

**SIMULTANEOUS ELECTRICAL CONDUCTIVITY
AND DTA MEASUREMENTS IN THE STUDY
OF THE PHOSPHONATE-PHOSPHATE REARRANGEMENT
AND ACCOMPANYING PROCESSES**

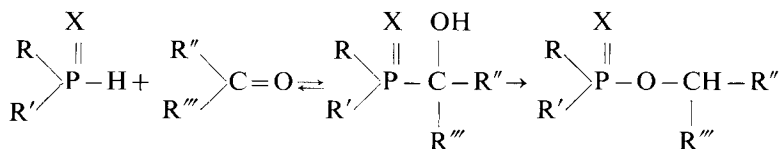
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The application of DTA with the simultaneous recording of electrical conductivity variation in the study of the thermal behaviour of α -oxyalkylphosphonates and their analogues is considered. The investigation of electrical conductivity variation during a reaction helps clarify certain problems of the phosphonate-phosphate rearrangement and the decomposition of α -oxyalkylphosphonates to their components.

Depending on the substituents near the α -carbon atom and on the electronic environment of the phosphorus atom, in the presence of an alkaline catalyst α -oxyalkylphosphonates undergo either phosphonate-phosphate rearrangement or decomposition to the initial components on being heated [1].



R, R' = Alk, Alko, Ph, OH, Et₂N; R'' = Alk, Ph, H, COOEt;
R''' = Alk, H, Ph, COOEt, COCH₃, P(O)(OEt)₂, CN; X = O, S.

We have earlier applied differential thermal analysis to the study of the phosphonate-phosphate rearrangement of α -oxyalkylphosphonic acid esters [2] and some of their analogues [3, 4] containing electron-acceptor substituents near the α -carbon atom. The exothermic effect on the curve corresponds to a rearrangement. The effects of various substituents in the α -oxyalkylphosphonates on their tendency to rearrange were traced by comparing the temperatures of the initial and maximum stages of the exothermic effects. When the carbon atom bonded to the hydroxyl group bears electron-donor or weak electron-acceptor substituents α -oxyalkylphosphonates normally decompose on heating to the initial components, the two processes occurring simultaneously in some cases [5]. On the curves, the decomposition of α -oxyalkylphosphonates is shown by an endothermic effect [6].

We have earlier suggested an ionic mechanism for the rearrangement in the presence of bases [2]. It was also considered very interesting to study the mecha-

nism of the thermal rearrangement of α -oxyalkylphosphonates and that of their decomposition in the presence of alkaline catalysts. In these cases the formation of intermediates of ionic structure could also be assumed.

To solve this problem we employed thermal curves with the simultaneous recording of the electrical conductivity [7].

Some results of these investigations were discussed in [8].

Experimental

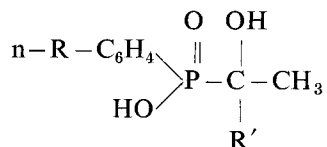
DTA and electrical conductivity variation curves were obtained on the low-frequency NTR-64 thermograph according to the procedure described in [7]. A chromel-alumel thermocouple and platinum electrodes were used. Calcined Al_2O_3 was used as reference. The samples were placed in narrow 110 mm long glass test-tubes ($d = 5$ mm). The thermocouple and electrodes enclosed in ceramic tubes were placed in two separate test-tubes. The ceramic tubes were tightly enclosed by the test-tubes. An elastic pipe was placed on the upper end of the test-tube protruding from the oven so that it also fitted tightly to the ceramic tube with the thermocouple and the electrodes.

There was a special outlet at the top of the test-tube to remove the displaced air and the evolved gases. The weight of the sample was 0.20–0.25 g.

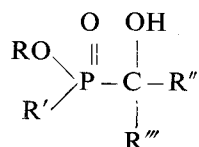
The frequency of the current was 10 kHz, the voltage on the electrodes 0.1 V and the heating rate 3–4°/min.

The ballast resistance of the galvanometer recording the electrical conductivity varied from 61 kohm to 40 ohm in parallel experiments, or was completely eliminated.

