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Kinetic Study of the Rearrangement of 0,0-dialkyl -2,2,2- tricloro-1-Hydroxyethylphoshonates

by

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Kinetic Study of the Rearrangement of 0,0-dialkyl -2,2,2- trichloro-1-hydroxyethylphoshonates

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SUMMARY

The kinetic study of the rearrangement of 0, 0-dimethyl-2, 2, 2-trichloro-1-hydroxyethyl phosphonat (Dipterex) and its ethyl analogous to diehlorovinyl dimethylphosphate D.D.V.P and its ethyl analogue in water was carried out by means of a new method. In the previous methods the concentrations were determined by means of P^{32} whereas no tracer has been used in this method. The rate of the reaction was followed in an automatic titrator so that the reaction conducted in the solution containing no buffer. In order to obtain a detailed kinetic picture of this consecutive reaction the kinetics of each step has been studied saparately.

It is found that the rearrangement of phosphonates to phosphates obeys first order kinetics with an acid-base equilibrium prior to the reaarangement. The hydrolysis of dialkylB, B-dichlorovinyl phosphates obeys second order kinetics: first order for hydroxyl ion concentration and first order for the phosphate concentration. The results were compared with the previous reports and a mechanism of the reaction is given.

INTRODUCTION

Mattson, Spillane and Pearce[1] have reported on their original discovery that 0,0-dimethyl -2, 2, 2 - trichloro-1-hydroxyethylphosphonate (Dipterex or Bayer L 13/59) (I) undergoes dehydrochlorination in the presence of alkali to yield a volatile, more toxic ester which they assigned a keto structure. Barthel, Giang and Hall[2] have proved that this new insectiside was dimethyl-2, 2-dichlorovinylphosphate, D. D. V. P. (II).

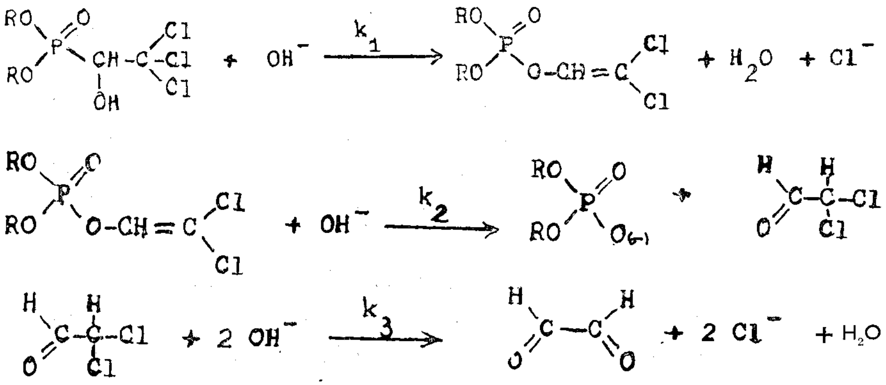
Lorenz, Henglein and Schrader[3] according to the infrared spect ra also proved that Dipterex undergoes a rearrangement reaction by the effect of alkali to give dichlorovinyl phosphate ester.

$$(CH_3O)_2P(O)CH(OH)CCl_3 \xrightarrow[-HCl]{OH^-} (CH_3O)_2P(O)OCH{=}CCl_2 \quad (1)$$

The first kinetic study on this rearrangement was performed by Müehlmann and Schrader[4] in Sörensen buffer and concentrations was determined by means of P^{32}. The kinetic study of the hydrolysis of dimethyl 2,2- dichlorovinylphosphate followed by the concentration of the unchanged DDVP labeled with P^{32}.

The second kinetic study on this reaction was performed by Metcalf and Fukuto[5] They also used P^{32} labeled Dipterex for kinetic measurments and Sörensen buffer for a fixed pH. They estimated concentration by three different methods: paper chromatography, separation by liquid-liquid partition, and cloride in determination.

