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On the Mechanism of Contact Eliminations

XXXIII. Effect of the Anion on the Activity and Selectivity of Lithium and Barium Salts in the HCl Elimination from 1- and 2-Chlorobutane

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The influence of the anion on the activity and selectivity of LiBr, Li_2SO_4, Li_2CO_3, Li_3PO_4, $BaCl_2$, $BaCrO_4$, $BaCO_3$, and $Ba_3(PO_4)_2$, has been studied by means of the pulse microcatalytic technique in the temperature range 80–430°C. As test reactions, the dehydrochlorination reactions of 1- and 2-chlorobutane have been used.

It has been found that the increase of anion basicity causes an increase in both activation energy and selectivity, the latter being expressed as the ratios butene-1/butenes-2, and *cis*-/*trans*-2-butene for 1-chlorobutane and 2-chlorobutane, respectively. The results suggest that an E-1 type of mechanism predominates in the more active catalysts, whereas an E-2 type of mechanism operates in the more selective ones.

INTRODUCTION

It is generally accepted that dehydrohalogenation reactions of alkyl halides over salt catalysts involve a double interaction between the reactant and the catalyst surface (*1*), facilitating the loosening of the atoms involved in the reaction. For this, the catalyst should have acceptor (cation) and donating (anion) centers, implying that the more active catalysts in this type of reaction are polar compounds such as metallic salts and oxides.

Basically, the activity of the catalysts depends upon their ability to polarize the carbon–halogen bond in such a manner that those catalysts having cations with a more electron-acceptor character, i.e., having greater charge and smaller volume, such as Mg^{2+} and Be^{2+}, will be the more active, whereas those having smaller charge and larger volume, such as K^+ and Cs^+, will exhibit a lower activity.

Since specificity and selectivity are coinciding concepts, differing only in that the first refers to the reactant, and the second to the catalyst, it will be most convenient to discuss both together.

As evidenced in (*1*), the basic concepts of Ingold's theory (*2*) are applicable to the heterogeneous gas–solid reactions of organic compounds. Accordingly, the mechanistic models often postulated in dehydrohalogenation reactions over polar catalysts are those known as E-1 and E-2 in the liquid phase, that is, the carbonium ion and concerted mechanism, respectively.

Reactions of E-2 type are in general specific, whereas those of E-1 type are not. Consequently, in the more active catalysts, due to their greater polarizing effect on the carbon–halogen bond, the E-1 mechanism will predominate, and by the free rearrangement of the reaction intermediate, those products which are thermodynamically

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more stable will be obtained. On the other hand, on the less active catalysts, the cation–halogen interaction is similar in magnitude to that of the anion with the β-hydrogen leading to a predominance of the concerted mechanism and hence to a greater selectivity.

The influence of the nature of the cation upon the catalyst activity and selectivity has been evidenced in previous work (*3*). However, the role of the anion in this type of reaction is not very clear. In the present work we shed some light on the latter problem by studying the HCl-elimination from 1- and 2-chlorobutane over several lithium and barium salts. The moderate activity and selectivity (*3*) of these catalysts implies that the cation–halogen interaction can be expected to be of the same magnitude as that corresponding to the anion with the β-hydrogen.

EXPERIMENTAL

The elimination of HCl from 1- and 2-chlorobutane have been studied by the pulse microcatalytic technique previously described (*4*). The reactor, made of a 25 cm long, 5 mm i.d. Pyrex glass tube was attached to a gas chromatograph fitted with a flame ionization detector. The separation of reactants from the reaction products was carried out by using a 1.5 m length and 6 mm o.d. column, packed with β–β' oxydipropionitrile 20 wt% on sterchamol 60–80 mesh, operated at 70°C in a helium flow of 30 ml min^{-1} (1.8 liter hr^{-1}). In these conditions, the unresolved butenes appeared as a single peak before that corresponding to the reactants. The butene isomers separation was achieved by using a 10 m length and 3 mm o.d. column of 20 wt% propylene carbonate on chromosorb P, 80–100 mesh, at 25°C and helium flow of 20 ml min^{-1} (1.2 liter hr^{-1}). High-purity reactants from Eastman Organic Chemicals and catalysts from Merck were used in all the experiments.

Catalyst Pretreatment

All the catalysts used in this study, i.e., LiBr, Li_2SO_4, Li_2CO_3, Li_3PO_4, $BaCl_2$, $BaCrO_4$, $BaCO_3$, and $Ba_3(PO_4)_2$ were dried at 110°C under moderate vacuum, prior to introduction in the reactor, followed by 3 hr heating in the reactor under helium flow, at 400°C. The amount of catalyst used ranged between 0.2 and 1.0 g depending upon the magnitude of the adsorption of reactants and products.

