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Stereomechanism of the Elimination of CH_3COOH from Gaseous 2-Butylacetate-3-d_1 over Phosphate Catalysts

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The elimination of CH_3COOH from 1-butylacetate, 2-butylacetate, *d,l*-erythro- and *d,l*-threo-2-butylacetate-3-d_1 as well as the isomerization of 1-butene and *cis*-2-butene were studied in the temperature range between 210 and 340°C, using microcatalytic and mass spectrometric techniques. Simultaneous *trans*-E2 and *cis*-E2 mechanisms were found with *trans* to *cis* ratios of 64/36, 58/42, 57/43 and 56/46 over $CaHPO_4$, $Ba_3(PO_4)_2$, $Ca_3(PO_4)_2$ and $AlPO_4$, respectively. All catalysts favored product distributions corresponding to the Saytzeff rule. In comparison with an analogous investigation using monodeuterated 2-butanols, the *trans* quota was significantly higher. This is probably due to the different size of the leaving groups. An essential detail is that both leaving groups of the ester can contact a plane catalyst surface even in case of *trans* elimination. Some relations are given between the mechanism of elimination and the crystal structure.

INTRODUCTION

An essential feature of the mechanism of elimination reactions is the number, stereochemistry and timing of the stages of the process. Usually E1, E1cB and E2 mechanisms are distinguished. E1 is a two step mechanism; the reaction starts with the (heterolytic) fission of the C–X bond. A carbonium ion with a definite lifetime is formed. A β-proton is abstracted in the second step. Another two step mechanism termed E1cB (cB = conjugated base) starts with the removal of a β-proton and formation of a carbanion. The E2 mechanism, which is also called a concerted or multicenter process, is characterized by the simultaneous abstraction of H^+ and X^-. In this case, the leaving groups can be abstracted from *cis* or *trans* (*syn* or *anti*) position.

With cyclic alcohols, Pines *et al.* (*1*) and also Blanchard and Canesson (*2*) have found that dehydration over Al_2O_3 is mainly *trans* elimination. Knözinger *et al.* (*3*) tried to distinguish between E1 and E2 using the kinetic isotope effect.

Another important technique for distinguishing these mechanisms is the use of compounds with two adjacent asymmetric C atoms. Noller *et al.* (*4*) found that dehydrochlorination proceeds by E1 and E2. Catalysts with strong electron pair acceptors (acidic sites), for example bivalent cations, favor E1. Catalysts with weaker acidic sites, e.g., monovalent cations, have more tendency towards E2, which was found to be mainly *trans*.

Trans dehydration over Al_2O_3 was confirmed by W. L. Hall (*5*), Narayanan and Pillai (*6*) recently by Kibby *et al.* (*7*). The last authors, furthermore, found preferred *cis* dehydration over hydroxyapatite.

While pyrolysis of esters has been studied rather frequently, little attention has hitherto been paid to the catalytic reaction. Andréu *et al.* (*8*) found the reaction of butylacetate to have more E2 character over $BaSO_4$ than over $MgSO_4$.