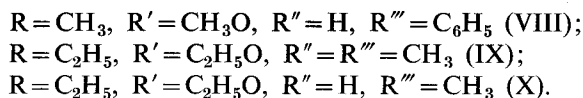
The objects of investigation were substituted α -oxyalkylphenylphosphinic acids [4]:



where $\text{R}=\text{H}$, $\text{R}'=\text{COOC}_2\text{H}_5$ (I); $\text{R}=\text{Br}$, $\text{R}'=\text{COOC}_2\text{H}_5$ (II); $\text{R}=\text{H}$, $\text{R}'=\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ (III); $\text{R}=\text{CH}_3$, $\text{R}'=\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ (IV); and α -oxyalkylphosphine acid esters [2, 3, 9].



where $\text{R}=\text{R}'=\text{C}_2\text{H}_5$, $\text{R}''=\text{CH}_3$, $\text{R}'''=\text{COOC}_2\text{H}_5$ (V);
 $\text{R}=\text{R}'=\text{C}_2\text{H}_5$, $\text{R}''=\text{C}_6\text{H}_5$, $\text{R}'''=\text{COOC}_2\text{H}_5$ (VI);
 $\text{R}=\text{C}_2\text{H}_5$, $\text{R}'=\text{C}_2\text{H}_5\text{O}$, $\text{R}''=\text{CH}_3$, $\text{R}'''=\text{COOC}_2\text{H}_5$ (VII);



The choice of these compounds is due to the fact that (I)–(VII) isomerize to the corresponding phosphates and their analogues, whereas (VIII)–(X) decompose to the initial components. To compare the electrical conductivity variation curves, DTA was performed with the simultaneous recording of the electrical conductivities of some other organophosphorus substances as well: diphenylphosphinic (XI) and phenylphosphonic (XII) acids, diethyl- α -phenylethylphosphate (XIII), dimethyldiphenylphosphonium iodide (XIV), and an equimolecular mixture of triphenylphosphite (XV) and benzyl iodide (XVI).

Results

1. Phenylphosphinic (I)–(IV), (XI) and phenylphosphonic (XII) acids and diethyl- α -phenylethylphosphate (XIII).

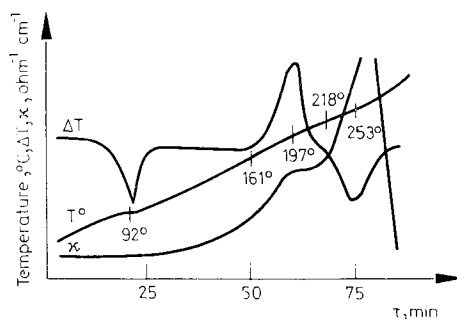


Fig. 1. DTA and electrical conductivity curves for α -oxy- α -carbethoxyethylphenylphosphinic acid ($R = 61 \text{ kohm}$)*

Let us consider the variation of the electrical conductivity on heating α -oxylalkylphenylphosphinic acids (I)–(IV) on the example of α -oxy- α -carbethoxyethylphenylphosphinic acid (I) (Fig. 1). As can be seen from Fig. 1, a conductive phase appears on melting (endothermic effect at 92°). A similar picture is also observed in the case of diphenylphosphinic (XI) and phenylphosphonic (XII) acids (Figs 2 and 3). On further heating the electrical conductivity increases smoothly.

The exothermic effect of the isomerization of α -oxyalkylphenylphosphinic acids (Fig. 1) is shown by an inflection on the electrical conductivity curve. On completion of the rearrangement and until the beginning of the endothermic effect the

* R is the ballast resistance of the galvanometer recording the electrical conductivity.

electrical conductivity stays at roughly the same level, since in the product of isomerization the hydroxyl near the phosphorus atom is retained. The inflection on the electrical conductivity curve at the beginning of the high-temperature endo-

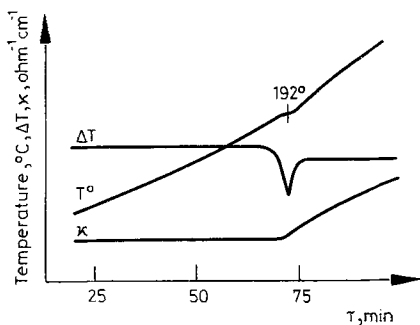


Fig. 2. DTA and electrical conductivity curves for diphenylphosphinic acid ($R = 61 \text{ kohm}$)

