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On the Mechanisms of Contact Eliminations

XXIX. The Elimination of CH_3COOH from Gaseous Ethyl, n-Propyl and n-Butyl Acetate over Salt Catalysts: The Influence of the Reactant Structure on the Reaction Rate*

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The decomposition of ethyl, n-propyl, and n-butyl acetate over $BaSO_4$, and of n-butyl acetate over $MgSO_4$ was studied using the microcatalytic pulse technique in the temperature range of 320–480°C. The activation energies obtained for both catalysts with the corresponding esters differed only slightly. 1-Butene was the only reaction product obtained from n-butyl acetate over $BaSO_4$. On the basis of these observations, a concerted reaction mechanism was concluded. The ρ^* values obtained from the Taft plot with the data from $BaSO_4$ are in accordance with the proposed mechanism, indicating however some ionic character in the transition state.

INTRODUCTION

On the basis of studies on the dehydrochlorination of alkyl halides over salt catalysts (*1*), it was concluded that the mechanism of elimination reactions is determined by a twofold interaction between the catalysts and the reactant molecules. The relative predominance, and consequently the type of mechanism operative, depends upon the nature of both the cation and the anion of the catalysts and the leaving atoms or groups of the reactants, which in turn are influenced by the neighboring substituents.

Due to the low strengths of the C–X bond, an almost exclusive carbonium ion (E1-like) mechanism with bromides ($X = Br$) (*1*, *2*) and an additional concerted (E2-like) one with chlorides ($X = Cl$) (*1*, *2*) has been observed on salt catalysts. In extensive studies with alcohols ($X = OH$) (*3*, *4*), the E2 mechanism was found to predominate.

Whereas the thermolytic decomposition of gaseous carboxylic esters at elevated temperatures has been developed during the last decades into elegant methods of synthesis (*5*), their catalytic reactions on surfaces have not been studied. As the process involves a C–O fission ($X = OCOR$), a mechanistic behavior in the E2 range similar to that of alcohols should be expected. The different esters chosen, viz., ethyl, n-propyl, and n-butyl acetates, enable us to study two factors significant for the mechanism: (i) the difference in the inductive effects of the alkyl groups, and (ii) the product distribution (in the case of n-butyl acetate) (*1*, *2*).

$BaSO_4$, which showed intermediate selectivity on the dehydrohalogenation reactions (*2*–*6*), was used as catalyst. Further, as an additional catalyst favoring the E1 character (*1*, *2*), $MgSO_4$ was employed to study the influence of the catalyst cation on the reaction mechanism.

EXPERIMENTAL

Equipment and Experimental Conditions

The experiments were carried out using the microcatalytic pulse technique (*7*). The

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* For the previous article of this series see reference (*6*).

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reactor employed has been described previously by one of us (*8*). Five-tenths to 2.0 μl of the reactants was injected into the carrier-gas stream as pulses which passed over the catalyst in about 0.1 sec to be subsequently analyzed on the appropriate chromatographic column. The gas chromatograph used was a Hewlett–Packard, model 700, provided with a flame ionization detector. For the separation of reactants and products, a column 5.5 m length and .3175 cm diameter, packed with 10% of SE-30 (Aerograph) on Firebrick 40–60 mesh (Johns–Manville) was employed. The column temperature was 26°C for ethyl, 65°C for n-propyl, and 75°C for n-butyl acetate, respectively.

As the butenes produced from n-butyl acetate were not resolved by this column, another column of 14 m length and .6350 cm diameter, packed with 37% of propylene carbonate (Curtin) on Chromosorb P, 30–60 mesh (Hewlett–Packard), and maintained at 10°C, was used. In both cases the carrier gas was nitrogen with a flow rate of 40 ml/min. Under these conditions, the butenes presented the following retention times: 1-butene, 16 min; isobutene, 16 min, 40 sec; *trans*-2-butene, 17 min, 45 sec, and *cis*-2-butene, 19 min, 38 sec. The identity of the different products was established by comparing their respective retention times with those of standards supplied by Phillips Petroleum Company.

Reactants

The ethyl acetate used was a Merck, AG product. n-Propyl and n-butyl acetate were prepared from the corresponding alcohols, according to (*9*).

