

# Kinetic Study by Proton Nuclear Magnetic Resonance Spectroscopy of the Reaction between Ethyl Pyruvate and Diethyl Phosphite Yielding 2-Diethoxyphosphonyl-2-Hydroxypropionic Acid Ethyl Ester

John Mikroyannidis, Athanasia Koliadima and George Karaiskakis<sup>†</sup>

Department of Chemistry, University of Patras, GR-26500, Patras, Greece

Mikroyannidis, J., Koliadima, A. and Karaiskakis, G., 1994. Kinetic Study by Proton Nuclear Magnetic Resonance Spectroscopy of the Reaction between Ethyl Pyruvate and Diethyl Phosphite Yielding 2-Diethoxyphosphonyl-2-Hydroxypropionic Acid Ethyl Ester. – Acta Chem. Scand. 48: 865–871 © Acta Chemica Scandinavica 1994.

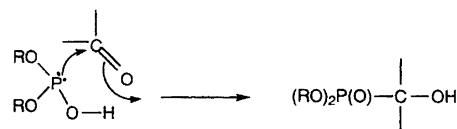
A kinetic study of the reaction of ethyl pyruvate (A) with diethyl phosphite (B) yielding 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester (C), an intermediate product for the preparation of 2-dihydroxyphosphonyl-2-hydroxypropionic acid, which can be used as a corrosion and scale inhibitor, was carried out in the present work by using the technique of proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy. The <sup>1</sup>H-NMR spectra of the reaction mixture show that the singlet at 2.07δ assigned to CH<sub>3</sub>COCOOEt (reactant A) was reduced, while that at 5.48δ assigned to the hydroxyl proton of the reaction product C was increased with the progress of the chemical reaction, making possible a kinetic study of the reaction mentioned. The reaction of A with an equimolar amount of B yielding C was found to be of second order (first order with respect to A and first order with respect to B). On the other hand the reaction between A and B when the reagent B is in excess (molar ratio  $n_A/n_B = 1:3$ ) was found to be of pseudo-first order with respect to A, although we believe that the apparent and not the intrinsic order of the reaction is changed by using a 1:3 ratio of reagents. Arrhenius activation parameters ( $E_a$ ,  $\ln A$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) were computed in both cases.

Most characteristics of nuclear magnetic resonance spectra are influenced to some extent by the various motions of the molecules, ions or atoms containing, or in the vicinity of, the nuclei observed. These effects provide several methods of studying a wide range of kinetic phenomena.

Among the many types of rate processes amenable to NMR study are (i) the formation of urethane,<sup>1</sup> (ii) the functionalization of polymethyl acrylate by reaction with ethanolamine,<sup>2</sup> (iii) the enzymatic hydrolysis of various disaccharides,<sup>3</sup> (iv) the immobilization of polymers,<sup>4</sup> (v) the cationic homo- and copolymerization of trioxane,<sup>5</sup> (vi) the thermal imidization of polymers,<sup>6,7</sup> (vii) the radical polymerization of diethylaminoethyl methacrylate,<sup>8</sup> (viii) the phase separation of various solutions,<sup>9</sup> (ix) the chemical kinetics of various sol-gel systems,<sup>10</sup> and (x) the hydrolysis, adsorption and dynamics of silane coupling agents of silica surfaces.<sup>11</sup>

Dialkyl phosphites add readily to the carbonyl groups

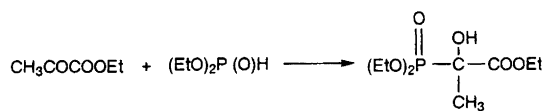
of simple aldehydes and ketones, to give 1-hydroxyalkyl-1-phosphonate esters.<sup>12</sup> The reaction is catalyzed by the presence of catalytic amounts of a strong base.<sup>13</sup> In some cases the reaction occurs in the absence of added base. Very strong electrophilic carbonyl compounds, such as chloral,<sup>14,15</sup> react with the neutral species even at room temperature. It is believed that the rate of the reaction with the tiny proportion of the phosphite form, (RO)<sub>2</sub>P(OH), is high enough with a very reactive substrate to account for the reaction. Nucleophilic attack of the phosphorus on the carbonyl carbon occurs; this is followed by a proton transfer that stabilises the adduct.<sup>16</sup>



Addition of dialkyl phosphites to be carbonyl group can be reversed, but equilibrium favours addition under normal conditions.