We found that Sörensen buffer can not keep its buffer effect along the reaction, that it can proceeds as pseudo-first order up to about 20-25 % completion. So we felt that a kinetic study over a wider pH range which the hydroxyl ion concentrations remain constant might help to explain the mechanism of this important type of rearrangement. Under the chosen conditions (pH 10-11 and 30-45 °C) the alkaline decomposition of Dipterex (I) and 0,0-diethyl-2,2,2- trichloro- 1,-hydroxyethylphosponate (III) is more complicated than expressed in equation (1) because of the hydrolysis of the rearragement products DDVP and diethyl-2,2- dichlorovinylphosphate (IV) to give dichloro acetaldehyde and alkyl phosphates and the hydrolysis of dichloro acetaldehyde:



In this work the hydrolysis of both phosphonate and phosphate esters was followed to approximately 75 % of completion. Hydroxide ion concentrations were kept constant by an automatic titration system.

The rearrangment reaction was found to obey first order kinetics although it was expected pseudo-first order according to the results of previous works. Figure 1 reprsents a rate curve for the rearrangement step (rearrangement of 2, 2, 2- trichloro-1-hyrdoxyethyldiethyl phosphonate at 30 ° and pH 10.)

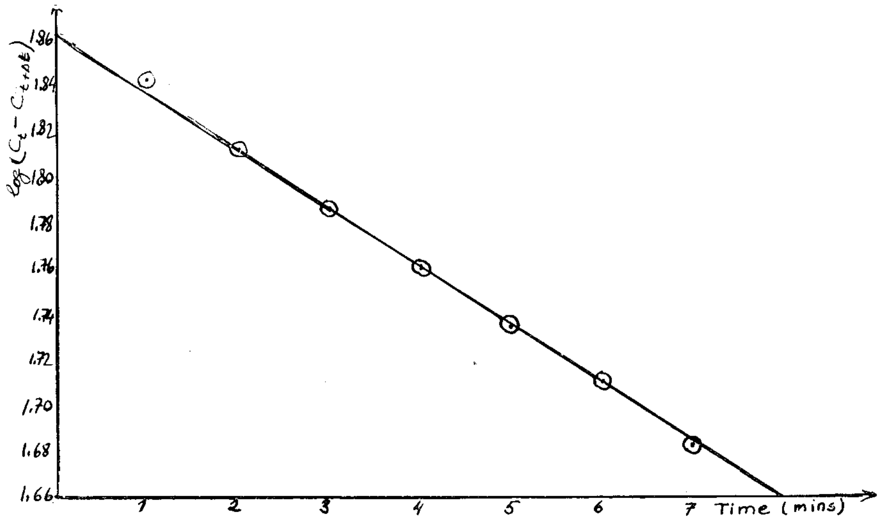


Figure 1

The rate constants given by Metcalf and Fukuto [5] for this rearrangement reaction at 37.5 °C are:

pH	k(min^{-1})	t 1/2 (min)
8	$1.1 \ 10^{-2}$	63
7	$1.8 \ 10^{-3}$	386
6	$1.3 \ 10^{-4}$	5340

The ratio of the rate constants at pH 8 and 6 is approximately 100 and the reaction seems as second order. In Table I and Table

II the rate constants for the reaarrangement step at various pH and temparatures are summarized for Dipterex and its ethyl analogous respectively. The rate constants at 30 °C for the reaarrangement of Dipterex and its ethyl analogous are plotted as function of pH in Figure 2 and 3 respectively. It. is seen that the rate of the rearrangement reaction is proportional with the hydroxide ion concentration at the beginning. Then it changed quickly A levelling-off of the rate when the system is sufficiently basic, indicates the prior equilibrium between substrate and hydroxide ion followed by rearrangement step.

