

The alcoholysis of 1,2,2-trimethylpropyl-methylfluorophosphonate

MLADJEN L. MIĆEVIĆ^a and SLOBODAN D. PETROVIĆ^{b#}

^aInstitute of Security, YU-11000 Belgrade and ^bDepartment of Organic Chemistry, Faculty of Technology and Metallurgy, P.O. Box 35-03, YU-11001, Beolgrade, Yugoslavia

(Received 12 April, revised 20 August 2000)

The alcoholysis of 1,2,2-trimethylpropyl-methylfluorophosphonate (soman) was examined with a series of alkoxides and in corresponding alcohols: methanol, ethanol, 1-propanol, 2-propanol, 2-methoxyethanol and 2-ethoxyethanol. Soman reacts with the used alkoxides in a second order reaction, first order in each reactant. The kinetics of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphonate and ethanol in the presence of diethylenetriamine was also examined. A third order reaction rate constant was calculated, first order in each reactant. The activation energy, frequency factor and activation entropy were determined on the basis of the kinetic data.

Keywords: decontamination, alcoholysis, 1,2,2-trimethylpropyl-methylfluorophosphonate, soman, alkoxides and diethylenetriamine.

INTRODUCTION

1,2,2-Trimethylpropyl-methylfluorophosphonate is a highly toxic compound of tetrahedral organic phosphorus. In the study of its chemistry, reactions in which non-toxic products are produced are of particular interest.¹ Of all the reactions, hydrolysis is the most studied, which is important not only because of decontamination, but also because of on-site monitoring of soman.²

Alcoholysis in tetrahedral organophosphorus compounds is a slower process than hydrolysis. The activation energies of alcoholysis are lower than the activation energies of hydrolysis. The number of effective collisions, as expressed by $\log A$ is also lower. As a result, the reaction rates of the examined reactions are also somewhat lower. This can be explained by lower bond energies in alcoholysis, on the one hand, and steric hindrance in alcoholytic reactions on the other.^{3,4}

The reaction of methylisopropyl fluorophosphonate, methanol and amine (triethylamine, diethylamine and piperidine) in pyridine as the solvent is third order, first order in each reactant. The product of the reactions are esters, contrary to amide formation

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in cases when chlorophosphonate is used as the phosphorylating agent. Amine plays the role of catalyst, assisting in deprotonation of the hydroxylic group in the transition state of the reaction of fluorophosphonate and methanol.⁵

EXPERIMENTAL

Materials

1,2,2-Trimethylpropyl-methylfluorophosphonate was synthesized and redistilled prior to use and found to have 98 % purity (GC-MS).⁶

1,2,2-Trimethylpropyl-*O*-ethylphosphonate (I) was synthesized from 1,2,2-trimethylpropyl-methylfluorophosphonate and sodium ethoxide in ethanol. The purity, as determined by gas chromatography, was 99 %.

Sodium methoxide, sodium ethoxide, sodium 1-propoxide, sodium 2-propoxide, sodium 2-methoxyethoxide and sodium 2-ethoxyethoxide were obtained by the usual Tishler procedure⁷ from sodium metal and corresponding alcohols, under dry nitrogen.

Diethylenetriamine (DETA), (Merck, for synthesis, 98 % GLC) was freshly distilled over sodium, under dry nitrogen. The applied materials were purified by standard laboratory procedures.

Determination

All the kinetic experiments were performed in a thermostated glass vessel ($\Delta T = \pm 0.1$ °C) equipped with a magnetic stirrer. The sodium alkoxides (5 ml) of defined concentration and dissolved in the corresponding alcohols (sodium methoxide $c_0 = 0.015$ mol dm⁻³, sodium ethoxide $c_0 = 0.0233$ mol dm⁻³, sodium 1-propoxide $c_0 = 0.0270$ mol dm⁻³, sodium 2-propoxide $c_0 = 0.0228$ mol dm⁻³, sodium 2-methoxyethoxide $c_0 = 0.0298$ mol dm⁻³ and sodium 2-ethoxyethoxide $c_0 = 0.0265$ mol dm⁻³), were thermostated for 30 min at the desired temperature.

1,2,2-Trimethylpropyl-methylfluorophosphonate was then added to the mixture in such an amount that the concentration in the total mixture was identical to the concentration of the corresponding alkoxides.

