# HETEROCYCLIC NITRO COMPOUNDS

# XII.* KINETICS OF THE REACTION OF 1-METHYL-3,5-DINITRO-1,2,4-TRIAZOLE WITH ALKOXIDE IONS

M. S. Pevzner, V. Ya. Samarenko,
and L. I. Bagal

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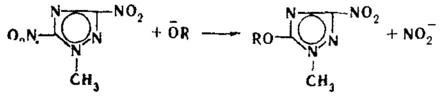
The kinetics of the reaction of 1-ethyl-3,5-dinitro-1,2,4-triazole (I) with methoxy and ethoxy anions in the corresponding alcohols were studied. The activation parameters of the reaction were determined. The existence of a linear dependence between the logarithms of the rate constants and the pK values for the autoprotolysis of water, methanol, and ethanol was demonstrated.

Continuing our investigation of nucleophilic substitution reactions in nitro derivatives of 1,2,4-triazole [1], we have studied the kinetics of the substitution of the nitro group in 1-methyl-3,5-dinitro-1,2,4-triazole (I) by methoxy and ethoxy groups.



I II, III II R=$CH_3$; III R=$C_2H_5$

Preliminary experiments demonstrated that the reactions proceed at a high rate. To decrease the observed rate and to reduce the reaction to pseudofirst-order, the measurements were carried out in buffered alcohol solutions (absolute alcohol–anhydrous sodium acetate–acetic acid) at constant (throughout a given experiment) concentrations of the nucleophilic reagent. In view of the insufficient reliability of the pH measurements in alcohols [2] and the inconvenience involved in using standard alcohol buffered solutions [2], we calculated the alkoxide anion concentrations from the Henderson formula [3], proceeding from the ion products of the corresponding alcohol ($K_S$) and the dissociation constant of acetic acid in a given alcohol ($K_A{}^S$).

$$[RO^-]=\frac{K_s[AcONa]}{K^s{}_A[AcOH]}\ ;\ K_s=[RO^-][ROH_2{}^+];$$

where [AcONa] and [AcOH] are the analytical concentrations of sodium acetate and acetic acid in a given alcohol buffer solution.

The following ion products of the alcohols and dissociation constants of acetic acid at 25° were used in the calculations: $CH_3OH$, $pK_S$ 16.92 [4], $pK_A{}^{CH_3OH}$ 9.625 [5]; $C_2H_5OH$, $pK_S$ 19.138 [6], $pK_A{}^{C_2H_5OH}$ 10.34 [7]. The $K_S$ and $K_A$ constants at other temperatures were calculated from the formula

$$\lg K_T=\lg K_{298.15}+\frac{\Delta H^0}{4.575}\left(\frac{T-298.15}{298.15T}\right)$$

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*See [1] for communication XI.

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TABLE 1. Dependence of the Rate Constant on the Concentrations of I and the Nucleophile

| $[OCH_3] \cdot 10^5$, mole/liter | $[I] \cdot 10^5$, mole/liter | t, °C | $k_1 \cdot 10^3$, sec⁻¹ | $k_2$, liter/mole·sec* |
|---|---|---|---|---|
| 0,225 | 24,27 | 31,7 | 1,65 | 733 |
| 0,225 | 12,33 | 31,7 | 1,72 | 763 |
| 0,251 | 24,48 | 25,1 | 1,08 | 440 |
| 0,491 | 24,72 | 25,1 | 2,28 | 467 |

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* $k_2 = k_1/[OCH_3^-]$.

TABLE 2. Effect of the Ionic Strength on the Rate Constant for the Reaction of I with the Methoxy Anion at 31.7°C

| [AcONa], mole/liter | $[AcOH] \cdot 10^2$, mole/liter | $[CH_3O^-] \cdot 10^5$, mole/liter | I | $k_1 \cdot 10^3$, sec⁻¹ | $k_2$, liter/mole·sec |
|---|---|---|---|---|---|
| 0,1707 | 0,4922 | 0,2269 | 0,22 | 1,72 | 768 |
| 0,5121 | 1,485 | 0,2242 | 0,66 | 1,63 | 735 |
| 0,6793 | 1,943 | 0,2273 | 0,87 | 1,76 | 780 |