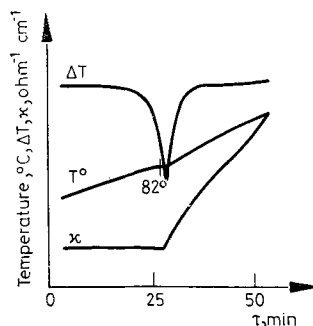
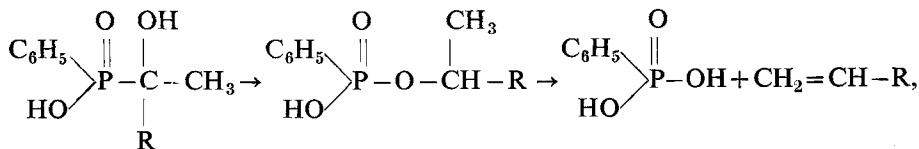


Fig. 3. DTA and electrical conductivity curves for phenylphosphonic acid ($R = 61 \text{ kohm}$)

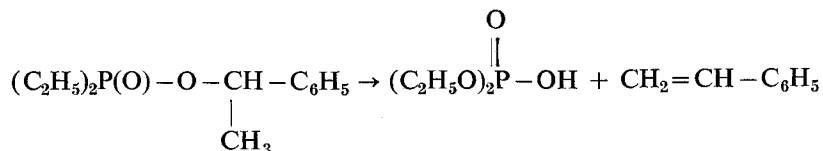
hermic effect reflects the appearance of the phosphoric acid in the system as a result of the decomposition of the products of isomerization [8]



where $R = \text{COOC}_2\text{H}_5$, $\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$.

(The electrical conductivity falls afterwards since a further decomposition of the products occurs.)

For the sake of comparison we obtained the curves for diethyl- α -phenylethylphosphate (XIII) (Fig. 4), which, as shown in [10], produces styrene and diethylphosphate on heating.



As can be seen from Fig. 4, in the endothermic effect region of the pyrolysis of (XIII) ($195 - 198^\circ$) there is in fact an inflection on the electrical conductivity variation curve.

2. Ethyl- α -oxy- α -carbethoxyethyl (V) (benzyl (VI)) phosphinates and diethyl- α -oxy- α -carbethoxyethylphosphonates (VII).

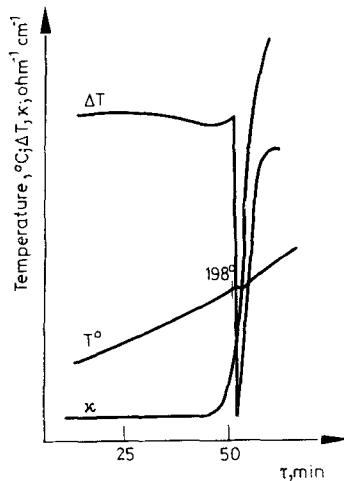


Fig. 4. DTA and electrical conductivity curves for diethyl- α -phenylethylphosphate ($R = 61$ kohm)

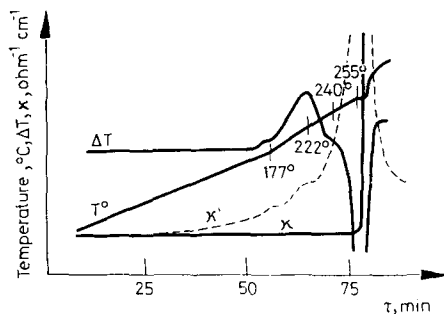
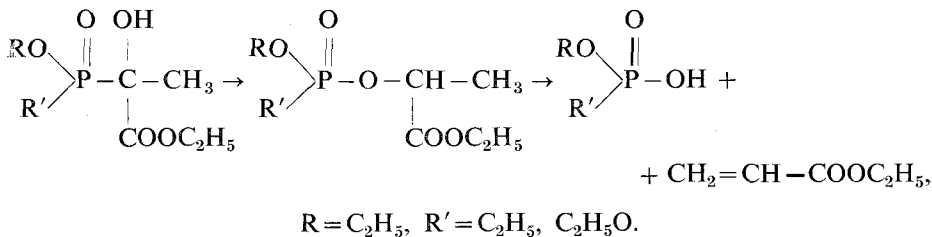