A mixture (5 ml) of diethylenetriamine dissolved in ethanol was thermostated for 30 min at the desired temperature. 1,2,2-Trimethylpropyl-methylfluorophosphonate (soman) was then added to the reaction mixture in such an amount that the concentration in the total mixture was 0.0322 mol dm⁻³. The concentration of DETA in the total reaction mixture was varied from 1.13 mol dm⁻³ to 9.05 mol dm⁻³. The concentration of ethanol in the total reaction mixture was varied from 2.13 mol dm⁻³ to 17.4 mol dm⁻³. At regular intervals, an aliquot of 0.1 ml was taken from the reaction mixture and transferred into a 50 ml calibrated flask containing 1 ml of 0.1 mol dm⁻³ HCl in ethanol for spectrometric analysis or for gas chromatography.

Spectrophotometric method

The spectrophotometric method, based on the hydroxybenzidine reaction (the Schöenman-reaction), using a wavelength of 420 nm was applied for the determination of 1,2,2-trimethylpropyl-methylfluorophosphonate.⁸

Conductometric method

The following equipment was used to analyze the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate (soman) and sodium alkoxide: a CDM3 RADIOMETER, conductometer, PP-1042 conductometric cells under dry nitrogen.

Gas chromatography method

A gas chromatograph 'Varian 3700', equipped with a flame ionization detector (FID) was used:

<i>for alcohols:</i>	<i>for alcohol-amine mixtures:</i>
column 5 % SE-30 + 5 % QF-1 on varaport-30	column SE-30 + QF-1
T detector: 200 °C	T detector: 240 °C
T injector: 200 °C	T injector: 200 °C
Program: 120 °C to 200 °C/ 5 °C/min	Program: 50 °C to 150 °C/ 10 °C/min
An external standard was used	An external standard was used
The retention time for 1,2,2-trimethylpropyl-methylfluorophosphonate was 3.62 min.	The retention time for 1,2,2-trimethylpropyl-methylfluorophosphonate was 5.35 min.

Identification of the reaction products

The products of the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate and sodium ethoxide in ethanol and of the same reaction catalyzed by diethylenetriamine were identified by gas chromatography, IR spectrometry and nuclear magnetic resonance ($^1\text{H-NMR}$). The product of the reaction, 1,2,2-trimethylpropyl-*O*-ethyl-methylphosphonate, was synthesized.⁹

IR -data (NaCl): 1380 and 1365 cm^{-1} [$\text{C}-\text{CH}_3$]₃, 1310 and 895 cm^{-1} [$\text{P}-\text{CH}_3$], 1240 cm^{-1} [$\text{P}=\text{O}$], 1015, 960 cm^{-1} [$\text{P}-\text{O}-\text{C}$], 2890 and 2990 cm^{-1} [CH_2-CH_2].

$^1\text{H-NMR}$ in CDCl_3 : δ 0.90 [9H, *s* (CH_3)₃], 1.28 [3H, *d*, OCCH_3], 1.30 [3H, *t*, $\text{O}-\text{CH}_2-\text{CH}_3$], 1.48 [3H, *d*, $\text{P}-\text{CH}_3$], 2.9 [2H, *t*, CH_2-C] and 3.85–4.40 [3H, unresolved multiplet, $\text{O}-\text{CH}_2$ and OCH].

The toxicity of the synthesized compound was determined and the following value was obtained $\text{LD}_{50} = 500 \text{ mg kg}^{-1}$ i.p. for rats.

RESULTS AND DISCUSSION

The reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium alkoxide in alcohol

The alcoholysis of 1,2,2-trimethylpropyl-methylfluorophosphonate was examined with sodium ethoxide. Soman reacts with sodium ethoxide in ethanol by a second order reaction, first order in each reactant. The reaction rate of soman was observed in the temperature range: $-15\text{ }^\circ\text{C}$ to $+25\text{ }^\circ\text{C}$. (Table I).