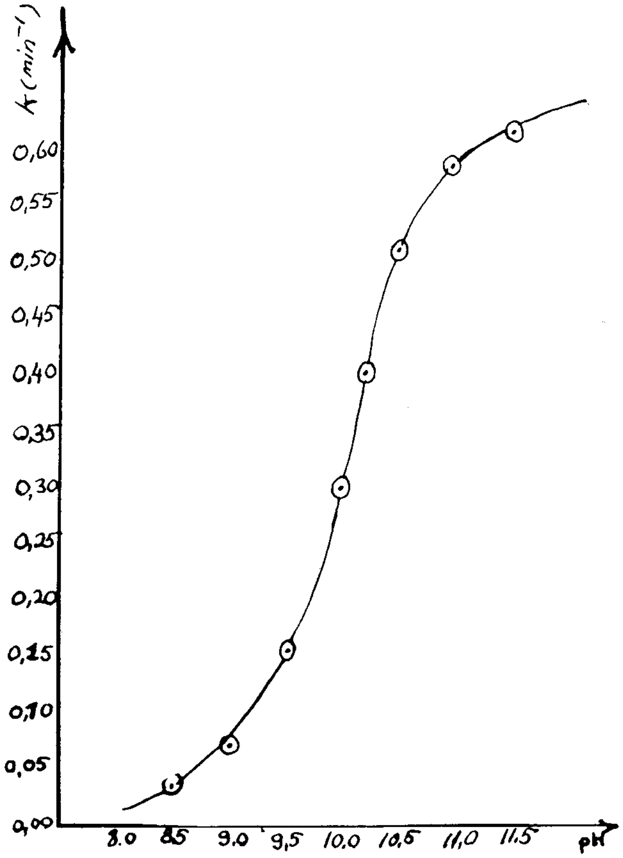


Figure 2

$$SH + OH^- \overset{K}{\rightleftarrows} S^- + H_2O$$

$$S^- \xrightarrow{k_1} \text{rearrangement products.}$$

The rate of the reaction depends on both k_1 and K.

$$\text{Rate} = k_1 [S^-] = k_1 K [SH] [OH^-]$$

TABLE 1

The rate constants of the rearrangement of Dipterex to DDVP

pH	temp. °C	k(min)$^{-2}$
8.5	30	2.92 10^{-2}
9.0	30	7.02 10^{-2}
9.5	30	1.54 10^{-1}
10.0	25	1.62 10^{-1}
10.0	30	2.91 10^{-1}
10.0	35	5.65 10^{-1}
10.2	30	3.96 10^{-1}
10.5	30	5.16 10^{-1}
11.0	22	2.14 10^{-1}
11.0	25	3.10 10^{-1}
11.0	30	5.90 10^{-1}
11.5	30	6.32 10^{-1}

TABLE II

The rate constants of the rearrangement of 2,2,2-trichloro-1-hydroxyethyldiethyl phosphonate to dichlorovinylphosphate

pH	Temp. °C	k(min^{-1})
8.5	30	1.52 10^{-2}
9.0	30	2.41 10^{-2}
9.5	30	3.91 10^{-2}
10.0	30	5.71 10^{-2}
10.0	35	1.09 10^{-1}
10.0	40	2.27 10^{-1}
10.2	30	9.02 10^{-2}
10.5	30	1.30 10^{-1}
11.0	30	1.51 10^{-1}
11.0	35	2.87 10^{-1}
11.0	40	5.71 10^{-1}

