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The Use of Hückel Theory Charge Densities and Localization Energies for the Prediction of Kinetic and Thermodynamic Factors Involved in an Assumed Model for the Hydrohalogenation of 1,3-Butadiene, Isoprene and Chloroprene

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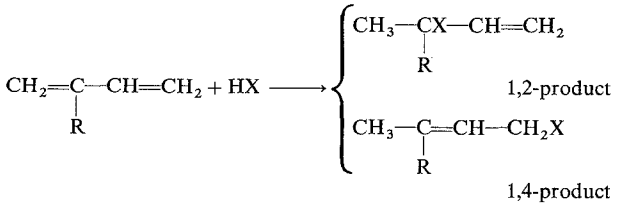
It is assumed that the first step in the hydrohalogenation of a diene under conditions such that an ionic mechanism is operative involves the formation of a linear carbonium ion *via* attachment of a proton to the 1-position and that the second step involves addition of the halide ion to either the 2- or 4-positions. If it is also assumed that hyperconjugation plays some non-negligible role in the carbonium ion intermediate, then it turns out that the use of Hückel theory charge densities and localization energies predict (1) that the 1,2-product is kinetically favored in the cases of butadiene and isoprene, (2) that the 1,4-product is kinetically favored in the case of chloroprene, and (3) that the 1,4-product is thermodynamically favored in all of the above systems. All of these predictions appear to be in agreement with available experimental results.

Bei der Addition von Halogenwasserstoffen an die hier untersuchten Diene wird im Reaktionsablauf ein lineares Carbeniumion angenommen. Das Proton wird in 1-Stellung addiert und in einem zweiten Schritt wird das Halogenion in 2- oder 4-Stellung angelagert. Weiter wird angenommen, daß Hyperkonjugation beim intermediären Carbeniumion eine Rolle spielt. Aus den mit der Hückeltheorie ermittelten Ladungsverteilungen und Lokalisierungsenergien läßt sich dann voraussagen, daß (1) das 1,2-Produkt bei Butadien und Isopren, (2) das 1,4-Produkt bei Chloropren kinetisch und (3) das 1,4-Produkt in allen Fällen thermodynamisch bevorzugt ist. Diese Voraussagen scheinen mit den bekannten experimentellen Resultaten übereinzustimmen.

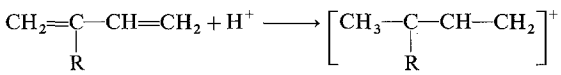
On admet que l'hydrohalogénation d'un diène dans des conditions où prévaut un mécanisme ionique comporte comme première étape la formation d'un ion carbonium linéaire par addition d'un proton à la position 1 et comme seconde étape l'addition de l'ion halogène à l'une des positions 2 ou 4. Si l'on admet par ailleurs que l'hyperconjuguaison joue un rôle non négligeable dans l'intermédiaire carbonium, l'emploi de la théorie de Hückel permet de prédire à l'aide des densités de charge et des énergies de localisation (1) que le produit 1,2 est favorable du point de vue cinétique dans les cas du butadiène et de l'isoprène (2) que le produit 1,4 est favorable du point de vue cinétique dans le cas du chloroprène et (3) que le produit 1,4 est favorable du point de vue thermodynamique dans tous ces systèmes. Toutes ces prédictions sont apparemment en accord avec les résultats expérimentaux disponibles.

Introduction

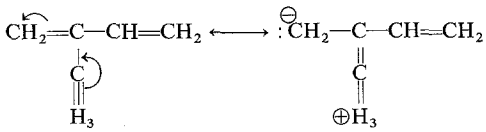
We consider the hydrohalogenation reaction

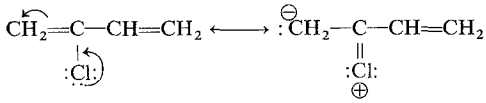


where the conditions are such that an ionic mechanism is operative. In this paper we limit outselves to the cases R = H (1,3-butadiene), R = CH_3 (isoprene or 2-methyl-1,3-butadiene) and R = Cl (chloroprene or 2-chloro-1,3-butadiene). We now assume that the above reaction may be viewed as if it takes place in two steps. The first step is assumed to involve the addition of a proton to the 1-carbon atom (R is attached to the 2-carbon atom of the butadiene framework) and may be written