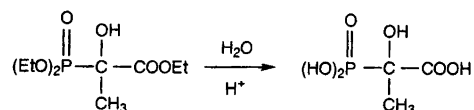
<sup>†</sup> To whom correspondence should be addressed.

The present investigation deals with the kinetic study by  $^1\text{H-NMR}$  of the reaction between ethyl pyruvate and diethyl phosphite on the basis of the simple integration curve of the  $^1\text{H-NMR}$  spectra. More particularly, the reaction of ethyl pyruvate with diethyl phosphite to afford 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester was selected.<sup>17</sup>



The carbonyl group of ethyl pyruvate is strongly electrophilic owing to the presence of the electron-withdrawing ester group in the  $\alpha$ -position, thus favouring the nucleophilic attack of phosphorus. A kinetic study of the reaction between ethyl pyruvate and diethyl phosphite was carried out in a molar ratio 1:1 and 1:3. In the latter case, diethyl phosphite acted both as a reagent and as reaction medium.

2-Diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester has been hydrolyzed in the presence of acids to the corresponding phosphonic acid, which can be used as corrosion and scale inhibitor.<sup>17,18</sup>



The reaction of ethyl pyruvate with diethyl phosphite is therefore of interest because affords an intermediate product for the synthesis of a hydroxy- and carboxy-substituted phosphonic acid. Phosphonic and bisphosphonic acids containing hydroxy and/or carboxy substituents have valuable properties as ferrous corrosion inhibitors and scale control additives for circulating water systems.<sup>17,18</sup> Along with polyelectrolytes, they are among the most effective scale inhibitors, and are able to retard or to block the growth process, even though their added concentrations are far below the stoichiometric quantity normally needed for coordination of the cations in solution.

## Experimental

**Reagents.** Diethyl phosphite (Merck) was purified by distillation under reduced pressure. Ethyl pyruvate (Aldrich) was used as supplied.

**Apparatus.** Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra were obtained on a Varian T-60A spectrometer operating at 60 MHz and at 30°C, the normal probe temperature, with an average deviation in total integral reproducibility of about 2%. Chemical shifts ( $\delta$ ) are given in ppm with tetramethylsilane as internal standard.

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer with NaCl cells.

Oil baths stirred and heated at a constant temperature ( $\pm 0.5^\circ\text{C}$ ) were used for the kinetic study of the chemical reaction.

**Preparation and characterization of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester.** A flask equipped with a magnetic stirrer and a condenser was charged with a mixture of ethyl pyruvate 98% (7.12 g, 60 mmol) and diethyl phosphite (8.28 g, 60 mmol). The mixture was stirred and heated at 70–75°C for 90 h. A small amount of the unreacted starting materials was subsequently removed from the reaction mixture by distillation under reduced pressure (0.9 mmHg). 2-Diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester was obtained as a viscous undistillable liquid (13.50 g, 93%).

IR (neat)  $\text{cm}^{-1}$ : 3480–3250 (OH stretching); 2960, 2926 (C–H stretching); 1744 (C=O stretching); 1408 (OH deformation); 1280 (C–O–C stretching); 1257 (P=O); 1070–995 (P–O–C).

$^1\text{H-NMR}$  (neat)  $\delta$ : 5.48 (s, 1H, OH); 3.83 (m, 6H,  $\text{OCH}_2\text{CH}_3$ ); 1.30 (d,  $J_{\text{PCCH}} = 16$  Hz, 3H,  $\text{PCCH}_3$ ); 1.05 (t, 9H,  $\text{OCH}_2\text{CH}_3$ ).

**General procedure for the kinetic study of the reaction between ethyl pyruvate and diethyl phosphite.** A flask equipped with a magnetic stirrer and a condenser was charged with a mixture of ethyl pyruvate (reagent A) and diethyl phosphite (reagent B) in a molar ratio 1:1 or 1:3. The mixture was heated by means of an oil bath at a constant temperature of 50, 60, 70, 80 or 100°C for various times, depending on the working conditions. The reaction was monitored by  $^1\text{H-NMR}$  spectroscopy. For this purpose, aliquots of the reaction mixture were obtained at regular times, and after cooling at ambient temperature they were immediately examined by  $^1\text{H-NMR}$ . All the experiments were repeated three times, so the given values of rate constants in Tables 1 and 2 are the average values of these three measurements. In all cases the reaction was monitored up to about 95%, as was justified from the NMR integration height of  $\text{CH}_3\text{COCOOEt}$  near 2.07 $\delta$ .