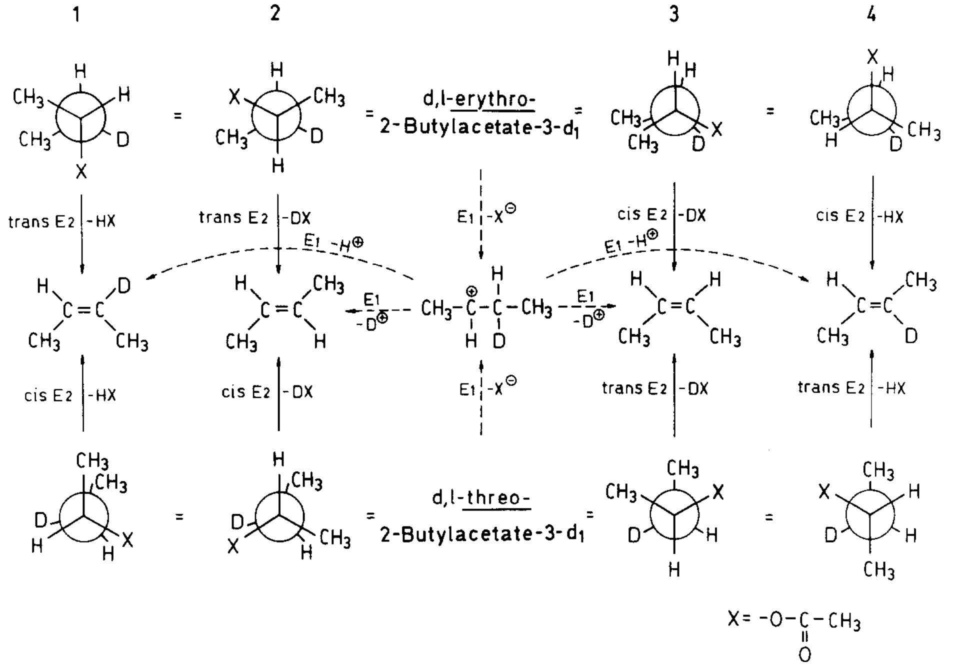

FIG. 1. Reaction scheme.

In this work, *d,l*-erythro- and *d,l*-threo-2-butylacetate-3-d_1 (E and T), both as a racemic mixture, were used. The scheme in Fig. 1 shows the information obtainable from the analysis of the products. In the case of an E1 mechanism, E and T should give the same product distribution, since the intermediate carbonium ion is the same for both reactants. In the case of a concerted mechanism, four elimination modes can be distinguished. An important criterion for a concerted mechanism is the difference of the product distribution obtained from E and T.

In most systems, E1 and E2 mechanisms are expected to be operative simultaneously. Recently Thomke and Noller (*9*) reported that, from a large number of catalysts, most gave a rather high E1 quota. Only with four catalysts was the E1 quota sufficiently low (approx 15%) to allow the application of the technique of diastereomeric reactants for studying details of the E2 mechanism. These catalysts were $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$, $CaHPO_4$, and $AlPO_4$, which gave a ratio of *cis* to *trans* mechanism of 85/15, 70/30, 70/30, and 45/55, respectively. The ratio of the concerted *cis* to *trans* mechanism suggested some relations with the crystal structure of the catalysts (*21*). The *cis* mechanism appeared to be favored by interatomic distances between the cation and the oxygen similar to the distance between the leaving groups in *cis*-(*syn*)-conformation.

The object of the present work was to study the elimination of acetic acid from butylacetate over the above-mentioned catalysts. A mechanistic behavior similar to that of the alcohols was to be expected. The comparison of butanol and butylacetate should show the influence of the size of the leaving group.

EXPERIMENTAL METHODS

Procedure

The microcatalytic or pulse technique was used. The reactor was a Pyrex tube with an inner diameter of 6 mm and a length of 20 cm. The catalyst (100 ± 1 mg) was held between two quartz wool plugs of 10 mg. Pulses of 0.5 μl of butylacetates and 0.2 ml of gaseous butenes (at room temperature and atmospheric pressure) were injected into the carrier gas stream, which passed over the catalyst in approximately 1 s and entered subsequently into a gas chromatograph for analysis. The reactor was heated in a tubular furnace, with a zone of uniform temperature (±0.5°C) of 8 cm in the middle.

For the experiments with undeuterated reactants a Pye-Unicam "model 4" gas chromatograph with FID was used (carrier gas: nitrogen, flow rate: 25 ml/min for all experiments). For the deuterated butylacetates a Varian Aerograph 1400-10 Special with an electron ionization detector (20 eV) connected to a mass spectrometer (Varian-MAT 111 GC/MS) for determination of the D content of the butenes was applied (carrier gas: helium, flow rate: 25 ml/min for all experiments).

