftarrows & (E)\text{-}III(K) \\ & & \Updownarrow & & \Updownarrow \\ & & (Z)\text{-}III(O) + H^+ & \rightleftarrows & (Z)\text{-}III(K) \end{array}$$

SCHEME 2

The value of the equilibrium constant *K* (Eq. (*1*)) was determined spectrophotometrically (see Experimental) in acidic triethylamine and basic acetate buffers. The ratio r_1 was determined from Eq. (*2*), where A^{II} is the absorbance of pure spiro adduct *II* in the given buffer (proportional to $[II]$ in this buffer), and $(A^{II} - A)$ is propor-

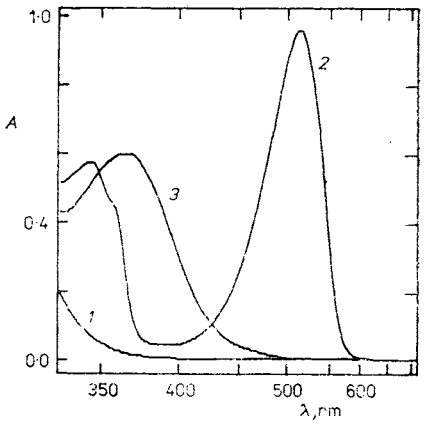


FIG. 2

The electronic spectra of 2-methylamino-N--methyl-N-(2,4-dinitrophenyl)acetamide hydrochloride (*III*) (spectrum *1*), spiro adduct *II* immediately after the addition of 20 µl 0·1M methoxide to the solution of compound *III* (spectrum *2*), and the N-methyl-N-(2,4--dinitrophenyl)glycine methylamide (*I*) formed after 16 h standing of the spiro adduct *II* (spectrum *3*). The concentrations of the compounds $3{\cdot}9 \cdot 10^{-5}$ mol l^{-1}

* The compounds which can exist as various charged forms are denoted with (A) anion, (K) cation, (O) without a charge.

tional to the sum of concentrations of the neutral and protonated forms of compound *III*.

$$K = [II(\mathrm{A})]\,[\mathrm{H}^+]/([(Z)\text{-}III(\mathrm{O})] + [(E)\text{-}III(\mathrm{O})]) = r_1[\mathrm{H}^+] \qquad (1)$$

$$r_1 = (A/(A^{II} - A))\,(1 + ([\mathrm{H}^+]/K^{III})) \qquad (2)$$

The reciprocal value of the expression $(1 + ([\mathrm{H}^+]/K^{III}))$ gives the proportion of the neutral forms of compound *III* in their mixture with the protonated forms, K^{III} is the overall dissociation constant of the protonated forms of compound *III*. The equilibrium constant K was calculated from Eq. (*3*) where r_2 means the ratio of concentrations of basic and acidic buffer components.

$$\mathrm{p}K = \log r_2 - \log r_1 + \mathrm{p}K_a \qquad (3)$$

The $\mathrm{p}K_a$ values of buffers were taken from literature: 10·9 for triethylammonium[7] and 9·27 for acetic acid[6] at $I = 0{\cdot}04$ mol l^{-1}. The pK value found for triethylamine and acetate buffers is 10·1 and 10·3, respectively (Eq. (*3*)). From the measurements of the protonated forms of compound *III* in acetate buffers it was found $\mathrm{p}K^{III} = 9{\cdot}65 \pm 0{\cdot}15$.

From the pK values of the reactions $II + \mathrm{H}^+ \rightleftarrows (Z)\text{-}III(\mathrm{O}) + (E)\text{-}III(\mathrm{O})$(pK = 10·2) and $(Z)\text{-}III(\mathrm{K}) + (E)\text{-}III(\mathrm{K}) \rightleftarrows (Z)\text{-}III(\mathrm{O}) + (E)\text{-}III(\mathrm{O})$ ($\mathrm{p}K^{III} = 9{\cdot}65$) it can be deduced that at pH ~ 9·9 it is $[II(\mathrm{A})]/([(Z)\text{-}III(\mathrm{K})] + [(E)\text{-}III(\mathrm{K})]) = 1$. The same relation applies to the analogous trinitroderivatives[1] at pH ~ 5·5, which means that the equilibrium constants of the reaction (*B*) have a value by c. 9 orders of magnitude (i.e. $2 \times \Delta\mathrm{pH}$) greater for the trinitro derivatives[1].