Fig. 5. DTA and electrical conductivity curves for diethyl- α -oxy- α -carbethoxyethylphosphonate (κ , when $R = 61$ kohm; κ' , R was taken out)

Let us consider the character of the electrical conductivity variation curve on heating (V) – (VII) on the example of diethyl- α -oxy- α -carbethoxyethylphosphonate (VII) (Fig. 5). As can be seen from the Figure, the increase of the sensitivity of the galvanometer recording the conductivity also made it possible to detect electric current in the circuit prior to the rearrangement accompanied by an endothermic effect. This may be caused by a weak ionization of the hydroxyl located near the α -carbon atom.

The inflection on the electrical conductivity curve in the region where the endothermic effect starts (240–255°) (Fig. 5) corresponds to the pyrolysis of the isomerization products, similarly to the above cases.



The electrical conductivity then also falls since a further decomposition of the products occurs.

3. α -oxyalkyl benzyl phosphonate (VIII)–(X) dialkyl esters.

As has already been mentioned, rearrangement products were not obtained during the heating of phosphonates (VIII)–(X). The curves of these substances show the endothermic effect due to phosphonate decomposition to the initial components in the range 150–200°.

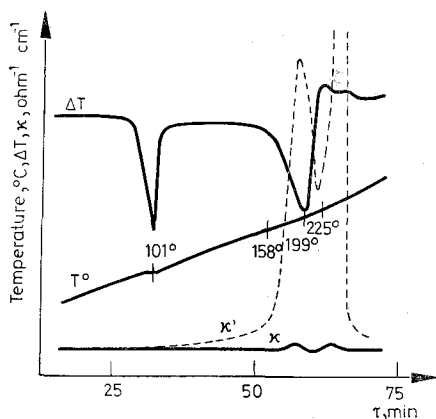
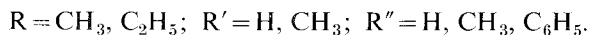
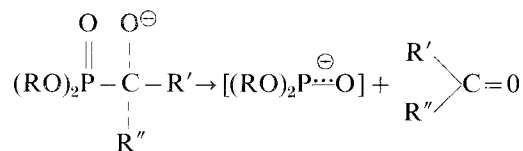


Fig. 6. DTA and electrical conductivity curves for dimethyl- α -oxybenzylphosphonate (κ , when $\text{R} = 61 \text{ kohm}$; κ' , $\text{R} = 40 \text{ ohm}$)

Let us consider the character of the electrical conductivity variation curve obtained on heating compounds (VIII)–(X) on the example of dimethyl- α -oxybenzylphosphonate (VIII) (Fig. 6). In this case also an increase in the sensitivity of the galvanometer recording the conductivity made it possible to detect the appearance of a conductive phase prior to the reaction. Already on the melting of a sample (the first endothermic effect) the electrical conductivity starts to increase smoothly. The infrared and NMR 31p. spectra of the melt of VIII and analysis of the vessel contents show that decomposition products are not formed at the melting point.

The sudden increase in conductivity on melting compounds (VIII)–(X) is probably caused only by the autoprotolysis of the phosphonate, similarly as for (V)–(VII). The inflection on the electrical conductivity curve corresponding to the second endothermic effect is caused by the appearance of phosphite anions as a result of the phosphonate decomposition.



The third endothermic effect shown on the curve corresponds to the pyrolysis of dialkylphosphite, an increase in electrical conductivity taking place initially. It probably corresponds for (VIII) to the formation of dimethylpyrophosphonic acid [11]. A further decomposition of the products then occurs and the electrical conductivity falls.