For separation of reactants and products a column of 4 m length and 0.125 in. diameter packed with 15% Silicon grease (Perkin-Elmer) on Chromosorb P/AW, 60–80 mesh was used. The column temperature was 105°C. Retention times; butenes, 1 min 20 s; acetic acid, 2 min 25 s; 2-butylacetate, 4 min 20 s; 1-butylacetate, 5 min 30 s.

The butene isomers were separated by the following technique: column: 4 m, 0.125 in.; 13.5% bis-(2-methoxyethyl)adipate and 6.5% diethyl-sebacate on Chromosorb R 60–80 mesh (Perkin-Elmer); retention times (at room temperature): 1-butene, 7 min 30 s; *trans*-2-butene, 9 min 25 s; *cis*-2-butene, 10 min 45 s.

Catalysts

$AlPO_4$ and $Ba_3(PO_4)_2$ chemically pure, produced by Riedel-de Haen (Germany), $CaHPO_4$ and $Ca_3(PO_4)_2$ analytical pure (BAR), produced by Baker Chemicals (Germany). The suspension in water of $AlPO_4$, $Ba_3(PO_4)_2$, and $Ca_3(PO_4)_2$ gave a pH between 6.5 and 7.5 showing that no traces of free phosphoric acid were present. The catalysts were stored in a dry box at 160°C. Before starting the experiments, the catalysts were treated in the reactor for 3 hr at 300°C in the carrier gas stream. The surface areas, determined with nitrogen according to BET technique, were: $AlPO_4$, 44; $Ca_3(PO_4)_2$, 40; $CaHPO_4$, 4.5; and $Ba_3(PO_4)_2$, 1 m²/g.

Reactants

1-Butylacetate was a p.a. Merck product. 2-Butylacetate, pur. from EGA, was further purified by distillation. 1-Butene, *trans*-2-butene and *cis*-2-butene were highly purified products from Baker Chemicals.

The deuterated compounds were synthesized in the following way:

cis-2-butene + *tert*-butylhypochlorite (*10*) → threo-2-chloro-3-butanol (*11*) $\xrightarrow{-\mathrm{HCl}}$
cis-2,3-epoxybutane (*12*) $\xrightarrow{+\mathrm{LiAlD_4}}$ *d,l*-threo-2-butanol-3-d_1 (*13*) $\xrightarrow{\text{acetic anhydride}}$
d,l-threo-2-butylacetate-3-d_1 (*5*) (T).

d,l-Erythro-2-butylacetate-3-d_1 (E) was prepared in the same way starting with *trans*-2-butene.

By mass spectrometric analysis 98% D was found in E and 93% D in T. The steric purity was checked by pyrolysis, which proceeds according to a stereospecific *cis*-E2 mechanism (*14*) at 450°C, and was found to be 96% for E and 90% for T.

RESULTS

The thermal stability of the reactants was investigated under reaction conditions in the absence of catalysts. 2-Butylacetate began to react at 320°C (pyrolysis). In order to study the catalytic mechanisms without influence of the thermal reaction, it was necessary to work below 320°C.

At 320°C, 2-butylacetate was completely converted to butene over 100 mg of $AlPO_4$ and $Ca_3(PO_4)_2$, and a conversion of approx 34% was achieved over 100 mg of $CaHPO_4$. Since with 100 mg of $Ba_3(PO_4)_2$ the butene yield was equal to that of the thermal reaction, 700 mg were used, which gave a conversion of 27% at 320°C, and allowed us to study the reaction in a suitable temperature range well below that of the thermal reaction. For 1-butylacetate, the temperatures of reaction were approx 80°C higher than for 2-butylacetate.

Test for E1 Mechanism

For testing the E1 quota, the 2-butene yield from 1-butylacetate was determined. The isomerization of 1-butene and cis-2-butene was also studied. Characteristic values are shown in Table 1. They are compared with the values obtained from 1-butanol (*9*).