$$(Z)\text{-}III(\mathrm{K}) + (E)\text{-}III(\mathrm{K}) \rightleftarrows II(\mathrm{A}) + 2\,\mathrm{H}^+ \qquad (B)$$

The kinetics of the reaction $II(\mathrm{A}) \rightarrow III(\mathrm{K})$ was studied by means of the stopped-flow technique. The reactions taking place after mixing solutions of compound *III* and methoxide are represented in Scheme 3.

$$\begin{array}{ccccccc} (E)\text{-}III(\mathrm{K}) & \xrightarrow{\text{very fast}} & (E)\text{-}III(\mathrm{O}) & \xrightarrow{\text{fast}} & [II(Z)] & \xrightarrow{\text{fast}} & II(\mathrm{A}) \\ & & \uparrow \text{slow} & & & & \\ (Z)\text{-}III(\mathrm{K}) & \xrightarrow{\text{very fast}} & (Z)\text{-}III(\mathrm{O}) & & & & \end{array}$$

SCHEME 3

The mixture of the protonated forms $III(\mathrm{K})$ is neutralized with methoxide instantaneously to give a mixture of neutral compounds $III(\mathrm{O})$ (the reaction half-life below

1 μs). The (*E*)-*III*(O) isomer is cyclized very rapidly to give the dipolar ion of spiro adduct *II*(*Z*) which (again very rapidly) is transformed into the anion *II*(A) = the final reaction product. The half-lives of both these reactions are shorter than the dead time of the spectrophotometer used (c. 2 ms) and, hence, the reactions cannot be spectrally followed. Therefore, the only spectrophotometrically measurable reaction is the isomerization (*Z*)-*III*(O) → (*E*)-*III*(O) whose rate constant $k_{iso} = 17{\cdot}0 \pm 0{\cdot}5\ s^{-1}$ is independent of the methoxide concentration. The absorbance ratio $(A_\infty - A_0)/A_0 = 1{\cdot}7$ (A_0 is absorbance of the spiro adduct formed by the very fast cyclization of compound (*E*)-*III*(O) which is present in an equilibrium with compound (*Z*)-*III*(O)) corresponds to the concentration ratio [(*Z*)-*III*(K)]/[(*E*)-*III*(K)]. The isomers ratio found by ^{1}H NMR is 1·9. The rate constant $k_{iso} = 17{\cdot}0\ s^{-1}$ found for the isomerization (*Z*)-*III*(O) → (*E*)-*III*(O) is 170× higher than that corresponding to the trinitro derivative[1] ($k_{iso} = 0{\cdot}1\ s^{-1}$). The difference between these rate constants is probably due to the greater sterical hindrance to the isomerization of the trinitro derivative due to the presence of the second nitro group at the ortho position.

Kinetics of the reaction of N-methyl-N-(2,4-dinitrophenyl)glycine methylamide (*I*) with methoxide is complicated by simultaneous formation of the nitroso compound *V*, its subsequent reduction-oxidation reactions, and the reverse reaction of spiro adduct *II* giving (also via the nitroso compound *V*) an unidentified product *VI* of the reduction-oxidation reaction (Scheme 1). Therefore, in the kinetic experiments the absorbance of spiro adduct does not reach a constant value but, after attaining a maximum value, it begins to decrease. The maximum concentration of spiro adduct is the smaller the lower is the methoxide concentration, because the rate of formation of spiro adduct *II* rapidly decreases with decreasing $CH_3O^{(-)}$ concentration, whereas the rate of the reverse reaction is slightly increased (Table I).