Catalysts

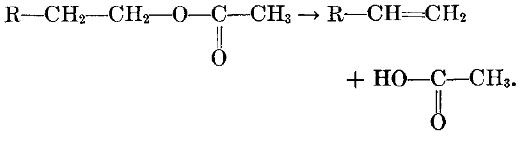
The catalysts used were: $BaSO_4$, p.a., and $MgSO_4 \cdot 7H_2O$, p.a., both from Merck, Ag (Germany). After drying both of them overnight at 180°C in a vacuum oven, $BaSO_4$ was additionally heated at 700°C for 4 hr. Samples of 0.3 g of the pretreated catalysts were introduced into the reactor tubing and heated again at 450°C during 1 hr in the reactor oven.

Activation Energies

The activation energies were calculated on the basis of the curves of disappearing reactant (see Figs. 1 and 2) as determined by means of at least 9 points (each one being the mean value of at least four measurements) obtained both with increasing and decreasing temperature, as indicated by the numbers of the points in Figs. 1 and 2. For this purpose a first-order kinetics, formerly found for elimination processes of this type (*2–10*), was assumed. A correction of the contact time was carried out in order to take into account the change in the flow rate of the carrier gas as the temperature of the experiment was varied (*2*). In these experiments no changes in catalyst activity was observed.

RESULTS

The thermal stability of all the reactants was investigated under the reaction conditions in the absence of the catalysts. The thermal decomposition of the different esters was negligible at 520°C, which was the maximum temperature obtainable with our equipment. The products of the various catalytic reactions correspond to those expected on the basis of a β-elimination process and are in accordance with the following reaction scheme:



$$R{-}CH_2{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \rightarrow R{-}CH{=}CH_2 + HO{-}\underset{\underset{O}{\|}}{C}{-}CH_3.$$

The percentage of conversion at various temperatures, the products formed, and the reaction parameters are given in Table 1. The differences in the activation energies observed are small and are only of mechanistic significance in so far as they are not caused by experimental error. As repeated measurements gave results in the same sequence, we regard the differences as mechanistically significant.

Figures 1 and 2 show the temperature dependence of the conversion of n-butyl acetate and the product distribution over $BaSO_4$ and $MgSO_4$, respectively. The product distribution obtained with the two

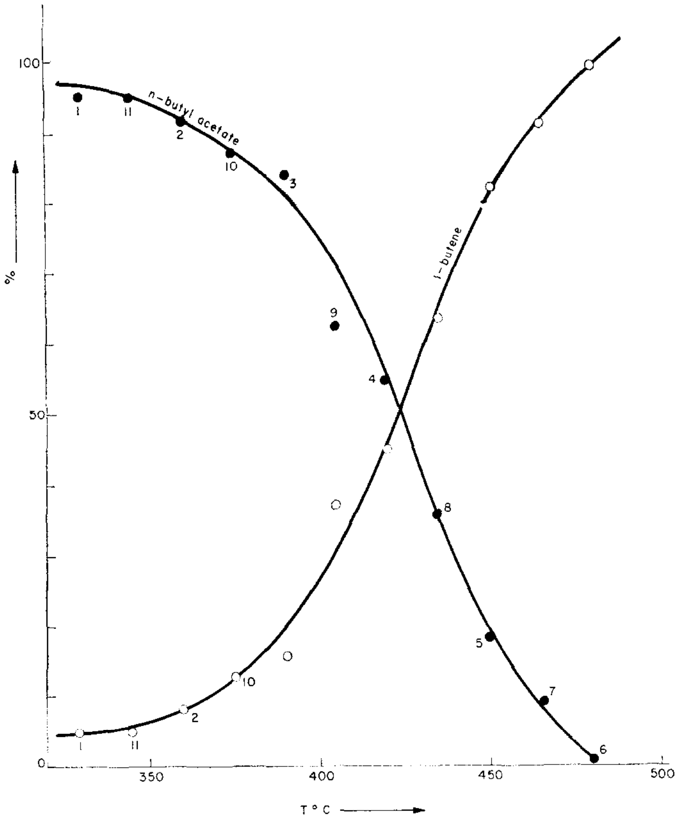


FIG. 1. Percentage of conversion and products formed as a function of temperature for the decomposition of n-butyl acetate over $BaSO_4$. Each point represents the mean value of at least four measurements and the numbers the sequence of them.

catalysts has significance for the interpretation of the mechanism and the selectivity of the catalysts, provided the products formed are primary ones. In our case, the relative product distribution remained unaffected when the extent of conversion was varied by changing the flow rate of the carrier gas (with a consequent variation of the contact time) at a given temperature. This has been shown *(11)* to be sufficient evidence for the primary nature of the products.

