Hydroxide Ion Initiated Reactions under Phase-Transfer-Catalysis Conditions. 5. Isomerization of Allylbenzene via Hydroxide Ion Extraction

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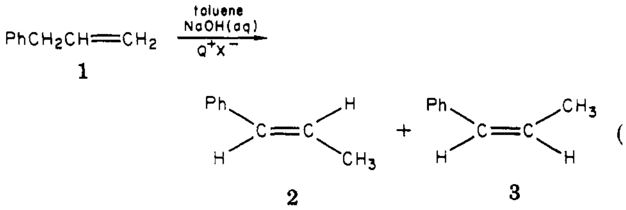
Kinetic data are reported regarding the isomerization of allylbenzene under phase-transfer-catalysis (PTC/OH^-) conditions. The dependency of these data on the stirring rate, catalyst structure, catalyst concentration, temperature, counterion, and aqueous hydroxide ion concentration are consistent with a hydroxide ion extraction mechanism.

The mechanism of hydroxide ion initiated reactions performed under phase-transfer-catalysis conditions (PTC/OH^- systems) has been the subject of much discussion. At first, it was thought that the hydroxide ion may be extracted from an aqueous reservoir into an organic phase with the aid of quaternary ammonium or phosphonium cations.[1,2] The Starks extraction mechanism[3,4] was believed to be applicable to the hydroxide ion as it was shown to be valid for other inorganic anions. Dehmlow later demonstrated[5] that the extraction constants of tetraalkylammonium hydroxides are quite low and pointed out possible sources of error in prior determinations of organic phase OH^- content. It was generally thought that the extraction of the hydrophilic hydroxide ion could not account for the behavior of PTC/OH^- systems. Makosza proposed an alternative mechanism for alkylation and carbene reactions in which deprotonation of the organic substrate by the hydroxide ion occurs at the interface.[6] According to this mechanism the role of the "quat" (R_4N^+ or R_4P^+ cation) is to remove the resulting organic anion from the interface into the bulk organic phase for subsequent reaction. Several studies have provided support for various aspects of the Makosza mechanism.[7-9]

We report the kinetic details of a systematic investigation of the isomerization of allylbenzene[10] under PTC/OH^- conditions and discuss the mechanistic implications of the results.

Results

Allylbenzene (1) was isomerized to *trans*- (2) and *cis*-β-methylstyrene (3) in the presence of toluene, aqueous NaOH, and catalytic amounts of a phase-transfer catalyst (see reaction 1).



(1)

Table I. Dependence of Rate Constant on Counteranion[a]

catalyst[b]	10^3k_{obsd}	induction time, min
TBA-HSO_4	114	<0.1
TBA-Cl	24	1.3
TBA-Br	2.4	10

[a] Reaction conditions: 1.42 M allylbenzene in toluene, 5 mol % of catalyst, 40% NaOH, 75 °C, 850 rpm. [b] TBA = tetrabutylammonium.

The reaction was run under varying conditions of mechanical stirring speed, quat structure, initial catalyst concentration, temperature, catalyst counterion, and aqueous NaOH concentration. Standard reaction conditions consisted of 1.42 M allylbenzene in toluene, 5 mol % tetrabutylammonium bromide (TBABr), 50% aqueous NaOH, 75 °C and stirring speed of 850 rpm.

The reactions follow pseudo-first-order kinetics (see eq 2) until Hoffman elimination of the quat becomes appreciable (catalyst decomposition may effectively stop the reaction at 70%–98% conversion, depending on reaction conditions). For almost all the reported values of k_{obsd} pseudo-first-order kinetics is obeyed up to 50–90% conversion (1–3 half-lives), depending on reaction conditions. In the very slowest reactions pseudo-first-order kinetics is observed for seven points up to at least a 2.5-h reaction time (≥0.4 half-lives).

$$\text{rate} = k_{obsd}[\text{allylbenzene}] \qquad (2)$$

In all the reactions an induction period was observed which was dependent on reaction conditions and will be discussed further.

The influence of stirring speed on k_{obsd} is shown in Figure 1. The reaction rate increases with increasing stirring speed up to 300 rpm above which the rate remains independent of stirring speed. The curve exhibited in Figure 1 is similar to that reported by Starks (Figure 4, ref 4). The effect of stirring speed on the induction period is shown in Figure 2. The induction period decreases as stirring speed increases and levels off to a constant value above 550 rpm.

The effect of quat structure on k_{obsd} is shown in Figure 3. As organophilicity increases from tetrabutylammonium to tetraoctylammonium k_{obsd} increases monotonically and reaches a maximum at tetradecylammonium. Substitution of one octyl group in tetraoctylammonium ($k_{obsd} = 13.3 \times 10^{-3}$ min^{-1}) by a methyl group results in a decrease in k_{obsd} to 4.4×10^{-3} min^{-1} for methyltrioctylammonium. Ethyltrioctylammonium undergoes extensive decomposition within 1.5 h due to the available ethyl group being convenient for Hoffman elimination. Quats below a minimum organophilicity (e.g., tetrapropylammonium) are ineffective.