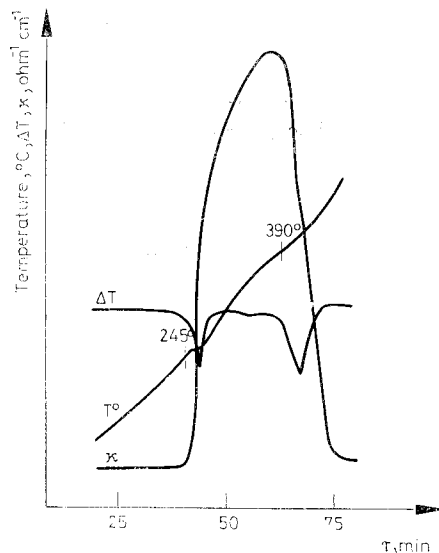


Fig. 7. DTA and electrical conductivity curves for dimethyldiphenylphosphonium iodide ($R = 61 \text{ kohm}$)

4. Dimethyldiphenylphosphonium iodide (XIV) and an equimolecular mixture of triphenylphosphite (XV) and benzyl iodide (XVI).

For comparison with the above experiments let us consider the curves obtained by recording simultaneously the electrical conductivities of a substance with ionic

structure $[(\text{CH}_3)_2\text{PPh}_2]^+\text{I}^-$ (XIV), and of the equimolecular mixture of triphenylphosphite (XV) and benzyl iodide (XVI), during the interaction of which the phenoxyphosphonium salt is assumed to be formed in the first stage [12].

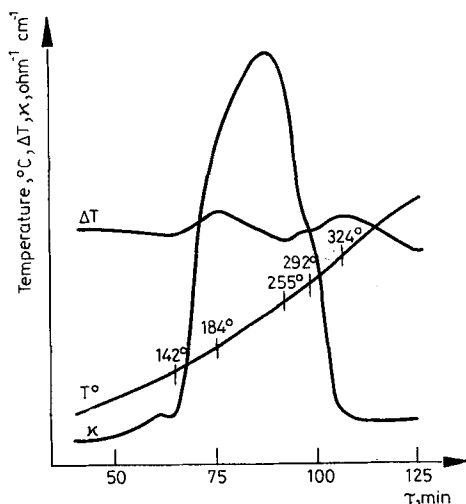
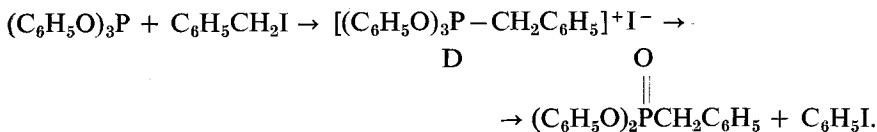


Fig. 8. DTA and electrical conductivity curves for an equimolecular mixture of triphenylphosphite and benzyl iodide ($R = 61 \text{ kohm}$; heating rate = $2.5^\circ/\text{min}$)

As can be seen from Fig. 7, on the melting of $[(\text{CH}_3)_2\text{PPh}_2]^+\text{I}^-$ (the first endothermic effect) the electrical conductivity variation curve deflects sharply from the zero line, whereas during decomposition (the second endothermic effect) it returns to the initial position. The electrical conductivity curve of the equimolecular mixture of triphenylphosphite (XV) and benzyl iodide deflects about as much as that of the ionic compound (Fig. 8). This can be explained by the fact that in the first exothermic effect region an adduct of XV and XVI (D) is formed, the latter decomposing the second exothermic effect to form benzylphosphonic acid diphenyl ester (XVII) [13].



The data obtained once again support the assumption of the ionic structure of the adduct (D) formed in the first stage of the Arbuzov rearrangement.

Mention should be made here of [14] in which the rearrangement of arsenicdialkylarylsulphides was also studied by simultaneous DTA and electrical conductivity measurements. The rearrangement products, as in our case, are practi-

cally non-conducting. However, in the Figure presented in the paper, after an inflection in the first exothermic effect region, the electrical conductivity curve stays at the same level, which appears very strange to us.