Before the actual catalytic experiments were made, the thermal reaction was examined in order to establish the maximum working temperatures. In the present study, they were found to be 470°C for the 1-chlorobutane and 410°C for the 2-chlorobutane.

RESULTS

Activation energies and preexponential factors have been calculated for both reactants over the two series of catalysts following the procedure described in (*3*), and a least-squares treatment has been used for the best fit of the experimental data. All values reported are averages of at least three determinations, and their deviations were always less than 3%. All runs were made in both ascending and descending order of temperature.

The Arrhenius parameters obtained in this way for the dehydrochlorination of 1- and 2-chlorobutane over the two series of barium and lithium salts are given in Tables 1 and 2, respectively. The preexponential factor values are of a relative nature since they have been calculated from apparent reaction rates (*3*).

Figure 1 shows the relationships between activation energies and the preexponential factors for the HCl elimination from 1- and 2-chlorobutane over the lithium and barium salt catalysts. Figure 2 shows the selectivities (expressed as the ratio butene-1/butenes-2) as a function of the reaction temperature, for the dehydrochlorination of 1-chlorobutane over the various lithium

TABLE 1

Reaction Parameters of the Dehydrohalogenation of 1- and 2-Chlorobutane over Different Barium Salts

Catalyst	Reactant	Temperature range (°C)	Conversion (%)	*Ea* (kJ/mol)	*A* (relative)
$BaCl_2$	1-Chlorobutane	214–394	7–94	58.58	1.1×10^8
	2-Chlorobutane	85–203	2–98	62.76	5.0×10^{10}
$Ba_3(PO_4)_2$	1-Chlorobutane	253–358	9–95	108.78	2.0×10^{12}
	2-Chlorobutane	105–222	3–99	66.94	1.0×10^{10}
$BaCO_3$	1-Chlorobutane	234–405	8–96	66.94	2.6×10^8
	2-Chlorobutane	106–201	4–97	83.68	7.2×10^{12}
$BaCrO_4$	1-Chlorobutane	164–265	9–95	75.31	1.0×10^{10}
	2-Chlorobutane	82–203	2–95	62.76	0.7×10^{10}

and barium salts, and Fig. 3 shows the corresponding selectivities (in this case as *cis-/trans*-2-butene ratio) obtained for the 2-chlorobutane reaction.

DISCUSSION

Activity and Reactivity

As pointed out in the Introduction, the activity of the salt catalysts is related to the ability of the cations (i.e., the electron-acceptor sites) to polarize the carbon–halogen bond. If in a series of salts having the same cation, the anion is changed, it is reasonable to think that the catalytic activity should decrease with increasing basicity, since the latter partially stabilizes the cationic charge, weakening therefore the polarizing effect on the carbon–halogen bond. According to this, the activity sequence of the catalysts used in this work should be

halides > sulfates > chromates
> carbonates > phosphates.

These anions may well be further divided into two groups of distinct basicity with the three more active ones in the group of lower basicity and the others in the higher

TABLE 2

Reaction Parameters of the Dehydrohalogenation of 1- and 2-Chlorobutane over Different Lithium Salts

Catalyst	Reactant	Temperature range (°C)	Conversion (%)	*Ea* (kJ/mol)	*A* (relative)
LiBr	1-Chlorobutane	290–430	5–90	62.76	4.3×10^7
Li_2CO_3	1-Chlorobutane	320–400	1–37	117.15	3.5×10^{11}
	2-Chlorobutane	190–300	2–100	104.60	4.8×10^{12}
Li_3PO_4	1-Chlorobutane	280–400	2–92	121.34	2.2×10^{12}
	2-Chlorobutane	150–260	3–100	104.60	9.7×10^{12}
Li_2SO_4	2-Chlorobutane	170–375	2–100	66.94	3.8×10^8