TABLE 1
2-BUTENE YIELD FROM DECOMPOSITION OF 1-BUTYLACETATE, DEHYDRATION OF 1-BUTANOL (*9*) AND ISOMERIZATION OF BUTENES

	2-Butene from:					
	1-Butylacetate		1-Butanol (*9*)		Isomerization	
Catalyst	°C	%[a]	°C	%[a]	°C	%[b]
$AlPO_4$	310	25	320	11	310	1
$Ca_3(PO_4)_2$	330	16	340	10	330	3.5
$Ba_3(PO_4)_2$	390	15	400	15	390	4
$CaHPO_4$	350	15	340	15	350	1

[a] Total butene = 100% (independent of conversion). The difference to 100% is the 1-butene yield.

[b] 1-Butene and *cis*-2-butene were pulsed separately. With each reactant nearly the same degree of isomerization (formation of the other butenes) was found. The average values are listed, indicated as sum of the butenes formed (all butenes, i.e., reactants and products = 100%).

Since the reaction over each catalyst was studied at temperatures below those given in Table 1 and since Noller *et al.* (*4*) and Knözinger *et al.* (*3*) have pointed out that the percentage of E1 diminishes with decreasing temperature, these values of the E1 percentage may be considered as an upper limit, and small enough to allow the application of the technique of diastereomeric reactants.

A further criterion is the deuterium content of 1-butene. In case of a pure concerted mechanism, 1-butene with 98% (93%) deuterium should be obtained from E (T), corresponding to the original content of D. This was found with all catalysts. Of course, this argument is somewhat indirect. However, it may be supported by a result obtained recently by Thomke and Noller (*9*) in a similar study with butanol: over BPO_4, which was shown to be a catalyst which prefers the E1 elimination for these reactions, the deuterium content of 1-butene was much lower than 90% (sometimes as low as 32%).

Under experimental conditions butene isomerization proceeds in a small amount. Therefore the butenes formed from the ester (and also from the alcohol) must be primary products, i.e., must be formed in the first adsorption step which leads to reaction.

Ratios of cis–trans-*Elimination Mechanisms*

The product distribution obtained from both 2-butylacetate and 1-butylacetate was independent of the number and chronological order of pulses. Previous adsorption of acetic acid reduced the catalytic activity, but did not affect the product distribution. Forty pulses at different time intervals and different temperatures showed a variation within 1%.

The results which give insight into the

TABLE 2

CONVERSION OF 2-BUTYLACETATE, PRODUCT DISTRIBUTION WITH *d,l*-ERYTHRO-(THREO)BUTYLACETATE-3-d_1 (E AND T) AND 2-BUTYLACETATE (BA), (SUM OF 1-BUTENE, *trans*-2-BUTENE, AND *cis*-2-BUTENE = 100%), PERCENTAGE OF DEUTERATED MOLECULES OF EACH SPECIES (IN PARENTHESES), RATIO OF *cis* TO *trans* MECHANISM, AND KINETIC ISOTOPE EFFECT (k_H/k_D)