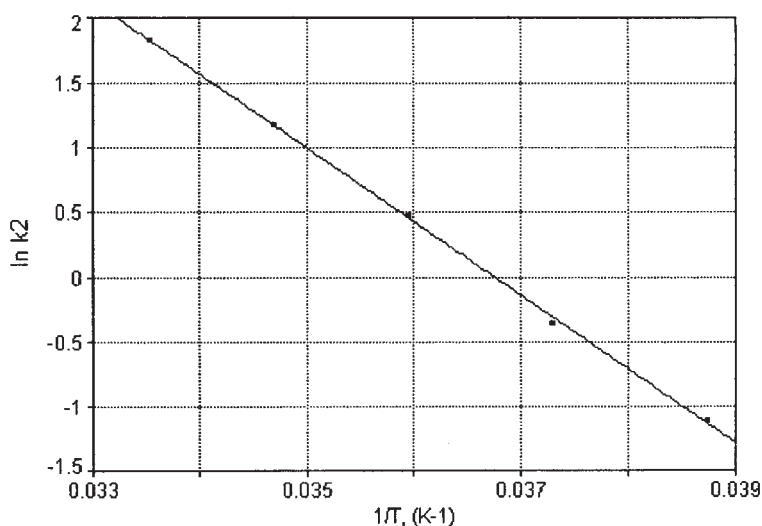


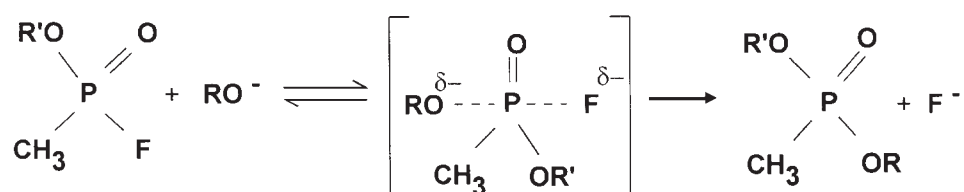
Fig. 1. Dependence of the reaction rate of the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium ethoxide in ethanol on temperature.

The activation energy, frequency factor and activation entropy were obtained on the basis of the kinetic data:

$$E_a = 47.3 \text{ kJ mol}^{-1}; \log A = 9.1; \Delta S^\ddagger_{25^\circ\text{C}} = -70.5 \pm 0.6 \text{ J mol}^{-1}\text{K}^{-1}$$

The experimentally determined activation parameters for the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium ethoxide in ethanol correspond to the values of S_N2 activation parameters ($\log A$ from 7 to 11, $\Delta S^\ddagger_{25^\circ\text{C}}$ from -125 to $-42 \text{ J mol}^{-1}\text{K}^{-1}$).^{11,12}

On the basis of the kinetic data for the activation parameters and reaction products, it can be assumed that the S_N2 (P) mechanism of nucleophilic substitution occurs:



R—ethyl, R'-1,2,2-trimethylpropyl

The alcoholysis of soman was examined in a series of alkoxides and corresponding alcohols: sodium methoxide, sodium ethoxide, sodium 1-propoxide, sodium 2-propoxide, sodium 2-methoxyethoxide and sodium 2-ethoxyethoxide.

TABLE I. Reaction rate constants and activation parameters of the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium alkoxides in the corresponding alcohols

Alkoxide	Reaction rate constants, $k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					Activation parameters		
	-15°C	-5°C	$+5^\circ\text{C}$	$+15^\circ\text{C}$	$+25^\circ\text{C}$	E_a kJ mol^{-1}	$\log A$	$\Delta S^\ddagger_{5^\circ\text{C}}$ $\text{J mol}^{-1} \text{ K}^{-1}$
CH_3ONa	0.17	0.30	0.59	—	1.67	36.8	6.67	-77.3
$\text{CH}_3\text{CH}_2\text{ONa}$	0.33	0.69	1.59	3.18	6.13	47.3	9.1	-72.7
$\text{CH}_3\text{CH}_2\text{CH}_2\text{ONa}$	1.09	2.32	4.71	—	14.88	41.7	8.5	-67.7
$\text{CH}_3\text{CH}(\text{CH}_3)_2\text{ONa}$	3.18	7.58	14.23	—	—	43.1	9.3	-62.6
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{ONa}$	1.56	3.34	5.23 4.95*	— 7.66*	— 16.68*	42.3	8.5	-66.2
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{ONa}$	2.17	4.39	8.93	—	—	40.7	8.6	-64.8

*In mixture dioxan/2-methoxy-ethoxide¹⁶

Soman react with the examined alkoxides in the corresponding alcohols by a second order reaction, first order in each reactant. The reaction rate of soman alcoholysis increases according to the following order of alkoxides: methoxide, ethoxide, 1-propoxide, 2-methoxyethoxide, 2-ethoxyethoxide and 2-propoxide.