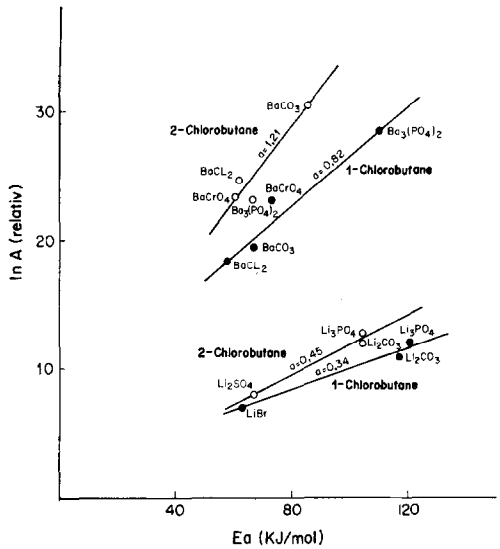

FIG. 1. Compensation effects of lithium and barium salts in the dehydrohalogenation of 1- and 2-chlorobutane.

basicity group. The anion basicity is related to its capacity of retaining a proton in aqueous media, that is, the pK_a of the corresponding acid. Nevertheless, there is no available information about the basicity of those anions on the surface of crystalline solids, and therefore, they might well be different from those in solution.

It can be observed from the activity sequence in the case of 1-chlorobutane (Fig. 1) that in general the activity decreases with increasing anion basicity. However, this does not always correspond with what would be expected from the above considerations, since for example $BaCO_3$ exhibits greater activity than $BaCrO_4$. This anomaly could be attributed to a possible reduction of the chromate to Cr_2O_3 by temperature effects, as pointed out in (*5*); such a reduction, although of small extent, could be enough to modify the catalyst activity.

In the case of 2-chlorobutane, the influence of the anion is less marked in the barium salts, $BaCO_3$ being the only one showing lower activity than the other catalysts.

As can be seen from the values given in Tables 1 and 2, over all the catalysts studied, with the exception of $BaCO_3$, 2-chlorobutane presents lower activation energies and reaction temperature ranges than 1-chlorobutane, being in consequence

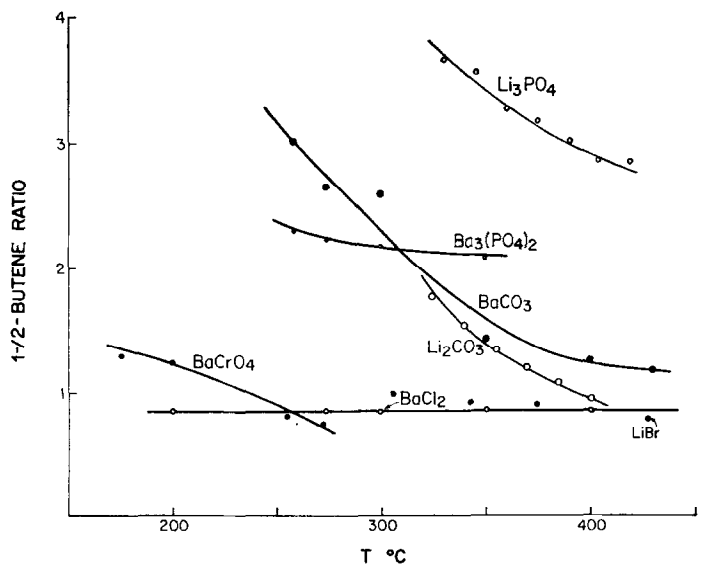

FIG. 2. Selectivity of lithium and barium salts in the dehydrohalogenation of 1-chlorobutane as a function of temperature.

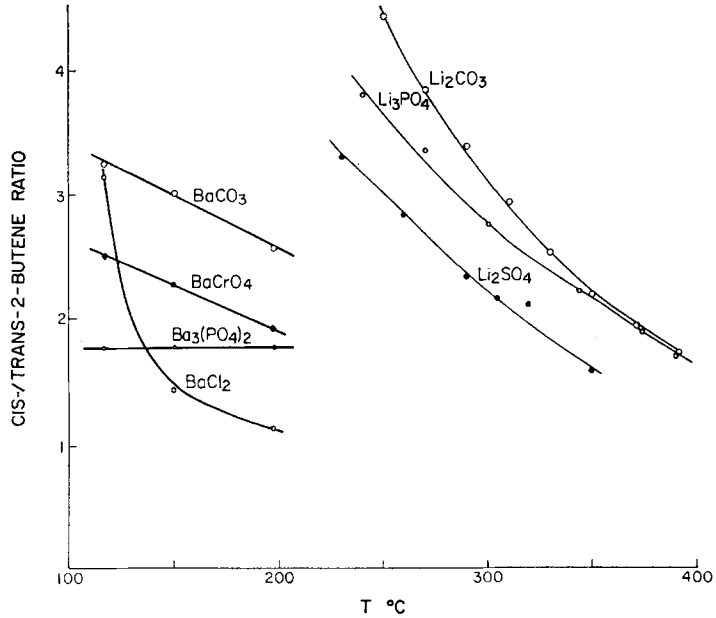

FIG. 3. Selectivity of lithium and barium salts in the dehydrohalogenation of 2-chlorobutane as a function of temperature.

more reactive than the latter in agreement with earlier results (*1*). Moreover, the slopes of the compensation lines as well as the preexponential factors of higher order shown by the 2-chlorobutane, in comparison with 1-chlorobutane over both series of catalysts, can be considered as indicative of its greater reactivity.