**Table 1.** Rate constants,  $k$ , determined by NMR spectroscopy, for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester with equimolar amounts of ethyl pyruvate and diethyl phosphite, at various temperatures.

T/K	$10^5 k^a / \text{l mol}^{-1} \text{s}^{-1}$
323.2	$2.14 \pm 0.02$
333.2	$4.34 \pm 0.26$
343.2	$9.17 \pm 0.30$
353.2	$17.84 \pm 0.67$
373.2	$64.36 \pm 0.33$

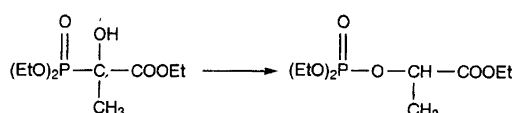
<sup>a</sup>All errors given in this and at the following tables are standard errors.

Table 2. Rate constants,  $k$ , determined by NMR spectroscopy, for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid from the reaction between ethyl pyruvate (A) and diethyl phosphite (B), when the reagent B is in excess ( $n_A:n_B=1:3$ ), at various temperatures.

$T/K$	$10^5 k/s^{-1}$
323.2	$1.22 \pm 0.08$
333.2	$3.24 \pm 0.14$
343.2	$5.45 \pm 0.83$
353.2	$8.49 \pm 0.58$
373.2	$39.98 \pm 0.21$

## Results and discussion

The reaction of ethyl pyruvate with diethyl phosphite afforded 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester.<sup>17</sup> The latter was characterized by IR and <sup>1</sup>H-NMR spectroscopy (see Experimental section). Upon heating the reaction mixture at 50–100°C, no isomerization of the reaction product to the corresponding phosphate was observed.<sup>17</sup>



Figs. 1 and 2 present the NMR spectra of ethyl pyruvate (A), diethyl phosphite (B) and 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester (C) mixture when  $n_A:n_B=1:1$  and  $n_A:n_B=1:3$ , respectively, as a function of the reaction time and at 333.2 K.

Upon comparing Figs. 1 and 2 it is seen that the progress of the reaction could be followed by <sup>1</sup>H-NMR. More particularly, the singlet near 2.07 $\delta$  assigned to  $\text{CH}_3\text{COCOOEt}$  was reduced, while that near 5.48 $\delta$  assigned to the hydroxyl proton of the reaction product was increased, with the progress of the chemical reaction. In addition, a doublet ( $J_{\text{pCCH}}=16$  Hz) associated with these methyl protons of the reaction product appeared around 1.30 $\delta$ . The right leg of this doublet overlapped with the left leg of the triplet near 1.05 $\delta$  assigned to the  $\text{CH}_3\text{CH}_2\text{O}$  protons. The reaction was completed when the singlet at about 2.07 $\delta$  disappeared. Furthermore, the proton of the singlet at 5.48 $\delta$  exchangeable with  $\text{D}_2\text{O}$  shows the presence of the hydroxyl group. Finally the multiplet near 3.83 $\delta$  was assigned to the methylene protons ( $\text{OCH}_2\text{CH}_3$ ) of the reagents ethyl pyruvate and diethyl phosphite, as well as of the reaction product (the ethyl ester of phosphonic acid and carboxylic acid). Note that the total number of methylene protons appearing near 3.83 $\delta$  remained constant during the reaction course. Therefore, the kinetic study of the reaction can be based either on the ratio of the NMR integration height of  $\text{CH}_3\text{COCOOEt}$  near 2.07 $\delta$  to that of  $\text{OCH}_2\text{CH}_3$  around 3.83 $\delta$  or on the ratio of the NMR integration height of