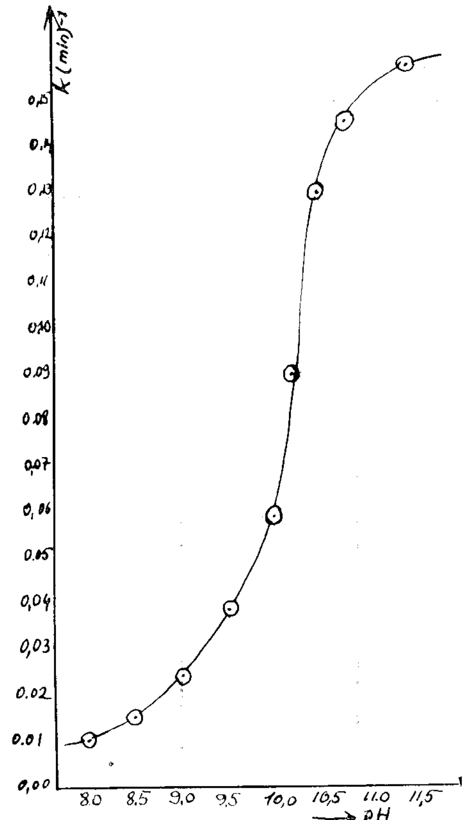


Figure 3

The difference between the results of various kinetic works depends on the difference between the chosen reaction conditions. At pH 10-11 there is an excess of hydroxide ion to convert all SH molecules into S^- anions, and the reaction obeys first order kinetics.

The rate constants for hydrolysis of D. D. V. P. and diethyl dichlorovinylphosphate are in the Table II and Table IV. The hydrolysis of dialkyldichlorovinylphoshates obeys second order kinetics, first order for hydroxide ion concentration and fisrt order for phosphate concentration. Since the hydroxide ion concentration was kept constant the rate must follow pseudo-first order kinetics. The rate constants in Table III and Table IV are in accordance with the theorie. For example: at 35° the rate constants are 1.83 10^{-2} for pH 11 and 1.81 10^{-1} for pH 12. The rate constants in Table III are 7.93 10^{-3} and 8.04 10^{-2} at pH 10 and 11 respectively for 35 °C.

The plot of the log k versus 1/T is shown in Figure 4 for Dipterex, in Figure 5 for its ethyl anologue, in Figure 6 for DDVP, From these figures it is clear that the reaction mechanism of these reactions do not change under the chosen conditions.

TABLE III

The rate constants for the hydrolysis of D.D.V.P.

pH	Temp. °C	k(min^{-1})
10	30	3.91 10^{-3}
10	35	7.93 10^{-3}
10	45	3.98 10^{-2}
11	30	4.22 10^{-2}
11	35	8.04 10^{-2}
11	40	1.49 10^{-1}

TABLE IV

The rate constants of the hydrolysis of 2,2-dichlorovinyldiethylphosphate

pH	Temp. °C	k(min^{-1})
10	47	5.42 10^{-3}
10	53	2.88 10^{-2}
10	55	3.96 10^{-2}
11	35	1.83 10^{-2}
11	40	7.30 10^{-2}
11	45	2.38 10^{-1}
12	30	3.98 10^{-2}
12	35	1.81 10^{-1}
12	40	6.94 10^{-1}

