STUDY OF THE TRANSITION STATES IN THE HYDROXYTHALLATION OF ALKENES*

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The properties of the transition states in the hydroxythallation of alkenes are characterized by means of two mechanistic methods, *viz.* the structure-reactivity profile method and the internal comparison method. In the case of $RCH=CH_2$ and $R^1R^2C=CH_2$ alkenes the transition state species is supposed to be a cyclic activated complex possessing a high positive charge localized at the multiply substituted carbon atom, whereas in the case of hydroxythallation of branched internal alkenes an acyclic transition state approaching in nature a carbonium ion is assumed.

The kinetics and mechanisms of chemical reactions are studied with a view to arriving at relevant data requisite for characterizing the structure and properties of the transition intermediates and activated complexes. A number of criteria have been suggested for establishing the nature, cyclic or acyclic, of the transition state in addition electrophilic reactions[1]. These can be divided into two groups: criteria based on free energy relationships, and those based on the reaction stereochemistry. Among promising criteria is the qualitative characterization of the transition state based on a comparison of the relative rates and/or the equilibrium constants of Ad_E reactions for selected unsaturated systems, representing a potential means for distinguishing between cyclic and acyclic transition states in addition electrophilic reactions.

Acid-catalyzed hydration (A) and addition of arenesulphenyl chloride (B) have been suggested[2,3] as models for the two limiting cases of Ad_E reactions:

$$\underset{\diagdown}{\overset{\diagup}{C}}=\underset{\diagdown}{\overset{\diagup}{C}} \xrightarrow[\text{slow}]{H^+} \overset{\diagup}{\underset{\diagdown}{C}}{}^{(+)}-\overset{|}{\underset{|}{C}}-H \xrightarrow{H_2O} HO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + H^+ \qquad (A)$$

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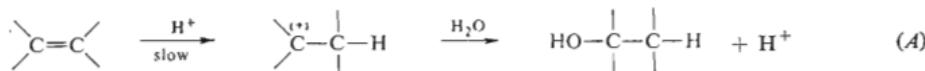
* Part IX in the series Extrathermodynamic Free Energy Relationships in the Oxidation of Alkenes by Thallic Salts; Part VIII: Chem. Zvesti 35, 165 (1981).
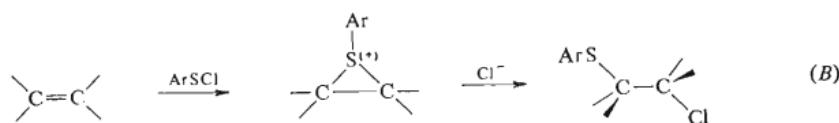
These reactions serve as standards with which the structure-reactivity profiles of other addition electrophilic reactions are compared; in this manner, information can be gained about the structure of the rate-determining transition states.

A suitable reaction for a study of the nature of the transition state is hydroxythallation of alkenes; this reaction has been extensively studied[4], yet there remain some aspects to be elucidated in it, particularly the structure of the transition state of the rate-determining stage.

EXPERIMENTAL

Chemicals

The thallic sulphate oxidant solution was prepared by electrochemical oxidation of thallous sulphate according to ref.[5]. The concentration of thallic ions was determined iodometrically[6].

2-Methyl-1-butene, chromatographically pure (99·6%), was prepared by pyrolysis at 480°C of 2-methyl-1-butanol acetate obtained by acetylation of 2-methyl-1-butanol (Fluka) with acetic anhydride. 2,3-Dimethyl-1-butene, 2-methyl-2-butene, and β-methylstyrene were commercial chemicals (Fluka). All the remaining alkenes were prepared according to ref.[7].

Reaction Kinetics

The hydroxythallation rates were determined spectrophotometrically[7] in the ultraviolet region. The kinetics of the reaction of olefins was measured on a Unicam SP-500 spectrophotometer in 1 cm cells at $25 \pm 0.1°C$. The rate constants given in Table I are average values from three to five independent measurements.

RESULTS AND DISCUSSION

The transition states of addition electrophilic reactions are variable, from the open ions structure A (Scheme (A)) to structures approaching the symmetric bridged-ions structure B (Scheme (B)). As the substituent effects on the two transition states are different, the dependences of the linearity of the free energies on the structure will be applicable to the study of the transition state nature to a limited extent only.