Catalyst	Temp (°C)	Reactant	Conversion (%)	1-Butene	*trans*-2-Butene	*cis*-2-Butene	*cis*/*trans* mechanism	k_H/k_D
$CaHPO_4$	260	E	—	20 (98)	14 (61)	66 (73)	33/67	2.1
		BA	8	25 —	19 —	56 —	—	—
		T	—	25 (93)	17 (72)	58 (49)	47/53	1.6
	340	E	—	28 (98)	19 (56)	53 (72)	35/65	1.8
		BA	57	30 —	23 —	47 —	—	—
		T	—	27 (93)	20 (71)	53 (44)	45/55	1.5
$Ca_3(PO_4)_2$	260	E	—	27 (98)	16 (58)	57 (68)	38/62	1.7
		BA	61	26 —	18 —	56 —	—	—
		T	—	26 (93)	19 (67)	55 (51)	50/50	1.5
	320	E	—	30 (98)	20 (57)	50 (66)	40/60	1.6
		BA	100	29 —	22 —	49 —	—	—
		T	—	30 (93)	20 (63)	50 (54)	49/51	1.4
$Ba_3(PO_4)_2$	280	E	—	28 (98)	17 (58)	55 (61)	43/57	1.5
		BA	9	29 —	20 —	51 —	—	—
		T	—	30 (93)	18 (67)	52 (45)	45/55	1.3
	340	E	—	33 (98)	20 (58)	47 (69)	38/62	1.8
		BA	47	33 —	23 —	44 —	—	—
		T	—	34 (93)	22 (61)	44 (50)	50/50	1.4
$AlPO_4$	210	E	—	16 (98)	35 (52)	49 (61)	45/55	1.3
		BA	42	15 —	39 —	46 —	—	—
		T	—	16 (93)	38 (76)	46 (67)	47/53	2.6
	290	E	—	22 (98)	35 (55)	43 (61)	46/54	1.4
		BA	98	21 —	37 —	42 —	—	—
		T	—	21 (93)	36 (71)	43 (67)	50/50	2.2

mechanism are compiled in Table 2. The data are representative for a large number of experiments at different temperatures.

As indicated in Table 2, deuterated and undeuterated 2-butenes were obtained simultaneously over each catalyst. According to the reaction scheme (Fig. 1), this must be interpreted as a simultaneous *cis*-E2 and *trans*-E2 mechanism, i.e., one fraction of the 2-butylacetate reacted via *cis*-E2, another via *trans*-E2. These parts may be calculated from the deuterium content and the product distribution of the 2-butenes in the following way (E over $Ca_3(PO_4)_2$ at 260°C is taken as an example): 16 molecules *trans*-2-butene and 57 molecules *cis*2-butene (deuterium content 58 and 68%, respectively) were formed from 100 molecules E. Nine molecules of these 16 molecules *trans*-2-butene were deuterated, 7 were not (calculated by 0.58×16 and 0.42×16, that is number of molecules multiplied by deuterium content). Hence 9 molecules of *trans*-2-butene were formed via *cis*-E2, 7 via *trans*-E2 (see Fig. 1).

Similarly, from 57 molecules *cis*-2-butene, 39 molecules were formed via *trans*-E2 and 18 via *cis*-E2. Hence $39 + 7 = 46$ molecules of 2-butene were formed via trans-E2, $18 + 9 = 27$ molecules via *cia*-E2. Thus the ratio of *cis* to *trans* mechanism, which is given in Table 2, is 37/63. It does not vary considerably with temperature.

Kinetic Isotope Effect

The mechanism is affected by the kinetic isotope effect, which leads to a higher formation of deuterated 2-butenes. A rough estimate of the effect will be attempted here.

There are four elimination modes for the E2 mechanism (Fig. 1), leading to deuterated *cis*-2-butene, undeuterated *trans*-2-butene, undeuterated *cis*-2-butene, and deuterated *trans*-2-butene. (With the undeuterated reactant, only two products can be distinguished, each corresponding to two elimination modes.) Provided the kinetics are similar to those usually found for monomolecular catalytic reactions, for example dehydrations [reviewed recently by Knözinger (*24*)], an acceptable form of the rate equation should be

$$\frac{dx_i}{dt} = k_i\theta_i,$$

where x is the amount of product, t the time [for simplicity, we use t instead of HLSV (W/F)], k the rate constant, and θ the fraction of the surface covered with reactant. θ is a function of the pressure and the surface characteristics. The index i runs from 1 to 4 and refers to the four (parallel) E2 elimination modes of Fig. 1. The reaction path leading to 1-butene and the E1 elimination mode are not considered here.