As is known, the nucleophilic ability increases in the following sequence: methyl-, ethyl-, propyl-, isopropyl-.¹⁰ With increasing basicity and ion dimensions, their nucleophilicity becomes more expressed and, consequently, their ability for nucleophilic substitution.¹⁰ In alcoholysis reactions of *p*-nitrophenyldiethyl phosphate with alkoxides, the reaction rates lie in the following sequence: ethoxide-, 1-propoxide-, 2-propoxide.¹¹

The reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate (soman) with ethanol and diethylenetriamine (DETA)

The product of the reaction is 1,2,2-trimethylpropyl-*O*-ethyl-methylphosphonate. The reaction rate constants are pseudo first order for soman and were obtained from the following equation

$$\ln(G_{\infty} - G_0) / (G_{\infty} - G_{\tau}) = k_1' \tau \quad (1)$$

Where: k_1' is the reaction rate constant, [min⁻¹]; τ – time [min]; G_0 – the initial conductivity [μ S/cm]; G_{τ} – conductivity at time τ [μ S/cm]; G_{∞} – the conductivity after completion of the reaction [S/cm].

A linear dependence of the logarithm of the conductivity, $\ln(G_{\infty} - G_0) / (G_{\infty} - G_{\tau})$ vs. time τ , is obtained, demonstrating that the reaction is first order with regard to soman. At higher concentrations of diethylenetriamine, the first order reaction rate also increases.

The considerable excess of amine with respect to soman makes it possible to consider the amine concentration constant and in this way determine its fraction in the constant k_1' from the dependence:

$$k_1' = f(c_{\text{DETA}}) \quad (2)$$

The results show that this dependence is also linear and that the reaction is first order with respect to the amine. First reaction orders with respect to both soman and amine lead to the conclusion that the concentrations of both reactants influence the reaction rate with the simultaneous formation of the products of the reaction between soman and alcohol. In order to establish whether the reaction also depends on the alcohol concentration, the amine to alcohol ratio was varied and the reaction rate observed at an initial soman concentration of $c_0 = 0.0322 \text{ mol dm}^{-3}$ (Table II).

Changes in the concentration of the reaction intermediates and the product with time are described by a differential equation:

$$dc_A/dt = -k_3 c_A c_B c_C \quad (3)$$

where: c_A – is the 1,2,2-trimethylpropyl-methylfluorophosphonate concentration [mol dm^{-3}], c_B – the ethanol concentration [mol dm^{-3}], c_C – the DETA concentration [mol dm^{-3}].

Table II gives the values of the following constants: k_1' , k_2' , k_3' . Constant k_2' was obtained by dividing k_1' by the concentration of diethylenetriamine and k_3' by dividing

k_2' by the alcohol concentration. Constant k_2' is not a real reaction rate constant because it decreases with decreasing ethanol concentration. k_3' is constant to approximately equimolar amine to alcohol ratios and then it decreases with decreasing alcohol fraction. Constant k_3' could be considered to be a true, total rate constant of a third order reaction, first order with respect to each reactant (soman, ethanol, diethylenetriamine). The decrease of the reaction rate constant at high amine concentrations can be interpreted by the influence of diethylenetriamine as a solvent when it predominates in the reaction system.

TABLE II. The rate constants of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphate with ethanol and (DETA)

Concentration, mol/dm ³		Reaction rate constants		
DETA	Ethanol	$k_1' \times 10^3 \text{ s}^{-1}$	$k_2' \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_3' \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
0	17.04	—	—	—
1.13	14.91	5.14	4.55	3.05
2.26	12.78	9.15	4.05	3.15
3.39	10.65	10.97	3.24	3.04
4.53	8.52	10.73	2.37	2.82
5.66	6.39	8.94	1.58	2.50
6.79	4.26	5.5	0.81	1.9
7.92	2.13	2.3	0.29	1.32
9.05	0	—	—	—

Knowing the rate constants at elevated temperatures enables the calculation of the reaction activation parameters: activation energy (E_a) and frequency factor (A) by using the Arrhenius equation.