In general, for a given activation energy, if we assume that the number of active sites is to be about the same in all the catalysts studied (all the catalysts have surface areas of the order of 1–5 $m^2 g^{-1}$), the larger preexponential factor characteristic of 2-chlorobutane will be caused by a greater entropy in the corresponding activated complex, indicative of an increased number of degrees of freedom. This would agree with the accepted mechanistic ideas of a more marked E-1 character for this reactant (*1*).

Selectivity

Catalyst selectivity, as stated earlier, depends upon the relative strength of the double interaction with the reactants.

As can be observed in Fig. 2, in the 1-chlorobutane case for the more active catalysts, the selectivity either decreases with increasing temperature (e.g., $BaCO_3$) or it is not exhibited at all, as happens with $BaCrO_4$ and $BaCl_2$. $Ba_3(PO_4)_2$ shows the highest selectivity throughout the entire temperature range studied. These results could be interpreted by accepting that over the less basic catalysts the Cl–cation interaction predominates, thus driving the mechanism to the E-1 type, whereas over $Ba_3(PO_4)_2$ both interactions are equivalent in the temperature range studied, the mechanism therefore being more E-2 like.

$BaCO_3$ would represent an intermediate case, hence the high sensitivity to temperature of its selectivity. At lower temperatures both interactions should be equivalent, the Cl–cation one predominating as the temperature is raised. A similar behavior, although somewhat polarized toward the E-1 mechanism, is shown by $BaCrO_4$. At lower temperatures this catalyst has a very low selectivity which disappears very quickly with increasing

temperature. The lithium salt catalysts studied exhibited a regular behavior since the phosphate has greater selectivity than the carbonate. Nevertheless, the selectivity of the carbonate is lower than could be expected from its higher basicity.

Being more reactive, 2-chlorobutane starts to decompose at lower temperatures. This fact favors higher selectivity, although on the other hand, it is lowered due to the greater polarizability of the C–Cl bond.

As can be seen in Fig. 3, at a very low temperature (115°C), $BaCl_2$ presents an abnormally high selectivity which quickly disappears with increasing temperature. On the other hand, $BaCO_3$ shows higher selectivity than $Ba_3(PO_4)_2$, and this in turn is lower than that of $BaCrO_4$. The behavior of the lithium salts toward 2-chlorobutane can be considered normal, since the more basic salts are the more selective ones. In general, as long as temperature increases, the cation–chlorine interaction becomes more marked, leading thus to loss of selectivity.

From the results above, it can be noted that the donating or basic character of a given anion seems to be a function of the cation to which it is bonded. Again we can observe that lithium salts are more selective than barium salts, since the corresponding butene ratios are in general greater in the former. This is indicative of a greater concerted character of the mechanism over the lithium salts, due to the smaller electrostatic field strength of this cation.

Finally, it should be pointed out that recent studies on the influence of water content over activity and selectivity of the above catalysts (*7*) lead us to consider the possibility that some of the observed anomalies may well be attributed to the effect of residual water molecules on the catalyst surface.

REFERENCES

1. Noller, H., Andréu, P., and Hunger, M., *Angew. Chem. Int. Ed.* **10**, 172 (1971).

2. Banthorpe, D. V., "Elimination Reactions," Elsevier, Amsterdam, 1963.

3. Andréu, P., Rosa-Brusin, M., Sanchez, C., and Noller, H., *Z. Naturforsch. B*, **22**, 809 (1967); **22**, 814 (1967).

4. Andréu, P., Hewlett–Packard Technical Paper No. 42 (1967).

5. Duval, C., "Inorganic Thermogravimetric Analysis," p. 534. Elsevier, Amsterdam, 1963.

6. Schwab, G. M., and Noller, H., *Z. Electrochem.* **58**, 762 (1954).

7. Villalba, S., and Noller, H., *Acta Cient. Venez. Suppl. 2* **24**, 165 (1973).