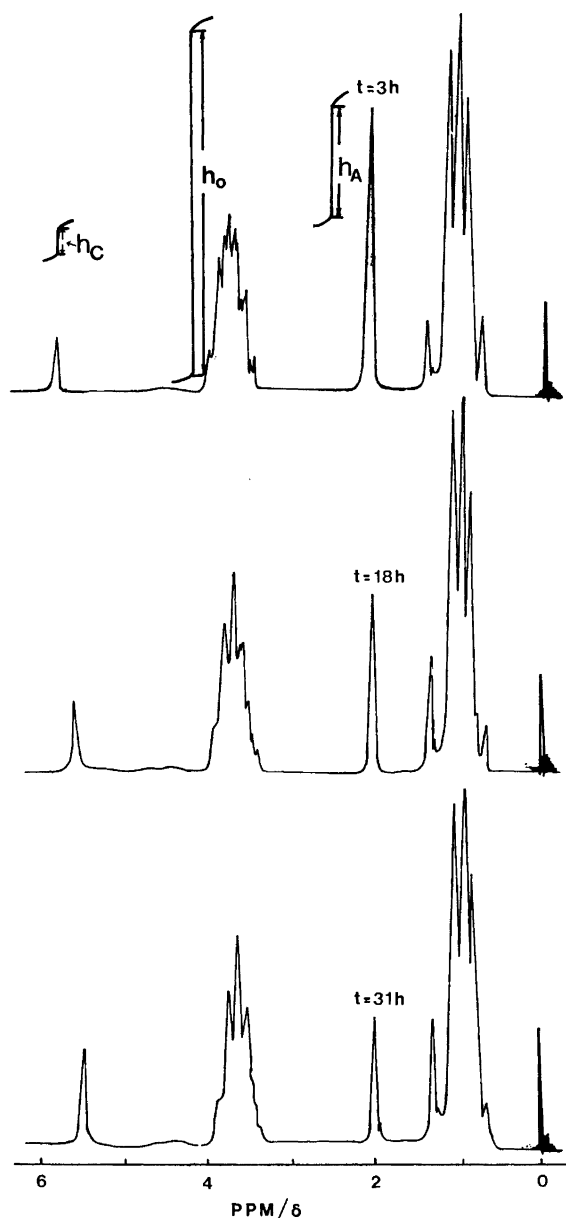


Fig. 1. <sup>1</sup>H-NMR spectra of ethyl pyruvate and diethyl phosphite equimolar mixture at various times and at a constant temperature ( $T=333.2$  K).

hydroxyl proton of the reaction product near 5.48 $\delta$  to that of  $\text{OCH}_2\text{CH}_3$  around 3.83 $\delta$ , which is kept constant during the whole experiment.

A reaction is classified as first-order if a plot of  $\ln c_A$  against  $t$  gives a straight line according to the equation

$$\ln c_A = \ln(c_A)_0 - kt \quad (1)$$

There are two possibilities for second-order reactions: the rate may be proportional to the product of two equal concentrations or to the product of two different ones. The first situation corresponding to equimolar amounts of the two reactants ( $n_A:n_B=1:1$ ) gives the eqn. (2),