Unfortunately our insight into the mechanism is not detailed enough to know whether θ for the four elimination modes is different. One may assume, however, that θ is equal for the (two) modes of *trans* mechanism, and also for the (two) modes of *cis* mechanism, i.e., $\theta_1 = \theta_2$ and $\theta_3 = \theta_4$. So we can readily find a relation between x_i and k_i dividing the corresponding equations by each other

$$\frac{dx_1}{dt} \cdot \frac{dt}{dx_2} = \frac{k_1\theta_1}{k_2\theta_2}$$

or, with $\theta_1 = \theta_2$,

$$\frac{dx_1}{dx_2} = \frac{k_1}{k_2},$$

which gives

$$\frac{x_1}{x_2} = \frac{k_1}{k_2}$$

(with the integration constant being zero since for $t = 0$, we have $x_1 = x_2 = 0$). Similarly, we obtain for the two modes of *cis* elimination

$$\frac{x_3}{x_4} = \frac{k_3}{k_4}.$$

With deuterated 2-butylacetate, x_2/x_1 is smaller, x_4/x_3 larger than with undeuterated 2-butylacetate, both by the isotope effect

$$f = \frac{k_H}{k_D}.$$

For calculating f we need two further assumptions: (a) f has the same value for *cis* and *trans* mechanism. (b) With the undeuterated reactant the *cis* mechanism gives the same ratio of *cis*- to *trans*-2-butene as the *trans* mechanism. With x_i being the values for the deuterated reactant we have the equation

$$\frac{fx_2}{x_1} = \frac{x_4}{fx_3} \quad \text{or} \quad f = \left(\frac{x_1x_4}{x_2x_3}\right)^{1/2}.$$

The values of the isotope effect calculated in this way are given in Table 2. The fluctuation of the values is rather high, especially with AlPO$_4$, for which the values from T are much higher than those from E. It must be noted, however, that similar differences were found for all runs over this catalyst within the whole temperature range studied. So it is likely that they are not due to experimental errors, but to mechanistic features of the reactions, although it is not possible to find an interpretation at the present stage.

The average values for a large number of runs (about 15 per reactant for each catalyst) carried out at different temperatures are shown in Table 3. The values are

TABLE 3
AVERAGE VALUES OF CONTRIBUTION OF ELIMINATION MECHANISM AND KINETIC ISOTOPE EFFECT

	From decomposition of butylacetate				From dehydration of butanol (9)			
			trans-E2 mechanism				*trans*-E2 mechanism	
Catalyst	Temp range (°C)	k_H/k_D	I[a]	II[b]	Temp range (°C)	k_H/k_D	I[a]	II[b]
$CaHPO_4$	260–340	1.6	64	67	300–340	1.6	30	30
$Ca_3(PO_4)_2$	260–320	1.5	57	62	280–320	1.6	15	13
$Ba_3(PO_4)_2$	280–340	1.5	58	61	300–450	1.9	30	28
$AlPO_4$	210–320	1.7	54	54	250–300	1.8	54	53

[a] The difference to 100% is *cis*-E2 mechanism. The values varied within ±5%.

[b] Values without consideration of kinetic isotope effect.

compared with those obtained with butanol (*9*).

DISCUSSION

The average values of the isotope effect are similar to those found by Thomke and Noller (*9*) for the dehydration of butanol and also to those reported by Knözinger and Scheglila (*3*a) for dehydration on alumina. Comparable values were also obtained in dehydrochlorination over salt catalysts (*4*). It may be noted that in the last cases average values over all elimination modes were observed. At temperatures below about 200°C the values of the isotope effect were found to be considerably higher.

All catalysts favor Saytzeff orientation, i.e., 2-butene is the main primary product. Saytzeff orientation is usually found with E2 and also E1 eliminations (less for E1cB) (*15*). Possibly Saytzeff orientation occurs, when the elimination reaction begins with the lengthening of the C–X bond (note that even in the case of E2 the reaction will not normally be exactly synchronous). In our case C–X lengthening probably precedes C–H separation, so that the stability of the products and hyperconjugation effects predominate over the acidity of the protons. Hoffmann orientation, i.e., predominance of 1-butene, is possibly more favored when the reaction begins with C–H lengthening.