TABLE III. The rate constants of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphate with ethanol and (DETA)

Temperature °C	Reaction rate constants $k_3' \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$		
	Conductometric method	Spectrophotometric method	Gas chromatography method
-15	—	0.27	0.25
-5	0.50	0.50	0.53
0	0.71	—	0.70
5	0.90	0.85	0.90
10	1.44	—	1.20
15	1.78	1.40	1.50
20	2.17	—	—
25	2.97	—	—

The kinetics of the reactions were observed by spectrophotometry, gas chromatography and conductometry and the following was concluded: the reactions are third order,

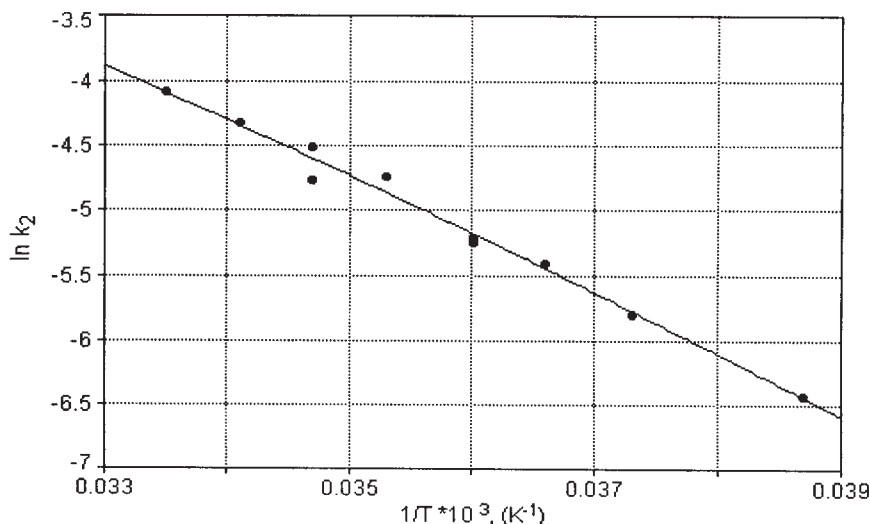


Fig. 2. Dependence of the rate constant k_3 of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphonate with ethanol and (DETA) on temperature.

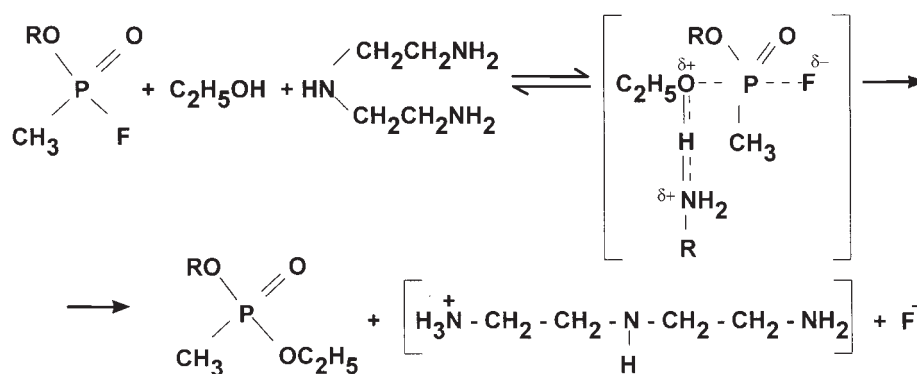
first order in each reactant; the reaction product is 1,2,2-trimethylpropyl-*O*-ethylmethylphosphonate (I), the activation parameters are: $E_a = 37.0 \pm 0.5 \text{ kJ mol}^{-1}$; $A = 3.04$; $\Delta S^\ddagger = -195 \text{ J mol}^{-1} \text{ K}^{-1}$.