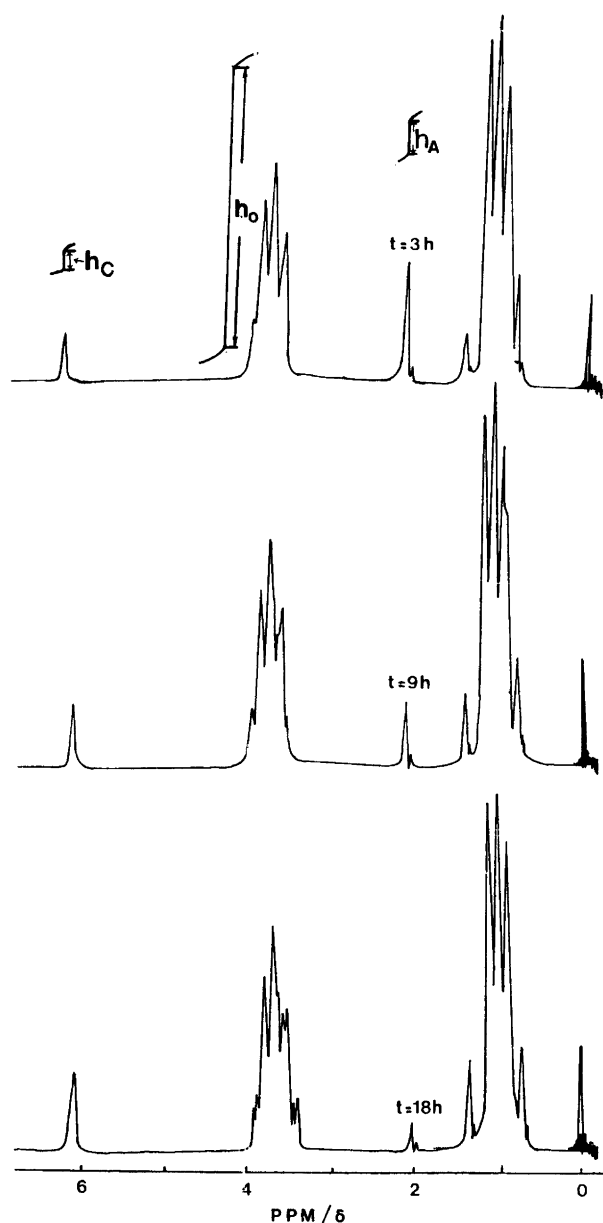


Fig. 2.  $^1\text{H-NMR}$  spectra of ethyl pyruvate (A) and diethyl phosphite (B) mixture, when the reagent B is in excess ( $n_{\text{B}}:n_{\text{A}}=3$ ), at various times and at a constant temperature ( $T=333.2\text{ K}$ ).

$$\frac{1}{c_{\text{A}}} = \frac{1}{(c_{\text{A}})_0} + kt \quad (2)$$

while the second, corresponding to the case in which reagent B is in excess ( $n_{\text{A}}:n_{\text{B}}=1:3$ ) gives the following relation:<sup>19</sup>

$$\ln \frac{c_{\text{A}}}{c_{\text{B}}} = \ln \frac{(c_{\text{A}})_0}{(c_{\text{B}})_0} + [(c_{\text{A}})_0 - (c_{\text{B}})_0]kt \quad (3)$$

It is characteristic of first- or second-order reactions that, as eqns. (1)–(3) show, all that need be measured to see whether or not a reaction is first- or second-order are

the concentrations of the reactants or of the product at various times. The measurement of any quantity that is proportional to these concentrations can therefore be used, and the actual concentrations need to be calculated. Thus, if some quantity, such as the heights  $h_{\text{A}}$ ,  $h_{\text{B}}$  and  $h_{\text{C}}$  of the steps obtained in the present work by the integral mode of the NMR spectra (cf. Figs. 1 and 2), are related to the concentrations  $c_{\text{A}}$ ,  $c_{\text{B}}$  and  $c_{\text{C}}$  or to the equivalent numbers of nuclei underneath the signals, by the proportionally equations:

$$c_i = \lambda h_i/h_0, \quad (c_i)_0 = \lambda h_i^0/h_0 \quad (4)$$

where  $i = \text{A or B or C}$ , then eqns. (1)–(3) become

$$\ln \frac{h_{\text{A}}}{h_0} = \ln \frac{h_{\text{A}}^0}{h_0} - kt \quad (5)$$

$$\frac{h_0}{h_{\text{A}}} = \frac{h_0}{h_{\text{A}}^0} + \lambda kt = \frac{h_0}{h_{\text{A}}^0} + (c_{\text{A}})_0 \frac{h_0}{h_{\text{A}}^0} kt = \frac{h_0}{h_{\text{A}}^0} + 1.07 kt \quad (6)$$

$$\ln \frac{h_{\text{A}}}{h_{\text{B}}} = \ln \frac{h_{\text{A}}^0}{h_{\text{B}}^0} + \left( \frac{\lambda}{h_0} (h_{\text{A}}^0 - h_{\text{B}}^0) \right) kt \quad (7)$$

Considering that during our experiments we can measure by the NMR technique only the heights  $h_{\text{A}}$  and  $h_{\text{C}}$ , which are proportional to the respective concentrations  $c_{\text{A}}$  and  $c_{\text{C}}$  as can be seen from Figs. 1 and 2, eqn. (7) can be converted into the following relation, applying the stoichiometric proportionalities ( $n_{\text{A}}:n_{\text{B}}=1:3$ ) used in the present study:

$$\ln \frac{h_{\text{A}}}{\left( \frac{h_0(c_{\text{B}})_0}{\lambda} - h_{\text{C}} \right)} = \ln \frac{h_{\text{A}}^0}{h_{\text{B}}^0} + \left( \frac{\lambda}{h_0} (h_{\text{A}}^0 - h_{\text{B}}^0) \right) kt \quad (8)$$

since

$$h_{\text{B}} = \frac{h_0 h_{\text{B}}^0}{h_0} - h_{\text{C}} = \frac{h_0(c_{\text{B}})_0}{\lambda} - h_{\text{C}} \quad (9)$$

