Evidence for Competing Bimolecular and Termolecular Mechanisms in the Hydrochlorination of Cyclohexene

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THE addition of acids to olefins *via* carbonium ion intermediates is a well documented reaction, but evidence on the stereochemistry of such additions does not conform to a simple pattern, varying from exclusive *trans*-addition to nonstereospecific addition, and to *cis*-addition depending upon the olefin structure and acidic reagent.[1] A study of the hydrochlorination of cyclohexene clarifies some of these variations.

Cyclohexene reacts slowly with hydrogen chloride in acetic acid to yield a mixture of cyclohexyl acetate and cyclohexyl chloride. The initial rates of reaction, $R = -\mathrm{d}[\text{olefin}]/\mathrm{d}t$, and chloride to acetate ratios were determined at less than 10% conversion by v.p.c. analysis. The stereochemistry of the addition was determined with 1,3,3-[$^2H_3$]-cyclohexene using the n.m.r. analysis method.[2]

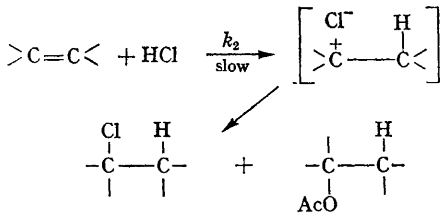
The results (*cf.* Table), show that cyclohexyl

TABLE

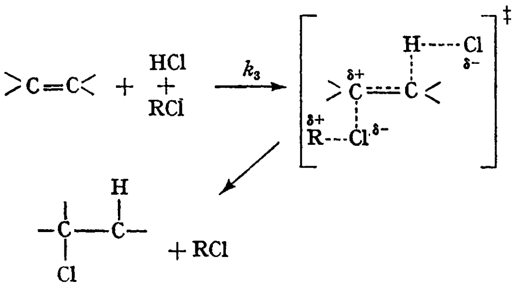
Temp. (°c)	[HCl] (M)	[NMe_4Cl] (M)	[H_2O] (M)	HOAc–Adduct % *cis*	HOAc–Adduct % *trans*	HCl–Adduct % *cis*	HCl–Adduct % *trans*	$10^7 R$ (mol. l.$^{-1}$ sec.$^{-1}$)
25·0	0·21	0	<·01	≤4	≥78	4·0	14	0·29
25·0	0·44	0	<·01	≤4	≥74	3·7	19	0·81
25·0	1·03	0	<·01	≤4	≥66	2·7	28	3·75
25·0	0·23	0	1·13	≤2	≥41	≤3	≥54	0·64
25·0	0·15	0·43	<·01	≤2	≥28	≤4	≥67	1·33
80·0	0·19	0	<·01	≤4	≥64	15	18	33·2
80·0	0·19	0·43	<0·1	≤2	≥29	≤4	≥65	—

acetate is always formed by a mainly *trans*-addition process but that cyclohexyl chloride can arise by *cis*- or *trans*-addition depending upon the reaction conditions. An increase in hydrogen chloride concentration increases the chloride to acetate ratio by increasing the amount of *trans*-hydrochloride formed, but an increase in temperature favours the formation of *cis*-hydrochloride. The presence of water or tetramethylammonium chloride enhances the reaction rate, the effect being predominantly an acceleration of *trans*-hydrochloride formation. The products were shown to be stable to the reaction conditions and no reaction was found to occur between cyclohexene and acetic acid in the absence of hydrogen chloride, either with or without added NMe_4Cl.

These observations are indicative of two competing reactions. One involves a bimolecular reaction between hydrogen chloride and cyclohexene to form a carbonium–chloride ion-pair which collapses largely to *cis*-hydrochloride and *trans*-acetate.



The other, a termolecular reaction, involves nucleophilic attack by R^+Cl^- ($R^+ = H^+$, $H_9O_4^+$ or Me_4N^+) in the rate-limiting step. It seems probable that an analogous termolecular process, with acetic acid serving as nucleophile, accounts for a substantial fraction of the *trans*-acetate formed.



The bimolecular addition *via* a carbonium-ion intermediate is a widely accepted mechanism for electrophilic addition. Termolecular *trans*-addition, however, has not been generally recognized as an important mechanism for addition of electrophilic reagents, although Hammond[3] has discussed such a mechanism as an alternative to formation of a π-complex intermediate in the *trans*-hydrohalogenation of 1,2-dimethylcyclohexene. Recent studies with hex-3-yne imply a similar mechanism for acid additions to acetylenes.[4] The bimolecular and termolecular mechanisms for addition are easily seen to be formally analogous to the reverse of E_1 and E_2 eliminations,[5] respectively.

Many of the variations observed in the steric course of acid additions to olefins may arise from competition between bimolecular and termolecular mechanisms of the type described here. In view of the possible intervention of termolecular pathways, caution should be exercised in interpreting reactions between olefins and acids exclusively in terms of carbonium-ion intermediates.

We thank the National Science Foundation for financial support.

(*Received, July* 31*st*, 1967; *Com.* 808.)

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