The obtained activation energy is somewhat lower than the characteristic activation energies for bimolecular nucleophilic substitution⁹ and is equal or slightly lower than the activation energies for the alkaline hydrolysis of $R_1R_2P(O)X$ type compounds. The low activation energy suggests a catalytic reaction. A catalytic reaction is also indicated by the very negative value of the activation entropy $\Delta S^\ddagger = -195 \text{ J mol}^{-1} \text{ K}^{-1}$.¹¹

According to this value, the activated complex has a much lower activation entropy than the reactants, which implies that it also presents a more ordered intermolecular state. Such low entropies are characteristic for reactions of non-ionogenic reactants and catalyzed reactions. The following established facts: third order reaction, first order reaction in each reactant, one reaction product of the structure 1,2,2-trimethylpropyl-*O*-ethylmethyl phosphonate (I), fit well into the assumed mechanism,¹² in the case of phosphorylating alcohols by phosphate esters in the presence of tertiary amines as catalyst. The reaction of soman with diethylene triamine and ethanol can also be explained by this mechanism.^{13,14}

The amine acts as a general base catalyst by facilitating the removal of the hydroxyl proton in the transition state of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphonate (soman) and ethanol. All the facts given above are consistent with this mechanism. A similar mechanism has been suggested by Dudek and Westheimer,¹⁵ for the propanolysis of tetrabenzyl pyrophosphate in the presence of lutidine or collidine, and by Hudson and Greenhalgh,⁵ for the hydrolysis of diisopropyl phosphorofluoridate with catalysis by butyl amine.

On the basis of the kinetic data for the activation parameters and the reaction products, it can be assumed that nucleophilic substitution take place by the $S_N2(P)$ mechanism.



In the presence of diethylentriamine, these reactions are accelerated, as a consequence of the general base catalysis by an amine for an $R_1R_2P(O)F$ type of compound. The influence of the mole ratio of alcohol and amine on the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with ethanol and diethylenetriamine was also examined.¹¹

The dependence of the reaction rate on the amine and alcohol concentration implies that in their mixture there is an optimal ratio between these two components at which the rate, *i.e.*, the constant, pseudofirst order regarding soman, is the highest.

To solve this problem, one starts from the assumption that the volume of the mixture is equal to the sum of the volumes of the components (amine and alcohol) and that the reaction will be the fastest under those conditions when the fraction of one or the other reactant is the highest.

Let the volume of the reaction mixture be constant:

$$V = V_1 + V_2 = \text{const.}, \text{ for } V_1 = n_1M_1/\rho_1 \text{ and } V_2 = n_2M_2/\rho_2$$

where V is the total volume, V_1 – the volume of ethanol, V_2 – the volume of DETA, n_1, n_2 – the number of moles of ethanol and DETA, ρ_1, ρ_2 – the specific densities of ethanol and DETA, M_1, M_2 – the molar masses of ethanol and amine.

As the reaction rate constant $k_1' = k_3 n_1 n_2$, it follows that

$$k_1' = k_3 (An_1 - Bn_1^2)$$

where: $A = V\rho_2/M_2$, and $B = M_1\rho_2/M_2\rho_1$.

The maximum value of k_1' is obtained when the first derivative of the constant in regard to n_1 is equal to zero:

$$dk_1'/dn_1 = k_3 (A - 2Bn_1) = 0$$

$$n_1/n_2 = M_2\rho_1/M_1\rho_2$$

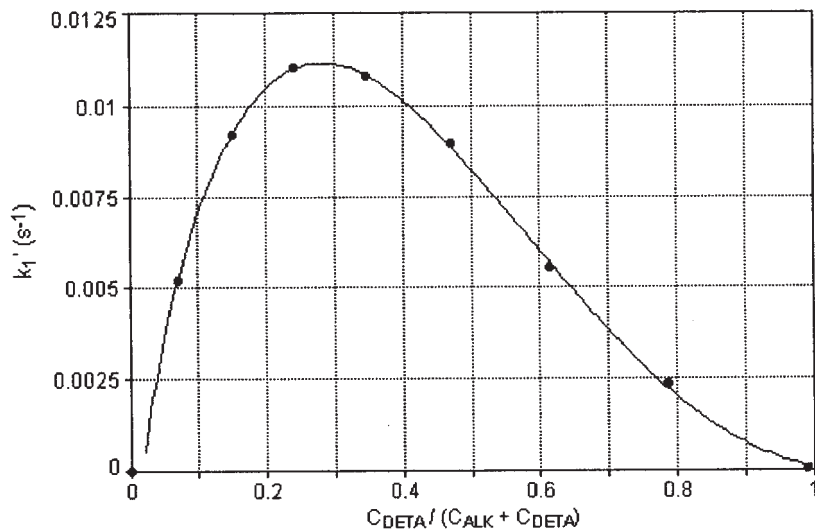


Fig. 3. Dependence of the rate constant k_3 of the reaction between 1,2,2-trimethylpropyl-methylfluorophosphonate with ethanol and diethylenetriamine (DETA) on the mole ratio of DETA and ethanol.