In the last two equations  $h_0$  is the height of the step in the integral mode of the NMR spectra assigned to  $\text{OCH}_2\text{CH}_3$ , which is kept constant during the whole experiment, since the methylene groups both of the reactants and the reaction product appeared in the same spectral region. The ratio  $h_i/h_0$  is used instead of the absolute height  $h_i$ , in order to avoid accidental experimental errors, because measurements of the heights of the integration steps were performed utilizing different spectral amplitudes in each case. The value of  $h_{\text{A}}^0$  corresponding to the NMR spectra of  $\text{CH}_3\text{COCOOEt}$  is referred to the initial concentration of ethyl pyruvate (zero reaction time), while a value of  $\lambda = 1.07\text{ mol l}^{-1}$  was found experimentally from the known values of  $(c_{\text{A}})_0$ ,  $h_0$  and  $h_{\text{A}}^0$ , via eqn. (4).

All the experimental data are plotted according to eqns. (5), (6) and (8) in order to verify the order of the reaction

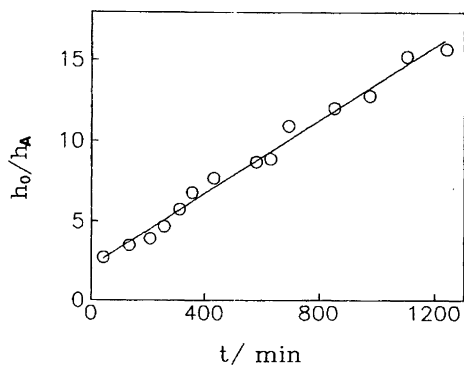


Fig. 3. Plot of eqn. (6). The experimental data were obtained from the NMR spectra of ethyl pyruvate and diethyl phosphite equimolar mixture ( $T=353.2$  K).

under the experimental conditions used. Figure 3 shows the variation of  $h_0/h_A$  vs.  $t$ , when equimolar amounts of the two reactants were used. This plot shows that the reaction between equimolar amounts of ethyl pyruvate and diethyl phosphite is of second order (first order with respect to ethyl pyruvate and first order with respect to diethyl phosphite), since all the experimental data obey only eqn. (6). On the other hand, Fig. 4 shows that the reaction between ethyl pyruvate (A) and diethyl phosphite (B), when reagent B is in excess ( $n_A:n_B = 1:3$ ), is of first order with respect to A, since all the experimental data are fitted only to eqn. (5). We believe that the apparent and not the intrinsic order of the reaction is changed by using the 1:3 ratio of reagent, since such a ratio is not large enough to assume that the reaction is going to be pseudo-first order.

The rate constants,  $k$ , for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester are given (with the aid of the reaction between ethyl pyruvate and

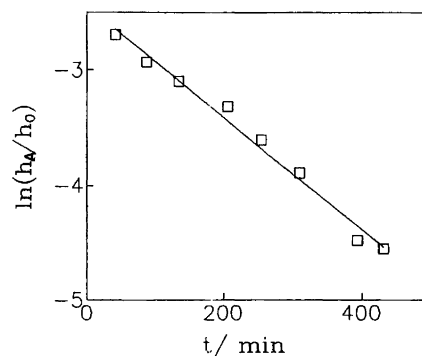


Fig. 4. Plot of eqn. (5). The experimental data were obtained from the NMR spectra of ethyl pyruvate (A) and diethyl phosphite (B) when  $n_B:n_A = 3$  ( $T=353.2$  K).

diethyl phosphite, obtained by the NMR spectroscopy) in Tables 1 and 2 and are shown as Arrhenius plots in Figs. 5 and 6. The best straight lines through the experimental points were calculated by a least-squares analysis.

The activation parameters  $E_a$  and  $\ln A$ , calculated from the known Arrhenius equation, are given in Table 3. In the same table are compiled the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  determined from the following relations:

$$\Delta H^\ddagger = E_a - R\bar{T} \quad (10)$$

$$\Delta S^\ddagger = \left[ \ln A - \ln \left( \frac{kT}{h} \right) - 1 \right] R \quad (11)$$

where  $\bar{T}$  ( $= 345.2$  K) is the average working temperature and  $k$  is Boltzman's constant.