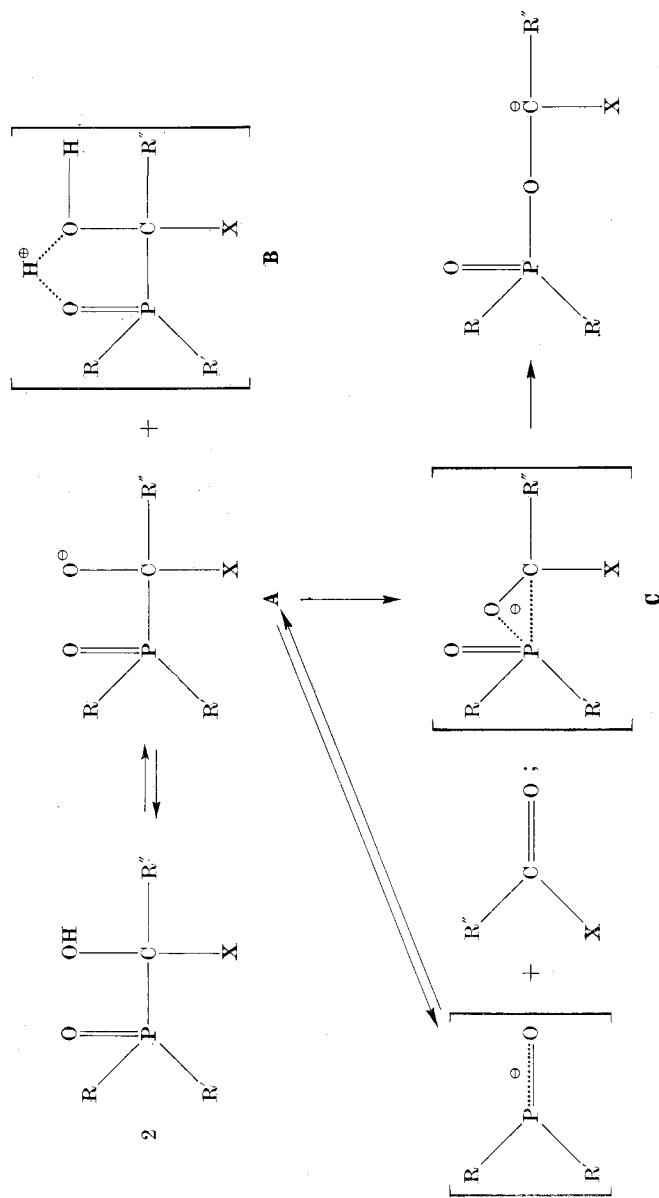
Discussion

A comparison of the DTA and electrical conductivity curves shows that the transformations occurring on heating the samples affect their electrical conductivities. By recording the electrical conductivity variation, the appearance not only of strong electrolytes such as phosphonium salts (Figs 7, 8), but also of substances of considerably lesser conductivity (Figs 1–5) can be ascertained. It should be noted that the conclusion about the non-conducting nature of such systems may sometimes be wrong if experiments are carried out at a single galvanometer sensitivity.

A conductive phase appears with α -oxyalkylphenylphosphinic acids (I–IV) on melting, similarly as with diphenylphosphinic and phenylphosphonic acids (Figs 1–3). An increase in the galvanometer sensitivity made it possible to record the electrical conductivity of α -oxyalkyl(benzyl)phosphonates (V)–(X), due to the weak ionization of the hydroxyl on the α -carbon atom. The acid nature of this group in similar compounds was shown earlier [15]. The electrical conductivity of (V)–(X) at 20°C was of the order of 10^{-6} ohm $^{-1}$ · cm $^{-1}$.

A smooth increase in electrical conductivity with a temperature increase is due not only to the variation of the ionization constant of the α -oxyalkylphosphonate, but also to a decrease in the medium viscosity and an increase of the ionic mobility on heating (Figs 1–5). The increase in electrical conductivity over the temperature range corresponding to the start of isomerization probably reflects a resultant effect of several factors. First and foremost, these are the ability of the carbinol to ionize, and the range of formation of rearrangement products. Since the rearrangement products (V)–(VII) practically do not conduct (their electrical conductivities being less than 10^{-8} ohm $^{-1}$), the overall electrical conductivity of the system should gradually decrease. However, in the initial period the rate of the formation of ionized molecules seems to prevail over that of their consumption and the electrical conductivity increases. The dilution of carbinol with the isomeric product also has an effect. Then, as expected, before the exothermic effect of the rearrangement reaches its maximum, the electrical conductivity starts to fall (Fig. 5). In the products (I)–(IV) on rearrangement of α -oxyalkylphenylphosphinic acid the hydroxyl near the phosphorus atom is retained. On completion of the rearrangement, therefore, the electrical conductivity does not fall, but remains almost constant to the beginning of the decomposition of the products (Fig. 1).