DISCUSSION

The most interesting point to be discussed is the mechanistic behavior of our systems. The principal mechanisms to be taken into account are those termed E1 and E2 (carbonium ion and concerted mechanism, respectively).

The mechanism of a catalytic reaction depends on both the catalyst and the reactant. As pointed out in former papers *(1, 2, 11)*, a bipoint interaction between catalyst and reactant must be taken into account, i.e., the cation of the catalyst interacting with the leaving group *X* and anion with the β-hydrogen. For a given reactant, the intensity of these interactions depends upon the acceptor and donor strengths of cations and anions, respectively. Whereas the activity of the cation was found to increase with increasing charge and decreasing size, that of the anion could rather be related to its basicity. The mechanism is determined by the relative intensity of these interactions *(1)*. Similarly, for a given catalyst, the mechanism should depend upon the relative strengths of the reactant bonds to be

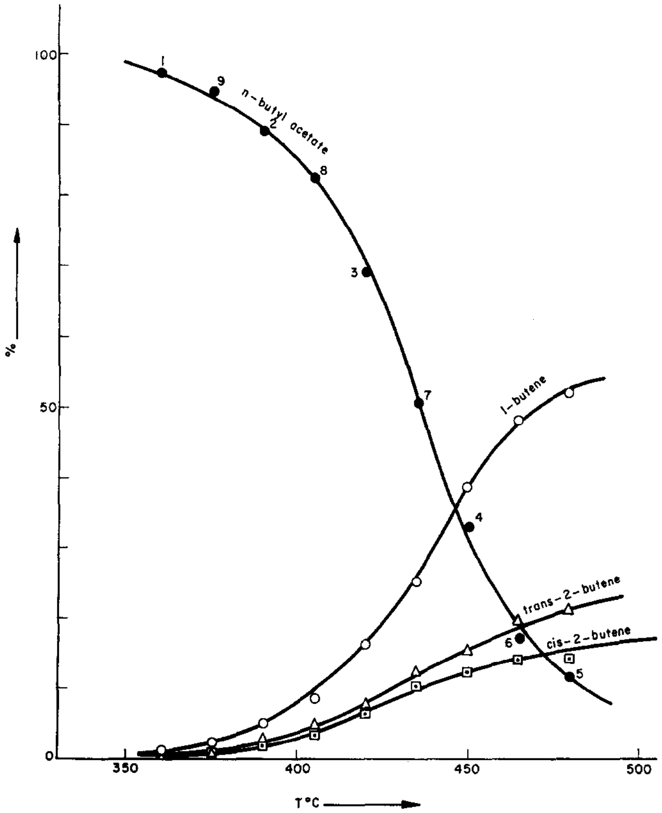


FIG. 2. Percentage of conversion and products formed as a function of temperature for the decomposition of n-butyl acetate over $MgSO_4$. Each point represents the mean value of at least four measurements and the numbers the sequence of them.

TABLE 1

REACTIVITY, PRODUCTS FORMED AND REACTION PARAMETERS FOR DECOMPOSITION OF ALKYL ACETATES

Catalyst	Reactant	Temp (°C)	Conversion (%)	log *k*	Reaction products	E_a (kcal/mole)	A relative
$BaSO_4$	Ethyl acetate	370	6.0	1.59	Ethylene	34	1.9×10^{30}
		412	24.6	2.29			
		470	85.0	3.15			
$BaSO_4$	n-Propyl acetate	370	6.6	1.63	Propylene	37	2.7×10^{30}
		412	29.8	2.38			
		470	85.3	3.30			
$BaSO_4$	n-Butyl acetate	370	11.0	1.74	1-Butene	37	3.5×10^{30}
		412	37.8	2.50			
		470	94.2	3.42			
$MgSO_4$	n-Butyl acetate	370	5.1	1.53	1-Butene	36	1.9×10^{29}
		412	12.0	1.94	*cis*-2-Butene		
		470	84.5	3.14	*trans*-2-Butene		