The rate constants of the acid-catalyzed hydration (k_{H^+}), hydroxythallation $(k_{Tl^{3+}})$, and addition of 4-chlorobenzene sulphenyl chloride in tetrachloromethane (k_{ArSCl}) for the alkene series under study are given in Table I. Obviously, no correlation occurs in the plot of log k_{H^+} vs log $k_{Tl^{3+}}$, hence, there is no similarity between the structure-reactivity profiles for alkene hydroxythallation and hydration (at least,

for the reactivity span in question). This warrants the statement that the transition state of the rate-determining step in the hydroxythallation of the compounds studied does not possess the open-ion structure. The plot of $\log k_{ArSCl}$ vs $\log k_{Tl^{3+}}$ is one of a loose linear correlation. The points corresponding to 2,4,4-trimethyl-2-pentene and 2-methyl-2-butene lie far off the regression straight line; in these compounds, particularly the former one, effects of steric nature obviously operate. Secondary effects, particularly hyperconjugation, may play here a part too. In contrast to bromination[8], the steric demands of the thallic ion and of arenesulphenyl chloride should be not very different owing to their similar geometry (the Van der Waals radii are[9] $r_S = 185$ pm, $r_{Tl^{3+}} = 178$ pm), but in the case of the addition of arenesulphenyl chloride the groups bonded at the sulphur atom can bring about interactions which cannot take place in the hydroxythallation.

The remaining data correlate as

$$\log k_{ArSCl} = 0{\cdot}30 \log k_{Tl^{3+}} + 1{\cdot}98 \quad (r = 0{\cdot}762, \ S = 58{\cdot}03\%) . \quad (1)$$

TABLE I

Rates (1 mol^{-1} s^{-1}) of hydroxythallation ($k_{Tl^{3+}}$), hydration (k_{H^+}), and addition of 4-chlorobenzenesulphenyl chloride (k_{ArSCl}) at 25°C

No	Alkene	$k_{Tl^{3+}}$	k_{H^+}[a]	k_{ArSCl}[a]
1	$CH_2{=}CH_2$	0·335	$0{\cdot}15 \cdot 10^{-14}$	65
2	$CH_3CH{=}CH_2$	9·423	$0{\cdot}238 \cdot 10^{-8}$	205
3	$C_2H_5CH{=}CH_2$	18·80	—	248
4	$n\text{-}C_4H_9CH{=}CH_2$	25·72	$0{\cdot}432 \cdot 10^{-8}$	133
5	$i\text{-}C_3H_7CH{=}CH_2$	35·01	—	140
6	$i\text{-}C_3H_7CH{=}CHCH_3$	81·90	—	325
7	$t\text{-}C_4H_9CH{=}C(CH_3)_2$	2·14	—	1 462
8	$C_6H_5CH{=}CH_2$	1·16	$0{\cdot}24 \cdot 10^{-6}$	62
9	$C_6H_5(CH_3)C{=}CH_2$	1·79	$0{\cdot}133 \cdot 10^{-3}$	265
10	$(CH_3)_2C{=}CHCH_3$	28·18	$2{\cdot}15 \cdot 10^{-4}$	3 030
11	$trans\text{-}C_6H_5CH{=}CHCH_3$	5·45	$1{\cdot}12 \cdot 10^{-7}$	118
12	$C_2H_5(CH_3)C{=}CH_2$	25·47	$0{\cdot}522 \cdot 10^{-3}$	611
13	$i\text{-}C_3H_7(CH_3)C{=}CH_2$	48·00	—	420
14	$n\text{-}C_3H_7(CH_3)C{=}CH_2$	27·80	—	—
15	$neo\text{-}C_5H_{11}(CH_3)C{=}CH_2$	13·00	—	—
16	$n\text{-}C_4H_9(C_2H_5)C{=}CH_2$	22·03	—	—
17	$n\text{-}C_3H_7CH{=}CH_2$	20·85	—	—
18	$C_2H_5(CH_3)C{=}CHCH_3$	49·60	—	—

[a] Ref.[2].

The purpose of this correlation treatment was not to obtain a tight fit by eliminating some of the data, but rather discern the tendencies in the structure-reactivity profiles based on all the available data. For this approach the data are sufficiently informative.

The overall tendency of the dependence (1) points to some similarities between the structure-reactivity profiles for addition of arenesulphenyl chloride and hydroxy-thallation (except for hydroxythallation of branched internal alkenes). This is consistent with the generally adopted mechanism, involving a bridge rate-determining transition state, for both reactions. However, as the correlation is rather loose, the transition state in the hydroxythallation should be represented by an asymmetric three-link cyclic activated complex possessing a high positive charge localized at the multiply substituted carbon atom (structure C) (for the $RCH=CH_2$ and $R^1R^2C==CH_2$ alkenes at least).

$$\left[\begin{array}{c} | \quad\quad | \\ -C\!\!\!-\!\!\!-\!\!\!-C-R \\ \diagdown_{Ti}\diagup^{9+} \\ \diagup\ \diagdown \end{array} \right]^{\ddagger} \qquad (C)$$
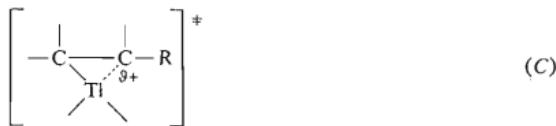
The Internal Comparison Method

The nature of the transition state in the hydroxythallation of alkenes can be further verified by using a new approach of the internal comparison method[10]. In this method the errors inherent in techniques employing for a given reaction series an external structure scale and substitution constants are eliminated. As required by this method, the hydroxythallation rate constants were determined for an isosubstituted series of alkenes: $RCH=CH_2$, $R^1R^2C=CH_2$, and internal alkenes (Table I).