TABLE 3. Second-Order Rate Constants and Activation Parameters for the Reaction of I with Alkoxy Anions

| Anion | T, °K | $k_2$, liter/mole per sec | Activation parameters |
|---|---|---|---|
| $CH_3O^-$ | 283,2 | 150 | $E_A$ 12,8 kcal/mole |
| | 290,6 | 242 | lg A 12,1 |
| | 298,2 | 450 | $\Delta H_{25}$ 12,2 kcal/mole |
| | 304,8 | 724 | $\Delta S_{25} - 5,3$ eu |
| $C_2H_5O^-$ | 293,2 | 5880 | $E_A$ 13,2 kcal/mole |
| | 297,8 | 7440 | lg A 13,6 |
| | 304,3 | 14000 | $\Delta H_{25}$ 12,6 kcal/mole |
| | 308,3 | 15800 | $\Delta S_{25} + 1,5$ eu |
| | 314,6 | 27200 | |

where $\Delta H^0$ are the corresponding enthalpies of ionization in calories per mole, and T is the experimental temperature in degrees Kelvin.

In the autophotolysis of methanol, $\Delta H^0 = 11{,}200$ cal/mole [8], while $\Delta H^0 = 11{,}560$ cal/mole [9] for the autophotolysis of ethanol, and $\Delta H^0 = 4450$ cal/mole [8] for the ionization of acetic acid in methanol. The $\Delta H^0$ value for the ionization of acetic acid in ethanol is apparently absent in the literature but, according to the data in [8], it can be assumed to be the same as in methanol.

The determination of the kinetic order with respect to the substrate and nucleophile demonstrated that the reaction is second-order overall – first order in each of the reagents – and this order is retained up to 90-95% conversion. The rate constants of the pseudofirst-order reaction and of the second-order reaction at various concentrations of I and the nucleophile are presented in Table 1. To ascertain the effect of acetate ions and the ionic strength (I) on the reaction rate, we performed experiments at various sodium acetate and acetic acid concentrations in buffered solutions with approximately the same concentration of methoxy anions (Table 2). The results demonstrate that, strictly speaking, the acetate ion concentration does not affect the second-order rate constant, and the reaction between I and acetate ions consequently does not occur. Within the limits considered, the ionic strength does not affect the reaction rate. It hence follows that a neutral molecule of I reacts with the alkoxide anion in the step that determines the rate of the process.

From an examination of activation parameters of the reaction (Table 3), it follows that the difference in the rates of reaction of I with methoxy and ethoxy anions is due mainly to entropy factors, since the energies of activation of the two reactions are close. This is apparently associated with the different degree of solvation of the starting material and the intermediate complex in methanol and ethanol. The energies of activation of the studied reactions are considerably lower than for the substitution reactions of the nitro group in other substrates (o- and p-dinitrobenzene [9] and 2- and 4-nitropyridine-1-oxides [10, 11]), where the energies of activation are 18-25 kcal/mole. Thus the high rates of substitution of the nitro group in I as compared with other activated systems are primarily due to the comparatively low energies of activation. The rates of the reaction of I with alkoxide ions are considerably higher than those for the reaction with the hydroxyl ion [1]. The relative order of the reactivities of the investigated anions is $C_2H_5O^- >$ $CH_3O^- > OH^-$, while the ratio of the rate constants at 25° in this series is 270 : 15 : 1. This order of the reactivities is in agreement with the values observed in aromatic nucleophilic substitution reactions [12].

A linear dependence is observed between the logarithm of the rate constants for the solvolysis of I and the pK values for the autoprotolysis of water, methanol, and ethanol,* which serve as a measure of the basicities of the corresponding anions. The slope of the line is 0.6. Similar linear dependences were observed by Murto [14]. This fact is apparently evidence that, within the limits of a given homologous series, the reactivities of the anions are determined to a considerable degree by their basicities.

## EXPERIMENTAL

The methanol and ethanol used for the kinetic experiments were rendered absolute by the method in [15]. Chemically pure glacial acetic acid was additionally purified by two freezings out. Chemically pure anhydrous sodium acetate was calcined at 250° before use. All of the reagents were checked for the absence of the nitrite anion. The preparation and purification of methyldinitrotriazole (I) were described in [1, 16]. The kinetic trend of the reaction was monitored by measuring the nitrite anion concentration. The method used for the investigation was presented in [1]. The experimental error was evaluated by the methods of mathematical statistics. The second-order rate constants were determined with an accuracy of ±4% and a confidence probability ($\alpha$) of 0.95.

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*The corresponding pK values at 25° [13] are as follows: 17.49 ($H_2O$), 19.70 ($CH_3OH$), 21.60 ($C_2H_5OH$).