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NOTE

On the Mechanism of Contact Eliminations

XXVIII. The Influence of Reactant Structure on the Reaction Rates of HCl Elimination from a Series of *n*-Alkyl Chlorides over $BaSO_4$ as Catalyst*

Correlations between reactant structure and reaction rates have been attempted in solution and are known as extrathermodynamic or linear free energy relationships (LFER) (*1*). Recently, the Taft equation has been applied to catalytic heterogeneous reactions as reviewed in (*2*), which empirically expresses the influence on the logarithm of the reaction rates of the polar effect of a series of aliphatic compounds undergoing the same reaction on a given catalyst. In the equation

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

k/k_0 is the relative constant with respect to a standard reaction (ethyl chloride in this case) and σ^* represents the alkyl substituent parameter which is a measure of the inductive effect. Values of σ^* for a number of substituents are tabulated in the literature (*1*). The reaction parameter ρ^* is characteristic of the type of reaction and the properties of the catalyst. Its value depends further on the direction and extent of electron shifts leading to the formation of the activated complex, thus giving insight into the mechanism. Negative ρ^* values are indicative of polar-like carbonium ion mechanisms, which become positive for apolar or concerted reactions.

Kraus and Kochloeffl (*3*) obtained negative ρ^* values for the dehydration of secondary aliphatic alcohols over SiO_2 and ZrO_2 and positive values over Al_2O_3; with this catalyst, negative ρ^* values are obtained for 1-phenyl ethanols (*4*). For the formation of ethers from alcohols over Al_2O_3 catalysts, Knözinger and Bühl (*5*) observed a positive ρ^* value. These values are concordant with mechanisms proposed.

Applying the Taft equation, we evaluate in this note our published results (*6*) on the reactivity of a series of *n*-alkyl chlorides over $BaSO_4$ as catalyst. Apparent rate constants at 220 and 280°C are calculated on the basis of a first order reaction as described in (*7*). Table 1 gives the values obtained together with the corresponding σ^* values. The small range of σ^* values studied has the advantage of introducing small changes into the nonreactive part of the reactant molecules, which is expected to affect the nature of the mechanism only slightly.

TABLE 1
σ^* CONSTANTS AND RELATIVE RATE CONSTANTS FOR HCl ELIMINATION OF *n*-ALKYL CHLORIDES OVER $BaSO_4$

Reactant	σ^*	log *k* 220°C	log *k* 280°C
Ethyl chloride	−0.100	1.49	1.85
n-Propyl chloride	−0.115	1.83	2.45
n-Hexyl chloride	−0.126[a]	2.38	2.81
n-Pentyl chloride	−0.127[a]	2.50	3.00
n-Butyl chloride	−0.130	2.52	3.10

[a] Values calculated as described in (*8*).

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* Part XXVII of this series: G. Martin, P. Andréu, and H. Noller, *An. Soc. Espan. Fis. Quim.*, **65**, 977 (1969).

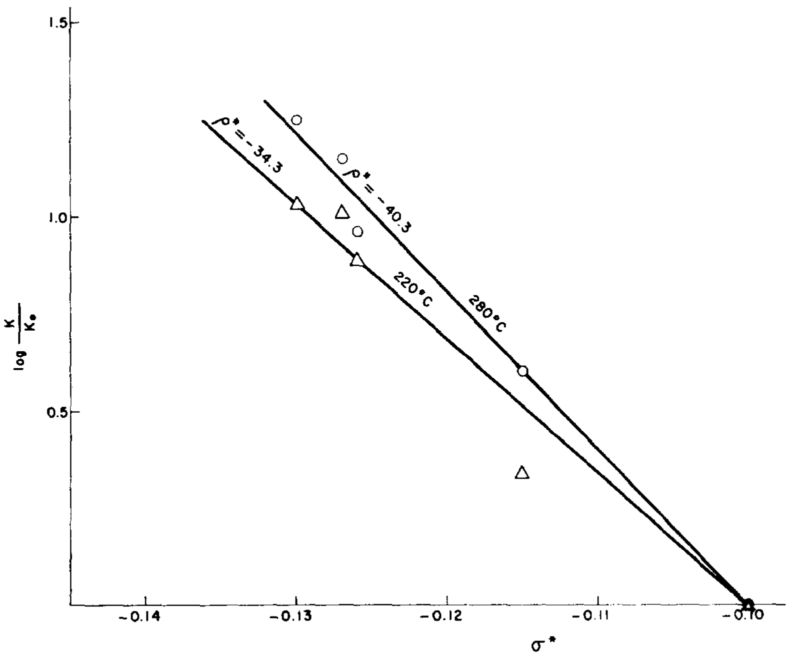

FIG. 1. Linear relation between the dehydrochlorination rate of alkyl chlorides and Taft σ^* values over $BaSO_4$.

Figure 1 shows a plot of the values from Table 1 giving a good fit to the Taft equation. The strong negative ρ^* values obtained show that over $BaSO_4$ this reaction series has a marked polar character. This is in accordance with the carbonium ion mechanism proposed formerly (*6*). The C–H bond is little broken in the transition state.

The ρ^* value is more negative, i.e., the reaction is more polar, at higher temperature. We would recall here former results about the occurrence of concerted and carbonium ion mechanisms as a function of temperature (*9*). Whenever both mechanisms could be observed with a given reaction system, the concerted, i.e., less polar, mechanism occurred at lower temperature and the transition from the one to the other mechanism was continuous. Thus it may be concluded that there exists a continuous sequence of mechanistic behavior, within which a given system covers a certain range, which is shifted with the variation of the conditions. As shown in Table 2, the butenes formed at 280° correspond to the thermodynamic distribution, while differing from it at 220°C, the difference usually being attributed to thermodynamic and kinetic control, respectively. We might suggest that the thermodynamic control at higher temperature is due to the carbonium ion character being more pronounced. For example the lifetime of the carbonium ion could be higher and also the difference in breakage of the C–Cl and C–H bond.

The deviation from linearity observed for *n*-propyl chloride at 220°C may also be due to a less carbonium ion (or even partial concerted) character of the mechanism

TABLE 2
RELATIVE DISTRIBUTION OF BUTENE ISOMERS OVER $BaSO_4$

Isomer	220°C Formed (%)	220°C Equilibrium[a] (%)	280°C Formed (%)	280°C Equilibrium[a] (%)
trans-2-Butene	31.7	54.0	49.0	50.8
cis-2-Butene	32.5	31.8	32.2	31.1
1-Butene	35.2	14.2	18.8	17.8

[a] According to (*10*).

with this reactant as compared to the others. This difference disappears at higher temperature.

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