TABLE 2

MECHANISTIC SHIFTS AS CAUSED BY VARIATIONS OF CATALYST AND REACTANT

1. Increasing acceptor strength of the cation	$\xleftarrow{\text{E1} \qquad \text{E2}}$
2. Increasing donor strength of the anion	$\xrightarrow{\text{E1} \qquad \text{E2}}$
3. Increasing C–X bond dissociation energy[a]	$\xrightarrow{\text{E1} \qquad \text{E2}}$
4. Increasing C–H bond dissociation energy[a]	$\xleftarrow{\text{E1} \qquad \text{E2}}$

[a] This should refer to the heterolytic rather than to the homolytic bond dissociation energy.

broken. The bond dissociation energy to be taken into account should be the heterolytic one rather than the homolytic one.

With the above concepts in mind, a prediction should be possible as to the direction in which the mechanism is shifted when the system is varied. These shifts are indicated in Table 2. Only the E1 and E2 mechanisms have been considered, but the scheme could easily be extended toward E1cB.

The most significant result for mechanistic considerations is the primary product distribution obtained from n-butyl acetate. Since only 1-butene is formed over $BaSO_4$, we conclude that an E2 mechanism is operative. Over $MgSO_4$, 2-butene is also formed, indicating that the mechanism is shifted toward E1 (line 1 of Table 2). In a former study of dehydrochlorination, all three linear butenes were obtained from n-chloro and n-bromobutane over $BaSO_4$ as well as over $MgSO_4$, indicating an E1 mechanism in each case. Since the C–Br and C–Cl. bonds are less strong than the C–O bond of an ester, this is the expected shift (line 3 of Table 2). The thermolysis of esters is considered to be a concerted heterolytic mechanism in many cases (*5*). C–O breakage plays a less important role than C–X breakage in alkyl halides. With alkyl halides the mechanism has an obviously higher tendency toward E1 than with esters, which also corresponds to line 3 of Table 2.

The activation energies are of relatively little mechanistic significance. Since the activation energy of the catalytic reaction with ethyl chloride is more than 10 kcal/mole below that of the thermolysis, we assume that the catalytic reaction is also heterolytic, as pointed out formerly for dehydrohalogenation reactions over polar catalysts (*1, 2, 11*). As can be seen from Table 1 the influence of the alkyl group on the activation energy is small. For both E1 and E2 mechanisms a small effect on the reactivity is expected from β-alkyl substitution. If an E1 mechanism were operative the variation of the activation energy should be due to the inductive effect of the β-alkyl group. However, the sequence may be affected also by anchimeric assistance as found elsewhere (*12, 13*). In case of an E2 mechanism the sequence of activation energies depends upon two effects which are opposite to each other, viz., the decrease of the acidity of the β-hydrogen because of the electron releasing effect of the alkyl group, and the stabilization by hyperconjugation of the double bond being formed.

The concepts E1 and E2 being only extreme cases and rather qualitative, it is desirable to obtain further insight into the transition state. For this purpose we analyze the data according to the Taft equation (*15, 16*):

$$\log k/k_0 = \rho^*\sigma^*$$

as discussed in our preceding paper of this series (*6*). In Fig. 3, the Taft equation plots show an increase of the relative reaction rates with the inductive effect of the alkyl substituents, given by their σ^* values, for different temperatures. Consequently, negative ρ^* values are obtained, which signify a transition state with some partial ionic character (*6–16*).