With butylacetate the ratio of *trans* to *cis* elimination was similar for all catalysts. *Trans* elimination was slightly favored, whereas in dehydration of butanol *cis* elimination was markedly preferred (*9*). This may (at least in part) be attributed to the different size of the leaving groups. Since the activated complex for *trans* elimination is probably formed from the (more stable) staggered conformer, it is easy to understand that the percentage of *trans* elimination is higher with the ester.

However, there is another interesting difference between ester and alcohol. While it is difficult to see how the leaving groups of an alcohol may contact a plane surface simultaneously, unless inclination of the reactant is assumed as proposed by Knözinger *et al.* (*3*) or reaction in caves as proposed by Pines and Manassen (*16*), such a contact is possible with the ester. This was found with Stuart–Briegleb molecular models and is represented in Fig. 2 (the molecule is only shown schematically and not in the exact steric position).

As pointed out by Noller *et al.* (*4*) and by other authors (*17*), elimination reactions need electron pair acceptor (EPA) sites, for example cations, and electron pair donator (EPD) sites, anions, on the surface of the catalyst.

The bonds must be assumed to be broken heterolytically, i.e., the acetate group is abstracted as an EPD, the β-proton as an EPA. So the interaction between reactant and catalyst is an EPD–

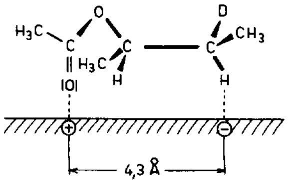

FIG. 2. Schematic drawing of adsorption complex.

EPA interaction on each point. Consequently the distances in the reactant and the catalyst should be well matched. The distance between O in C=O and β-H in the conformer of Fig. 2 is approx 4.3 Å (estimated from the Stuart model). Actually, a great many of the cation–oxygen distances in $CaHPO_4$, $Ba_3(PO_4)_2$ and $AlPO_4$ lie between 4.1 and 4.6 Å (calculated from the data given in Refs. (*18–20*). Data for $Ca_3(PO_4)_2$ were not available.

On the other hand, the dehydration of butanol also proceeds by EPD–EPA interaction. In the eclipsed conformation of 1-butanol, the oxygen atom of the hydroxyl group and the β-H(D) contact a plane surface at a distance of approx 2.5 Å (*21*). The distances of cation and oxygen of $Ca_3(PO_4)_2$ and $Ba_3(PO_4)_2$ are between 2.4 and 2.7 Å and are therefore favorable for *cis* elimination. Thus the higher *cis* quota may be ascribed to this coincidence of relevant distances and the lower size of the leaving group.

In the above discussion the EPA and EPD sites were considered to be cations and O^{2-} ions, respectively. Of course, it is also possible that the EPA sites might be protons. This could be the case with $AlPO_4$, the surface of which is covered with OH groups as reported recently by Peri (*22*).

The elimination mechanisms of both ester and alcohol were found to be independent of temperature. This is different from the results reported by Knözinger *et al.* (*3*) and also from those found in dehydrochlorination (*4,23*), where a shift towards E1 was observed with increasing temperature. These findings may be related to what one could call synchronization of the separation. The E2 mechanism usually is considered as a concerted mechanism, which means that the two leaving groups are abstracted in one step, but the movement must not necessarily be exactly synchronized; one group can precede the other one, as discussed for example by Banthorpe (*15*). The only condition for being termed E2 is that there is no stage in which rotation about the C–C axis could occur.

Now, the shift towards E1 possibly depends upon the degree of desynchronization. If it is low no shift is observed, while if it is high, as probably in dehydrochlorination, the mechanism is shifted towards E1 with increasing temperature.

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