The least squares method afforded the regression straight lines

$$\log k_2 = 0.98 \log k_1 + 0.16 \quad (r = 0.999, \ S = 99.80\%) \qquad (2)$$

for $R^1R^2C=CH_2$ alkenes (omitting n-$C_4H_9(C_2H_5)C=CH_2$), and

$$\log k_3 = 0.80 \log k_1 + 0.70 \quad (r = 0.999, \ S = 99.80\%) \qquad (3)$$

for internal alkenes (omitting t-$C_4H_9CH=C(CH_3)_2$; the subscripts 1, 2, and 3 refer to the $RCH=CH_2$, $R^1R^2C=CH_2$, and branched internal alkenes, respectively) (Fig. 1). The slope of the straight line B in Fig. 1 (for $R^1R^2C=CH_2$ alkenes) is nearly unity, so that the straight line can be considered parallel to the reference straight

line A (for $RCH=CH_2$ alkenes). However, more important than the achieved better fit are the relative positions of the straight lines in the plot. Independent of any other data, the relative slopes of the straight lines B and C give information on the nature of the transition state in the reaction[10]. The $R^1R^2C=CH_2$, and the branched internal alkenes could be expected to form intermediates with the character of the carbonium ion A; their behaviour with respect to the polar substituent effect should be different as compared with that of the $RCH=CH_2$ alkenes (straight line A). In fact, however, the straight lines A and B are parallel, which indicates that the transition states in the hydroxythallation of $RCH=CH_2$ and $R^1R^2C=CH_2$ alkenes are of similar nature, $viz.$ the asymmetric bridged-ion entity C.

The slope of the straight line C (for branched internal alkenes) is significantly different from unity. Its value indicates that the transition state in the hydroxythallation of branched internal alkenes is of a different nature. As pointed out above, the substituent effects in the transitions states A and B are different. In the hydroxythallation of alkenes, differences have actually been observed[7]. Moreover, the ground and the transition states of the reactions will be affected also by other phenomena such as the intramolecular and intermolecular steric effects, solvent effects, and electronic effects, which may differ from those for which the substituent constants have been defined.

Based on the different behaviour, the hydroxythallation of branched internal alkenes can be assumed to involve a transition state with an asymmetric structure,
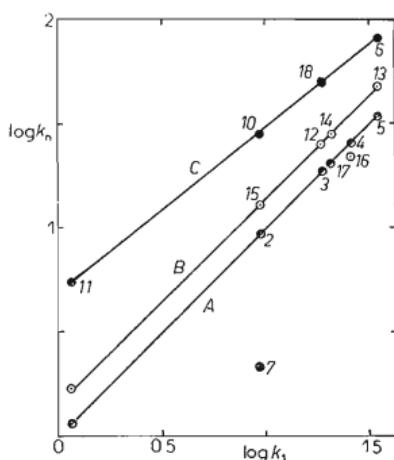

Fig. 1

Experimental course of hydroxythallation of $RCH=CH_2$ (A), $R^1R^2C=CH_2$ (B) and branched internal alkenes (C), k_n, where $n = 1, 2$, and 3 for the three alkene types, respectively

approaching that of the carbonium ion D:

$$\left[\begin{array}{c} R \\ | \\ R-C-C-R \\ | \ \ \ + \\ Tl \\ \diagup \diagdown \end{array} \right]^{\pm} \qquad (D)$$
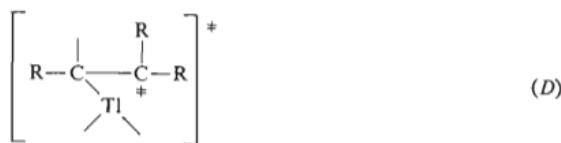
The degree to which this structure participates should be dependent upon the relative significance of the $2p\pi \rightarrow 6s$ charge transfer contribution.

The concept of the nature of the transition state in the oxidation of $RCH{=}CH_2$ alkenes[7] is, moreover, supported by the study[11] of oxidation of substituted styrenes, indicating that the activated complex in the oxythallation to a high extent bears the character of a π-complex. The rearrangement of the π-complex to the σ-organothallic species is consistent with the stereochemical studies of cyclohexene systems[12,13]. By employing the Amis relation, Treindl and Melicherčík determined the critical distances $r = 0.43$, 0.33, and 0.48 nm for acrolein[14], crotonaldehyde, and methacrolein[15], respectively, corresponding probably to the distance between the Tl^{3+} ion and the double bond in the intermediate π-complex. These limited data are consistent with the concept of oxythallation of unbranched linear alkenes proceeding via a cyclic activated complex.

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