It can be seen from Table 3 that the activation parameters found in the present work for the two cases applied ( $n_A:n_B = 1$  and  $n_A:n_B = 1:3$ ) are almost identical. This suggests that the energy barrier for the synthesis of

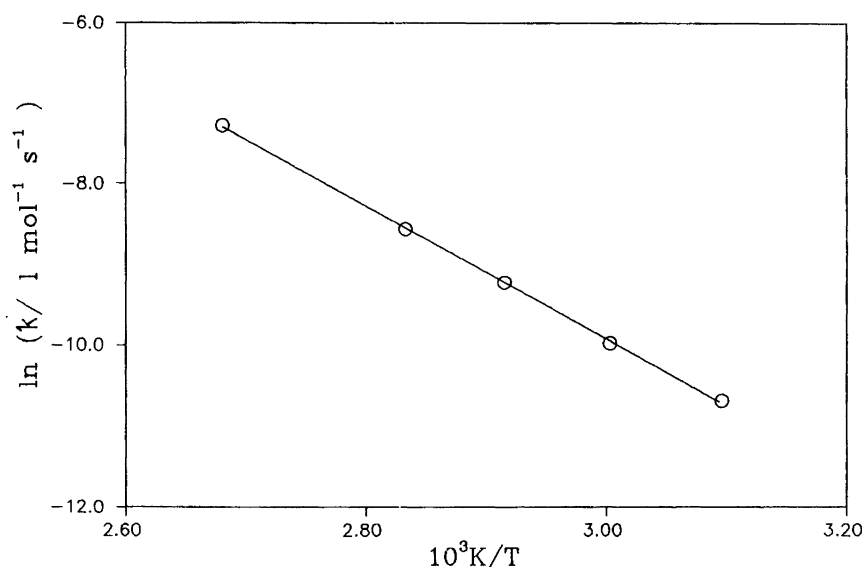


Fig. 5. Arrhenius plot for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester with equimolar amounts of ethyl pyruvate and diethyl phosphite.

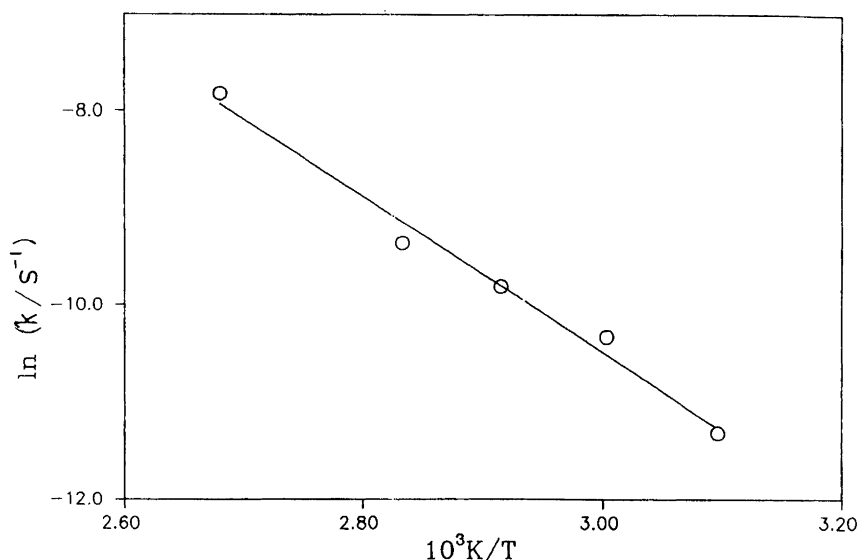


Fig. 6. Arrhenius plot for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester from the reaction between ethyl pyruvate (A) and diethyl phosphite (B) when  $n_B:n_A=3$ .

2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester is independent of the ratio of the reactants used, since as it was pointed out earlier the apparent and not the intrinsic order of the reaction is changed by varying the ratio of the reagents from 1:1 to 1:3. A similar result was obtained by Jönsson and Flodin<sup>1</sup> in a kinetic study of the formation of polyurethane, which has been followed by *in situ* <sup>1</sup>H-NMR. Another important conclusion can be drawn from the negative values of the entropy of activation,  $\Delta S^\ddagger$ , according to which the less free translations and rotations are lost and are replaced by vibrations, although solvation is an appreciable factor in determining the entropy of the system.

The reaction was kinetically studied for a long period of time (20 h in the case of  $n_A:n_B = 1:1$  and 7 h in the case of  $n_A:n_B = 1:3$ ) and it was almost completed, as the experimental data show. The linearity of the curves in Figs. 3 and 4 over the whole timescale shows that the dilution caused by the production of the product and the changes in polarity and viscosity during the whole experiment do not influence the determined rate constants.