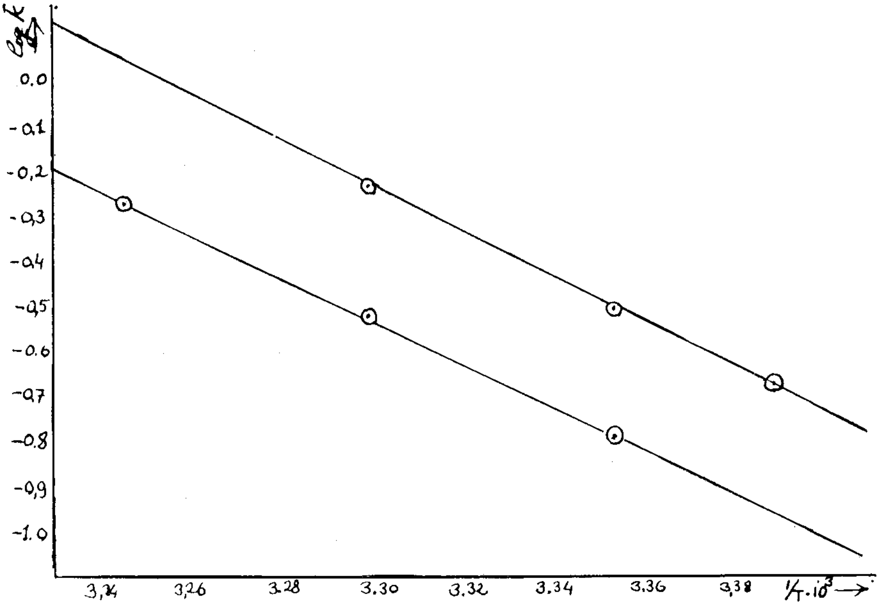


Figure 4

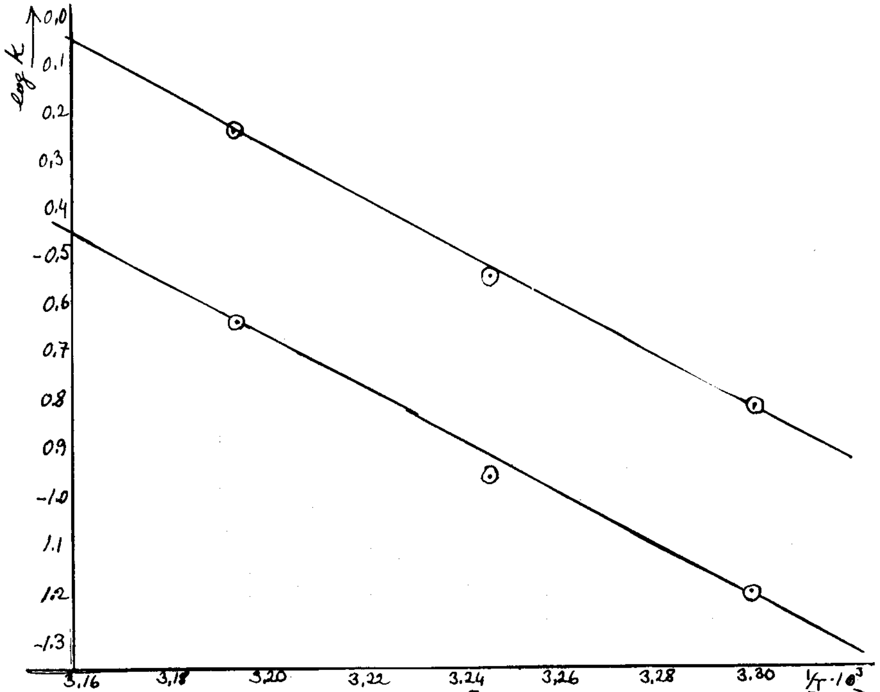


Figure 5

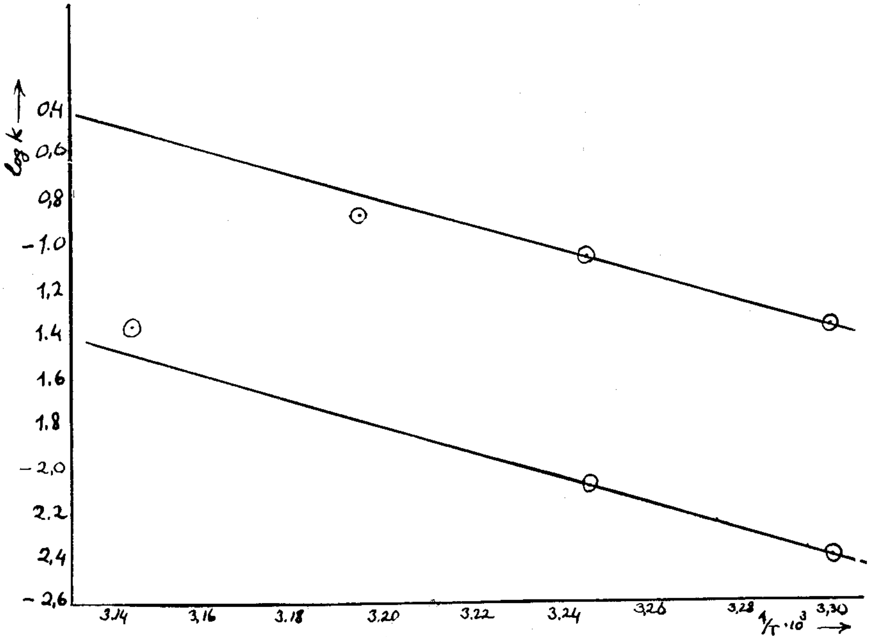


Figure 6

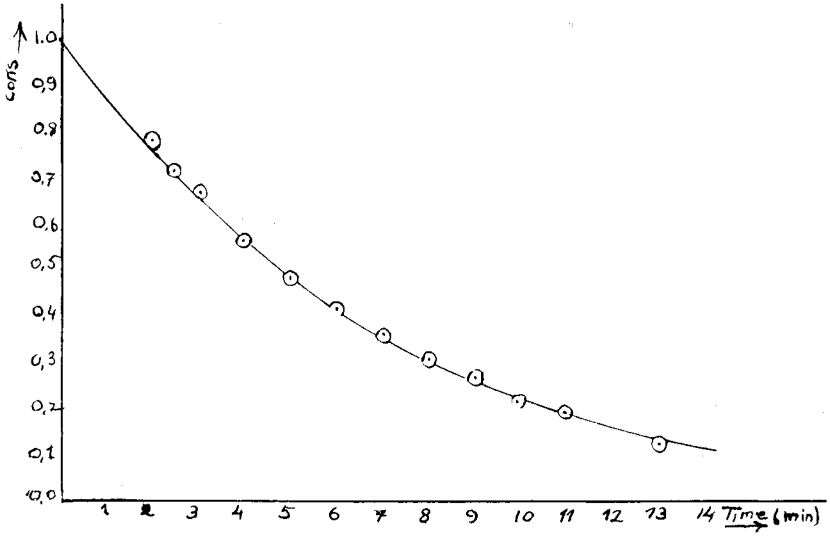


Figure 7

EXPERIMENTAL

Materials:

1. Dipterex was prepared by Lorenz[6] method. The impurities removed by vacuum destilation at 35-37 °C /9 mm. White cristals from ether. m. p. 82 °C Yield: 84 %

Reported values: 78.5-79 °C[1] and 78-80 °C[2]

2- 2, 2, 2- trichlorolro-l-hydroxyethyl diethylphonate

This ester is described as a liquid with a density of d = 1.3850 by Meier-Bode and Kötz[7]. Melnikov[8] gave a melting point for it. (47.5-48 °C) It is also decribed in Field's patent[9] as a liquid (that decomposes over 100 °).

We prepared pure diethyl ester from diethyl phosphite and chloral. It was not to get cristal from the product although it solidifies after cooling. After removed the impurities at 9 mm Hg using a steam bath the solid product was crystallized from ether. m. p 59 °C Yield 81 %

Calculated	C	H	P	Cl
Calculated	25.24	4.24	10.85	37.26
Found	25.30	4.37	10.92	37.04

3- D. D. V. P. Dimethyl 2,2- dichlorovinylphosphate

was prepared from chloral and trimethyl phosphite by Perkow[10] method. b. p. 110 °C /9 mm Hg n_D^{20} 1. 4540 Reported b. p. 100-4 ° / 2,5 mm n_D^{20} = 1.4541

4. Diethyl 2,2-dichlorovinylphosphate - was prepared from chloral and triethyl phosphite by Kharash and Begeldorf[11] method. b. p. 120-1 ° /9 mm Hg, n_D^{20} = 1.4480 Reported: b. p. 69-71 ° /0.5 mm n_D^{20} = 1.4498.

Kinetic measurement for rearrangement reaction:

The rearrangement of Dipterex and its ethyl analogous were performed in vater at varying hydroxide ion concentration (pH = 9-11) and different temparatures (30-45 °). The initial concentrations of the two compound were the same (2.857 10^{-2} M).