where the intermediate is a *linear* carbonium ion (as opposed to, say, a *bridged* structure) in which the positive charge is distributed over conjugated portion of the system. In a usual first-order approximation one would indicate that the positive charge is distributed only over atoms 2, 3 and 4 (of the butadiene framework) but we refrain from such an indication for reasons soon to be apparent. In the case of butadiene, the attachment of H^+ to the 1-carbon atom is rationalized on the basis of the Hückel theory result that F_1 (the *free valence number* of the 1-carbon atom) is 0.838 as opposed to 0.391 for F_2. Although the free valence number appears to be more appropriate as an index of free radical nature than as an index for ionic reactions, the Pullmans [8] have demonstrated that this quantity appears to be a *universal index of chemical reactivity* of alternant hydrocarbons, serving almost equally well for free radical and ionic reactions. The Pullmans have also shown that there exists an accurate linear relationship between the free valence number and the *atom self-polarizability* $\pi_{r,r} = \partial q_r/\partial \alpha_r$. The latter quantities [$\pi_{1,1} = 0.626$ and $\pi_{2,2} = 0.402$ (in units of β_0^{-1}) for butadiene] lead to the same conclusions as does use of the much more easily computed free valence numbers. In the case of isoprene and chloroprene the analogous attachment is rationalized on the basis of the classical resonance structures:





The main question now pertains to the second step of the reaction, viz., to which of two possible sites (carbon atoms 2 or 4 of the butadiene framework) does the halide ion add? In order to answer this question it is convenient to examine two different aspects of the reaction, viz., (1) the pre-transition state aspect (kinetic control) and (2) the post-transition state aspect (thermodynamic control). The former is concerned with the question of which position is more favorable to attachment from a strictly *rate* consideration and the second is concerned with the

point of *thermodynamic equilibrium* between the 1,2- and 1,4-products. Needless to say, there is no necessary relationship between these two aspects of the reaction.

As discussed by the Pullmans [8], the Hückel molecular orbital (HMO) approximation can be made to provide a plethora of indices for the characterization of chemical reactivity.

Webster [9] has pointed out that it is convenient to classify the reactivity indices into three categories based on the particular aspect of chemical reactivity best described by given indices: (1) indices which characterize the reaction at some stage prior to the transition state, (2) indices which characterize the reaction at some stage beyond the transition state, and (3) indices which characterize specific reaction mechanisms. On this basis we conclude that the simplest relevant indices for categories (1) and (2) are the *electron charge density* and the *localization energy*, respectively. The former is defined by

$$q_r = 2 \sum_{j=1}^{\text{occ}} c_{rj}^2 \tag{1}$$

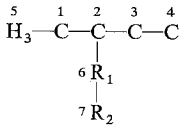
where c_{rj} is the rth component of the jth molecular orbital (MO) and the summation is over the occupied MO's. The localization energy is given by [6, 10]

$$L_r^{(n)} = T_r^{(n)} - E_\pi \tag{2}$$

where $T_r^{(n)}$ is the sum of the energies of the occupied MO's of the residual molecule (that portion of the conjugated molecule remaining after removal of the rth carbon atom and n π-electrons from the conjugated system) plus the energy of n π-electrons localized on the isolated rth carbon atom in the sp^2 valence state and where E_π is the total π-electronic energy (twice the sum of the energies of the occupied MO's) of the molecule (in our case the carbonium ion). Since the halide ion X^- is nucleophilic, one uses $n = 0$ in Eq. (2). The most reactive position with respect to addition of X^- is indicated by the atom with the lowest (most positive) value of q_r (kinetic control) and by the atom with the lowest value of $L_r^{(0)}$ (least energy needed to keep the π-electrons away from atom r). The latter reflects the thermodynamic control of the reaction and is related to the empirical *law of maximum conjugation.*

Calculations

It is convenient to represent the linear carbonium ion intermediate as



R_1	R_2	Parent molecule	Number of π-Electrons
H	—	1,3-butadiene	4
C	H_3	isoprene	6
Cl	—	chloroprene	6

where H_3 represents a pseudoatom used to indicate cognizance of hyperconjugative effects. It is immediately apparent that if one carries out an HMO calculation by