A comparison of the present results with others in the literature is not possible, because as far as we know the

Table 3. Activation parameters ( $E_a$ ,  $\ln A$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) determined by the NMR spectroscopy, for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester from the reaction between ethyl pyruvate (A) and diethyl phosphite (B).

Parameter	$n_A:n_B = 1:1$	$n_A:n_B = 1:3$
$E_a/kJ\ mol^{-1}$	$68.4 \pm 0.7$	$67 \pm 5$
$\ln(A/l\ mol^{-1}\ s^{-1})$	$14.7 \pm 0.3$	$\ln(A/s^{-1})$
$\ln A$	$14.7 \pm 0.3$	$13.6 \pm 2$
$\Delta H^\ddagger/kJ\ mol^{-1}$	$65.6 \pm 0.7$	$64 \pm 5$
$\Delta S^\ddagger/J\ mol^{-1}\ K^{-1}$	$-132 \pm 3$	$-142 \pm 14$

kinetic study of the reaction between ethyl pyruvate and diethyl phosphite is presented for the first time here.

From the results presented in this paper it is demonstrated that the simple methodology of NMR spectroscopy based on the heights of the steps of the integration curve can be used successfully in a kinetic study of the very important reaction between ethyl pyruvate and diethyl phosphite for the synthesis of 2-diethoxyphosphonyl-2-hydroxypropionic acid ethyl ester, which can be used as a ferrous corrosion or scale inhibitor.

*Acknowledgments.* We thank Mrs. M. Barkoula for her kind assistance.

## References

- Jönsson, K. J. and Flodin, P. *Br. Polym. J.* 23 (1990) 71.
- Yu, Y. and Brown, G.R. *Macromolecules* 25 (1992) 6658.
- Rudi, W., Mario, K., Horst, L., Sigrid, M. and Horst, F. *Carbohydr. Res.* 235(4) (1992) 259.
- Junshi, W. and Thomas, E. *Carbohydr. Polym.* 20(1) (1993) 51.
- Lu, N., Collins, G. L. and Yang, N. L. *Polym. Prepr. Div. Polym. Chem., Am. Chem. Soc.* 31(1) (1990) 85.
- Ning-Jo, C. and Jann-Wen, H. *Polym. J.* 22(8) (1990) 725.
- Mikhailova, N. V., Antonov, N. G., Shustrov, A. B., Denisov, V. M. and Kol'tsov, A. I. *Polym. Sci. USSR* 31(9) (1989) 2142.
- Bune, Y. V., Sheinker, A. P., Bogechev, Y. S., Zhuravleve, I. L. and Telezhov, E. N. *Eur. Polym. J.* 27(6) (1991) 509.
- Golub, A. A., Goncharov, V. A., Mikheev, V. A., Rusnak, V. P. and Shvarts, V. A. *Phys. B* 165 (1990) 819.
- Roger, A. and Bruce, K. *Ann. Rev. Mater. Sci.* 21 (1991) 491.
- Blum, F., Meesiri, W., Kang, H.-J. and Gambogi, J. J. *Adhes. Sci. Spectrosc.* 5(6) (1991) 479.
- Abramov, V. S. *Dokl. Akad. Nauk SSSR* 73 (1950) 487; *Chem. Abstr.* 45 (1991) 2855.

13. Pudovik, A. N. and Kitaev, J. P. *Zh. Obshch. Khim.* 22 (1952) 467.
14. Barthel, W. F., Giang, P. A. and Hall, S. A. *J. Am. Chem. Soc.* 76 (1954) 4186.
15. Lorenz, W., Henglein, A. and Schrader, G. *J. Am. Chem. Soc.* 77 (1955) 2554.
16. Kirby, A. J. and Warren, S. G. *The Organic Chemistry of Phosphorus*, Elsevier, New York 1967, p. 58.
17. Mikroyannidis, J. A. *Phosphorus and Sulfur* 32 (1987) 113.
18. Xyla, A. G., Mikroyannidis, J. A. and Koutsoukos, P. G. *J. Colloid Interface Sci.* 153 (1992) 537.
19. Moore, W. J. *Physical Chemistry*, 3rd. edn., Prentice-Hall, NJ 1962, p. 262.

Received March 24, 1994.