The pH was adjusted to the appropriate pH with 0,4 N NaOH using a Radiometer Titrator (T TT I C) and kept there by automatic titration. The amount of sodium hydroxide used at constant pH was registered automatically as function of time A syringe burette of 0.5 ml was used with the titrator. The recorder chart is divided 100 parts and permits to read 5.10^{-3} ml accurately.

To determine k_1 and k_2 independently the reaction was stopped after fixed time intervals by adding small amount of concentrated nitric acid to the reaction mixture and the content of the (reaction cup) washed down into a conical flask and Cl^- ion concentration was determined by semimicro Wolhard method (improved by Caldwell and Mayer[12]

Since the rate studies depend on the determination of Cl^- amount a Hg / Hg_2SO_4 electrod was used as reference instead of calomel and the potential was compensated by a pHA SO_2 mV. Compensater.

The third step of the reaction gives also some Cl^- ions but the experiments showed that this one is so small in compare with the Cl^- amount which comes from the first step.

For example: in the hydrolysis of DDVP at 30 °C and pH=10 the Cl^- after 12 minutes is equivalent to 0,003 ml of 0.05 N silver nitrate whereas under the same condition the Cl^- which comes from the Dipterex $+ OH^- \longrightarrow$ Reaction is equivelent to 2.688 ml of 0,05 N silver nitrate.

The runs were repeated under the same condition and they were stopped after different time intervals from the zero time, (if the reaction enough rapid for example first, second third and forth et. c. minutes. If it is a slow one in every forth minutes 4.8. 12, 16 and 20 minutes.) The estimated Cl^- amounts for a number of runs which performed under the same reaction condition plotted versus time. Figure 2 Shows a representative rate curve obtained by Guggenheim[13] method from this (first) curve-The k_1 values evaluted from the slopes are shown in Table I and Table II

Kinetic Measurements for hydrolysis of phosphate ester.

To determine the rate constant k_2 independently the dichlorovinyl phosphates were prepared and hydrolysis were performed in water at various hydroxide ion concentrations pH = 10-12) and different temperatures (30-60 °). The initial (Starting) concentrations were $2,857.10^{-2}$ M. The pH was adjusted to appropriate pH and kept there by automatic titration. The amount of sodium hydroxide used at the constant pH was automatically registered as function of time.

After various time intervals the reaction was stopped by adding small amount of conc. nitric acid and Cl^- ion concentration was determined by semimiero Volhard method.

The difference between the total base (OH^- amount) consumed for overall raaction and Cl^- ion which only comes from the second step of the reaction, gave the amount of the OH^- ions which used up for only the first step. (Because no Cl^- forms in the first step.) Table III shows. the data obtained at pH 11 and 40 °for the hydrolysis of D. D. V. P.

TABLE V

Time	Syringe NaOH	NaOH 0,05N	Cl^-	OH^- -Cl^-	Hydrolysis %	Rest %
1.5	13.5	0.568	0.046	0.522	14.06	85.94
2.0	17.5	0.737	0.070	0.667	22.23	77.77
2.5	22.0	0.926	0.088	0.838	27.93	72.07
3.0	26.2	1.103	0.103	1.000	33.33	66.67
4.0	34.8	1.465	0.191	1.274	42.46	57.54
5.0	43.0	1.810	0.270	1.540	51.33	48.67
7.0	60.5	2.358	0.541	1.817	60.56	39.44
8.0	68.0	2.863	0.809	1.954	68.46	31.54
9.0	76.0	3.200	1.037	2.163	72.10	27.90
10.0	84.5	3.458	1.106	2.352	78.40	21.60
11.0	90.0	3.747	1.313	2.434	81.10	20.90
13.0	99.8	4.200	1.565	2.635	87.83	12.17

A concentration-time curve depending on the figures in Table V is shown in Figure 7. Figure 8 Shows the rate curve obtained using the Guggenheium method. The k_2 values evaluated from the slopes are shown in Table III and Table IV.

Figure 9 is the plot of ml silver nitrate (equivalent to Cl^- ion) as a function of the time, for the hydrolysis of DDVP.