The optimal mole ratio for ethanol and diethylenetriamine was established, based on the reaction rate (theoretically $n_1/n_2 = M_2\rho_1/M_1\rho_2$, $n_1/n_2 = 1.84$, experimentally $n_1/n_2 = 2$).

CONCLUSIONS

1. 1,2,2-Trimethylpropyl-methylfluorophosphonate (soman) reacts with sodium ethoxide in ethanol in the mole ratio 1:1. As the product of the reaction 1,2,2-trimethylpropyl-*O*-ethylmethylphosphonate is obtained. The whole reaction is second order, first in each of the reactant. The product of the reaction of alcoholysis of soman is slightly toxic ($LD_{50} = 500$ mg/kg i.p. on rats). The experimentally obtained activation parameters for the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium ethoxide in ethanol are: $E_a = 47.3$ kJ mol⁻¹, $\log A = -9.1$, $\Delta S^\ddagger_{25^\circ\text{C}} = -70.5 \pm 0.6$ J mol⁻¹ K⁻¹. The assumed mechanism of the nucleophilic substitution reaction is $S_N2(P)$.

2. The constants were defined for the velocity of the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with sodium methoxide, sodium ethoxide, sodium 1-propoxide, sodium 2-propoxide, sodium 2-methoxyethoxide and sodium 2-ethoxyethoxide in the appropriate alcohol.

The activation parameters were calculated for all the quoted reactions. The experimental data on the velocity constants for the reactions of 1,2,2-trimethylpropyl-*O*-ethyl-methylphosphonate with alkoxides show that the velocity of the reaction increases in the order methoxide, ethoxide, 1-propoxide, 2-methoxyethoxide, 2-ethoxyethoxide and 2-propoxide.

3. It has been established that the reaction of 1,2,2-trimethylpropyl-methylfluorophosphonate with ethanol and diethylenetriamine is a third order reaction, first order in each reactant. The product of the reaction is 1,2,2-trimethylpro-

pyl-*O*-ethyl-methylphosphonate. The activation parameters of the reaction are: $E_a = 37$ kJ mol⁻¹, $\log A = 3.04$ and $\Delta S^\ddagger_{25^\circ\text{C}} = -195$ J mol⁻¹ K⁻¹. It was assumed that alcoholysis of soman occurs in the reaction mixture by an S_N2(P) reaction mechanism, with catalysis by amine. The optimal mole ratio of ethanol and diethylenetriamine, concerning the velocity of the reaction, is 2:1.

ИЗВОД

АЛКОХОЛИЗА 1,2,2-ТРИМЕТИЛПРОПИЛ-МЕТИЛФЛУОРОФОСФАТА

МЛАЂЕН Л. МИЋЕВИЋ¹ и СЛОБОДАН Д. ПЕТРОВИЋ²

¹Институт за безбедносћ, 11000 Београд и ²Каџедрa за орѓанску хемију, Технолошко-металуришки факултет, б. бр. 35-03, 11001 Београд

Испитана је алкохолиза 1,2,2-триметилпропил-метилфлуорофосфоната (соман) са низом алкоксида у одговарајућим алкохолима: метанол, етанол, 1-пропанол, 2-пропанол, 2-метоксиетанол и 2-етоксиетанол. Соман реагује са испитиваним алкоксидима у реакцији другог реда, првог реда према сваком реактанту. Испитана је и кинетика реакције између 1,2,2-триметилпропил-метилфлуорофосфоната и диетилентриаминa у етанолу. Реакција је укупно трећег реда, првог према сваком реактанту. За испитиване реакције су израчунате: енергије активације, фактори фреквенције и ентропије активације.

(Примљено 12. априла, ревидирано 20. августа 2000)

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