In the preceding study of dehydrochlorination of a similar series of alkyl chlorides over $BaSO_4$ (*6*), ρ^* values be-

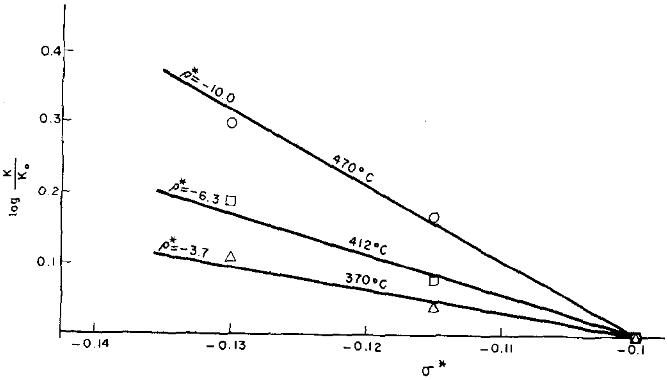


FIG. 3. Relationship between the decomposition rate of alkyl acetates and Taft σ^* values over $BaSO_4$. Ethyl, $\sigma^* = -0.100$; n-propyl, $\sigma^* = -0.115$; n-butyl, $\sigma^* = -0.130$.

tween −30 and −40 were obtained. Since negative ρ^* values are indicative of an ionic mechanism, we see once more that the elimination reaction with esters is closer to an E2 mechanism than with alkyl halides. As charge separation with alkyl halides is higher than with esters, isomerization is also higher in the first case. With increasing temperature ρ^* becomes more negative, indicating a parallel increase of the ionic character of the reaction. This seems to be a general feature of elimination reactions. With all catalysts that gave an E2 mechanism in the dehydrochlorination of 2,3-dichlorobutane a gradual transition to an E1 mechanism was found with increasing temperature (*1*). Whenever a system presented both mechanisms, E2 appeared at lower, E1 at higher temperature. Corresponding conclusions have been reached by Knözinger *et al.* (*17*) studying the magnitude of primary isotopic effects on the dehydration of alcohols over Al_2O_3. A concerted mechanism (E2 type) was proposed to be operative; however, from the decrease of the isotopic effect (α) with increase of temperature, they also conclude a corresponding increase of the ionic character of the mechanism.

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REFERENCES

1. NOLLER, H., ANDRÉU, P., SCHMITZ, E., ZERAIN, S., NEUFANG, O., AND GIRÓN, J., *Int. Congr. Catal., 4th,* paper No. 81, Moscow, 1968.
2. ANDRÉU, P., ROSA-BRUSIN, M., SÁNCHEZ, C., AND NOLLER, H., *Z. Naturforschg.* **22–b,** 809, 814 (1967); *Anal. Quim.* **65,** 141 (1969).
3. PINES, H., AND MANASSEN, J., *Advan. Catal. Relat. Subj.* **16,** 49 (1966).
4. KNÖZINGER, H., *Angew. Chem., Int. Ed. Engl.* **7,** 791 (1968).
5. BANTHORPE, D. V., "Elimination Reactions," p. 167 and following. Elsevier, 1963.
6. LÓPEZ, F. J., ANDRÉU, P., BLASSINI, O., AND PÁEZ, M., *J. Catal.* **18,** 233 (1970).
7. KOKES, R. J., TOBIN, H., AND EMMETT, P. H., *J. Am. Chem. Soc.* **77,** 5860 (1955).
8. ANDRÉU, P., HEWLETT-PACKARD, Technical Paper No. 42, 10 (1967).
9. VOGEL, A. I., "Practical Organic Chemistry," p. 382. Longmans, 1959.
10. ROSA-BRUSIN, M., URDANETA, E., ANDRÉU, P., AND NOLLER, H., *An. Soc. Espan. Fis. Quim.* **65,** 965 (1969).
11. NOLLER, H., HANTSCHE, H., AND ANDRÉU, P., *J. Catal.* **4,** 354 (1965).
12. ANDRÉU, P., BELLORÍN, J., CUNTO, C., AND NOLLER, H., *Z. Phys. Chem., N. F.* **64,** 71 (1969).
13. ANDRÉU, P., LÓPEZ, F. J., BLASSINI, O., PÁEZ, M., AND NOLLER, H., *An. Soc. Espan. Fis. Quim.* **65,** 899 (1969).
14. GRIMALDO, Y., Trabajo Especial de Grado

(Master Thesis), Universidad Central de Venezuela, (1969).

15. Pal'm, V. A., *Russ. Chem. Rev.* **30,** 471 (1961).

16. Kraus, M., *Advan. Catal. Relat. Subj.* **17,** 75 (1967).

17. Knözinger, H., Scheglila, A., *Z. Physik. Chem. N. F.* **63,** 197 (1969).