assuming that the carbonium ion intermediate is an allylic cation $(C_2—C_3—C_4)^+$ with no account taken of the other groups, then one finds that $q_2 = q_4$ and $L_2^{(0)} = L_4^{(0)}$, i.e., 2- and 4-addition of X^- are favored *equally* in both kinetic and thermodynamic aspects of the reaction. Since this result fails to account for the experimentally demonstrated non-equivalence of the 2- and 4-positions, one is forced to consider second-order conjugative effects, viz., interactions between the carbonium ion $(C_2—C_3—C_4)^+$ and the methyl (or methyl and chloro) groups. This means that one includes hyperconjugative participation of methyl groups and, for reasons of consistency, conjugative participation of chlorine in the case of chloroprene. Of course, such second-order conjugative effects are implied by the resonance structures depicted earlier. The big difficulty one is now faced with involves choosing reasonable parameters to describe the pseudoatoms and carbon atoms in the methyl groups and the chloro group. For the methyl groups we first chose the parameters used by Coulson and Crawford [1] to describe certain features of molecules such as toluene and propylene. For the chloro group we employed parameters used earlier by Hayashi *et al.* [2] in an MO treatment of the polymerization of vinyl monomers. We then tested the sensitivity of the results to these choices by varying all of the parameters (one at a time and in unison) so as to cover a reasonable range of values as reflected by choices made by others in a great variety of HMO calculations. Since the qualitative aspects of the results were virtually intensitive to the variations so considered, we report only the results of the first choice. The results, shown in the table, are indicated on the basis of HMO *electronegativity parameters*, h_r, appearing in the coulombic integral expression

$$\alpha_r = \alpha_0 + h_r \beta_0 \tag{3}$$

where α_0 and β_0 are unspecified reference values for a standard coulombic integral and standard resonance integral, respectively, and HMO *resonance parameters*, k_{rs}, given by

$$\beta_{rs} = k_{rs} \beta_0 \,. \tag{4}$$

Discussion

The reactivity indices given in the table predict that the kinetically controlled products are 1,2- in the cases of butadiene and isoprene but that the 1,4-products are thermodynamically more stable. Experimentally, it is found that at $-80°$ C HBr addition to butadiene produces 80% of the 1,2-product and 20% of the 1,4-product. At $+80°$ C the ratio of products is reversed [4]. Furthermore, prolonged heating of *either* pure 1,2- or pure 1,4-products at $+80°$ C eventually leads to an equilibrium mixture identical with the reaction products at that temperature. The lower-temperature results clearly indicate that the 1,2-product is favored kinetically. Rearrangement to a preponderance of 1,4-product would be expected to be very slow at $-80°$ C but is apparently quite rapid at a 160° higher temperature. Jones and Chorley [3] have shown that hydrochlorination of isoprene leads to a preponderance of 1,2-product, however, Ultée [11] has demonstrated that this is followed by rearrangement to the 1,4-product.

In the case of chloroprene our results predict that the 1,4-product should be in preponderance in *both* the pre-transition state and post-transition state of the

Table. *HMO parameters, electronic charge densities and localization energies for the linear carbonium ions formed from 1,3-butadiene, isoprene and chloroprene. (Charge densities are in units of e, localization energies are in units of* $-\beta_0^{-1}$. *All* h_r *and* k_{rs} *values not given are 0.0 and 1.0, respectively.)*

	Parent molecule		
	1,3-Butadiene	Isoprene	Chloroprene
h_1	−0.1	−0.1	−0.1
h_2	0.0	0.0	0.3
h_5	−0.5	−0.5	−0.5
h_6	—	−0.1	1.8
h_7	—	−0.5	—
k_{12}	0.7	0.7	0.7
k_{15}	2.5	2.5	2.5
k_{26}	—	0.7	0.6
k_{67}	—	2.5	—
q_2	0.527	0.537	0.648
q_4	0.531	0.559	0.540
$L_2^{(0)}$	1.008	1.600	1.026
$L_4^{(0)}$	0.868	0.906	0.852

reaction. Petrov [5] has studied the addition of HBr to chloroprene in glacial acetic acid at −5° C and found 72% of the 1,4-product. Since intramolecular conversion would be low at such a temperature, the 1,4-product must be the preponderant pre-transition state product. Insofar as we have been able to determine, the 1,4-product preponderance does not change with increasing temperature.

Conclusions

The above agreement between theory and experiment, albeit apparently strikingly good, is nevertheless based on too small a sampling to warrant over-optimistic generalizations to be made. We have noted, however, that a similar line of reasoning suffices to rationalize the otherwise anomalous comparitive chemistries of certain five-membered heterocyclic compounds, viz., furan, pyrrole and thiophene. HMO calculations of charge densities in these compounds predict preponderance of β-substitution products whereas it is the α-products which predominate experimentally. One also finds that the localization energies favor the α-products. This problem has been discussed in some detail by Pilar and Morris [7].

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