The inflections on the electrical conductivity variation curves in the region of the endothermic effects of decomposition of (VIII)–(X) to the initial components (Fig. 6) can be explained not only by an increase in the number of ionized α -oxyalkylphosphonate molecules, but also by the formation of phosphite anions as a



result of decomposition. It is the latter that brings about a considerably sharper electrical conductivity increase of the system as compared to its variation on rearrangement. The qualitative comparison of the deflection value of the electrical conductivity curve (Fig. 6) shows that it is close to that of the electrical conductivity curve obtained on the formation of the adduct of $(\text{PhO})_3\text{P}$ and PhCH_2I (Fig. 8).

This may serve as a confirmation of the above assumption that thermal rearrangement is not preceded by the decomposition of α -oxyalkylphosphonates to the initial components, while rearrangement proceeds by an intramolecular tricentre mechanism.

Reactions in the absence of a catalyst can be assumed to proceed without the prior splitting off of a proton from the hydroxyl near the α -carbon atoms. As has been shown, however, α -oxyalkylphosphonates are partially ionized even before the reaction. Since the nucleophilic character of the oxygen atom in the form (A) is higher than in a non-ionized molecule, it is reasonable to assume that the rearrangement proceeds through the formation of this anion (A). The anion (A) formed as a result of the autoprotolysis of α -oxyalkylphosphonate undergoes further transformations on heating. The negatively charged atom attacks the electrophilic phosphorus atom, as a result of which a transition state (C) occurs. The electron acceptor substituents near the α -carbon atom facilitate this transition and hence rearrangement.

The carbanion which is further formed adds a proton and an isomerized product. When electron-donor and weak electron-acceptor substituents are present near the α -carbon atom the decomposition of (A) to a phosphite anion and a carbonyl compound prevails.

Conclusion

1. The thermal behaviours of a number of α -oxyalkylphosphonates and their analogues, diethyl- α -phenylphosphate and dimethyldiphenylphosphonium iodide, and an equimolecular mixture of triphenylphosphite and benzyl iodide have been studied.

2. It was found that the thermal transformations of α -oxyalkylphosphonates and their analogues are preceded by the ionization of the hydroxyl near the α -carbon atom.

3. On the phosphonate-phosphate rearrangement of α -oxyalkylphosphonates containing electron-acceptor substituents near the α -carbon atom no prior decomposition to the initial components takes place, and rearrangement proceeds by an intramolecular tricentre mechanism.

4. By simultaneous DTA and electrical conductivity measurements the thermal behaviour of both high and low-conductivity substances can be studied. To make certain of the absence of conductivity in systems of this kind it is necessary to carry out experiments at different galvanometer sensitivities.

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RÉSUMÉ — Etude du comportement thermique des α -oxyalkylphosphonates et de leurs homologues par ATD en enregistrant simultanément la variation de conductivité électrique. Cette dernière méthode apporte des éclaircissements sur certains problèmes en rapport avec le réarrangement phosphonate-phosphate et la décomposition des α -oxyalkylphosphonates en leurs composants initiaux.

ZUSAMMENFASSUNG — Die Anwendung der DTA mit gleichzeitiger Registrierung der elektrischen Leitfähigkeitsänderungen wird bei dem Studium des thermischen Verhaltens von α -Oxyalkylphosphonaten und ihren Analogen erwogen. Die Prüfung der elektrischen Leitfähigkeitsänderungen während einer Reaktion trägt dazu bei einige Probleme der Phosphonat-Phosphat Umordnung und der Zersetzung von α -Oxyalkylphosphonaten in die Ausgangskomponenten zu klären.

Резюме — Рассмотрен вопрос о применении ДТА с одновременной регистрацией изменения электропроводности при исследовании термического поведения α -оксиалкилфосфонатов и их аналогов. Исследование изменения электропроводности в процессе протекания реакции способствует выяснению некоторых вопросов механизма фосфонат-фосфатной перегруппировки и распада α -оксиалкилфосфонатов на исходные компоненты.