The above-described reaction course is kinetically characterized by two relaxation times (τ_1, τ_2) which represent time constants of two exponential functions (Eq. (*4*)). Both the relaxation times are complex functions of all three rate constants[8] k_1,

TABLE I

The relaxation times τ_1, τ_2 and rate constants k_{-1}, k_1, k_2 of the reactions *II* ⇄ *I* → *VI*

$[CH_3O^-]$ mol l^{-1}	$\tau_1^{-1} \cdot 10^3$ s^{-1}	$\tau_2^{-1} \cdot 10^3$ s^{-1}	$k_{-1} \cdot 10^3$ s^{-1}	$k_1 \cdot 10^3$ l mol^{-1} s^{-1}	$k_2 \cdot 10^3$ l mol^{-1} s^{-1}	k_2/k_1
0·2	1·07	0·15	0·22	1·35	3·65	2·7
0·5	2·9	0·14	0·19	1·50	4·20	2·8
0·8	5·4	0·11	0·15	1·71	5·0	2·9
0·95	6·9	0·10	0·13	1·80	5·4	3·0

k_{-1}, k_2 (Scheme 1) (Eq. (5)). Values of the relaxation times τ_1 and τ_2 were determined by a known procedure[9]. The individual rate constants are best determined from combinations of the relaxation times (Eqs (6) and (7)).

$$A_t - A_\infty = a\,e^{-t/\tau_1} + b\,e^{-t/\tau_2} \tag{4}$$

$$\tau_{1,2}^{-1} = (1/2)\,[(k_1 + k_2)\,[CH_3O^{(-)}] + k_{-1} \pm \{[(k_1 + k_2)\,[CH_3O^{(-)}] + k_{-1}]^2 - 4k_{-1}k_2[CH_3O^{(-)}]\}^{1/2}] \tag{5}$$

$$\tau_1^{-1} + \tau_2^{-1} = (k_1 + k_2)\,[CH_3O^{(-)}] + k_{-1} \tag{6}$$

$$(\tau_1\tau_2)^{-1} = k_{-1}k_2[CH_3O^{(-)}] \tag{7}$$

In this case a precise evaluation of rate constants is made difficult by the fact that the used, relatively high methoxide concentrations (0·2–0·95 mol l^{-1}) are connected with a change of the medium, particularly its solvation ability, and hence also with changes in the rate constant values. Therefore, the evaluation of the rate constants approximatively presumes that at the lowest methoxide concentration used the k_{-1} value almost does not differ from the value of $2{\cdot}3 \cdot 10^{-1}$ s^{-1} found directly from the absorbance decrease of the spiro adduct at $[CH_3O^{(-)}] < 10^{-3}$ mol l^{-1}. At this methoxide concentration the spiro adduct *II* is decomposed practically quantitatively to the starting compound *I*. Then the $k_2[CH_3O^{(-)}]$value is calculated from Eq. (7) using the k_{-1} value, and the $k_1[CH_3O^{(-)}]$ value from Eq. (6). At the highest methoxide concentration the $(k_1 + k_2)\,[CH_3O^{(-)}]$ value is almost 2 orders higher than k_{-1} (Table I). Therefore, the reverse reaction is practically insignificant in the first phase. Ratio of the rate constants of these side reactions was determined from the absorbance value obtained by extrapolation of the descendent section of the time dependence of the absorbance of the spiro adduct to the time $t = 0$ and from the absorbance coefficients of the spiro adduct *II* and the final product *VI* (at the same wavelength). The linear extrapolation is justified in this case, since $\tau_2/\tau_1 = 70$. The k_1 and k_2 values were calculated in the first approximation from Eq. (6) neglecting the k_{-1} value. Then was the k_{-1} value calculated from Eq. (7) and introduced back into Eq. (6) to obtain the corrected k_1 and k_2 values. The same procedure was applied to calculation of the rate constants for $[CH_3O^{(-)}] = 0{\cdot}5$ and 0·8 mol l^{-1} with the presumption of a continuous change of the k_2/k_1 value with the methoxide concentration. The results are given in Table I. The k_1 and k_2 values increase and the k_{-1} value decreases with increasing methoxide concentration. The equilibrium constant of formation of the spiro adduct *II* is 6 and 14 l mol^{-1} at the lowest and the highest methoxide concentrations, respectively.

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