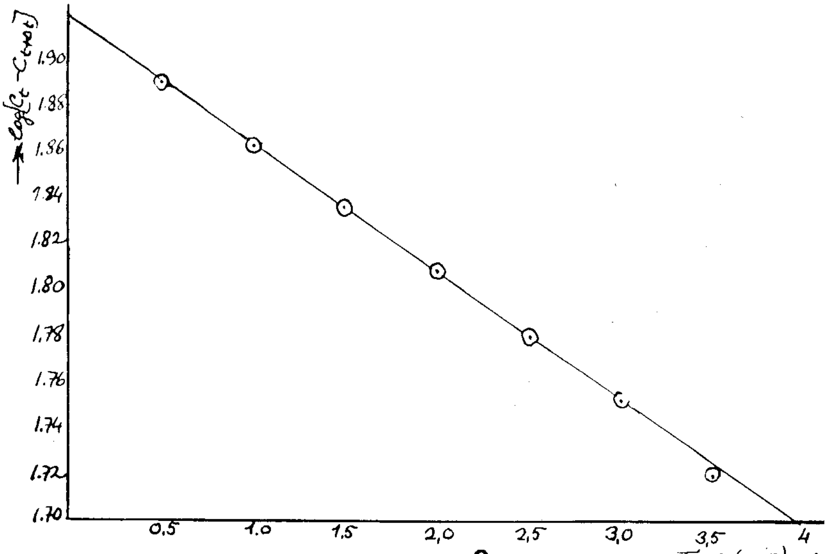


Figure 8

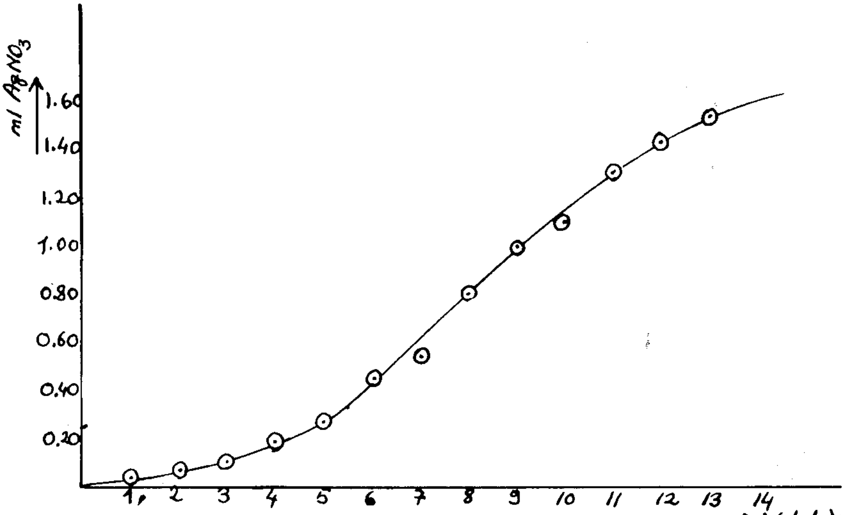


Figure 9

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ÖZET

0,0–dialkil–2, 2, 2–trikloro–1–hidroksietil fosfonatların sulu çözeltide hidroksil iyonlarının etkisile 2,2– diklorovinil dialkil fosfatlara çevrilmesinin kinetiği yeni bir yöntemle incelendi. Daha önceki çalışmalarda konsantrasyonlar P^{32} üzerinden tayin edilirken bu çalışmalarda konsantrasyonlar P^{32} üzerinden tayin edilirken bu çalışmada herhangibir iz element kullanılmamıştır. Reaksiyon hızları otomatik titrasyonla takip edildiğinden tampon çözeltilerde yürütülen çalışmalardakinden çok daha sabit bir pH ta çalışmak mümkün olmuştur. Reaksiyon ardaşık bir reaksiyon olduğundan her basamağı ayrı ayrı incelenmiştir.

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