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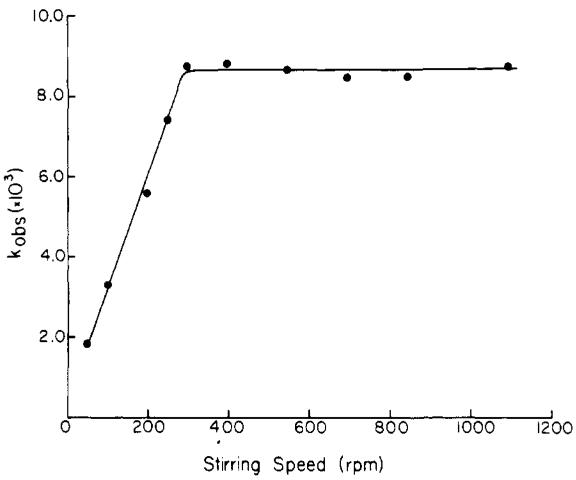

Figure 1. Dependence of k_{obsd} on stirring speed.

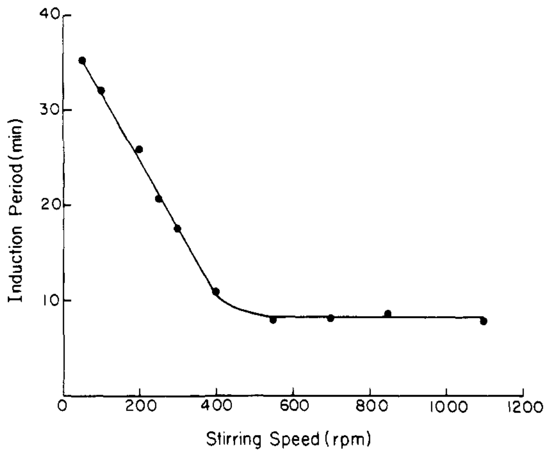

Figure 2. Dependence of induction periods on stirring speed.

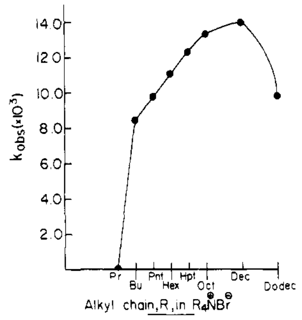

Figure 3. Dependence of k_{obsd} on quat structure.

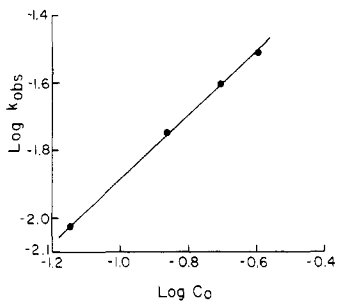

Figure 4. Determination of kinetic order with respect to catalyst (0.97).

When k_{obsd} is plotted opposite initial catalyst concentration, C_0, a slight deviation from linearity is observed apparently due to the change in the properties of the organic phase with increasing catalyst content (up to 10% catalyst by weight at 20 mol %). In Figure 4 log k_{obsd} is plotted opposite log C_0. A slope of 0.97 indicates nearly first order with respect to the catalyst.

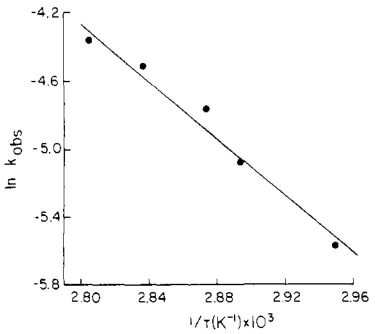

Figure 5. Arrhenius plot: dependence of k_{obsd} on temperature.

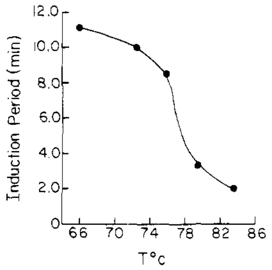

Figure 6. Dependence of induction period on temperature.

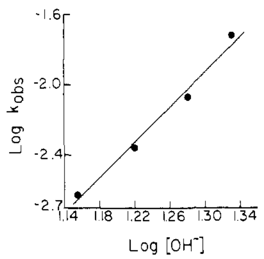

Figure 7. Dependence of k_{obsd} on aqueous hydroxide ion concentration.

The energy of activation for the reaction is on the order of about 17 kcal/mol as determined from the Arrhenius plot in Figure 5. The induction period is also temperature dependent, decreasing with increasing temperature (Figure 6).

The effect of the catalyst counterion was examined in the presence of 40% NaOH (in order to assure total solubility of the catalyst in the biphase system), and the results are presented in Table I.

As in all PTC/OH^- reactions, this reaction is very sensitive to the aqueous NaOH concentration. In Figure 7 log k_{obsd} vs. log $[OH^-]$ gives a slope of 5.0. In the presence of 50 mol % powdered solid NaOH a value of 38×10^{-3} for k_{obsd} was obtained. No reaction was observed after 90 min in the presence of 50 mol % powdered NaOH in the absence of catalyst.

The possibility of catalysis by a species other than the combination of the hydroxide ion with the quat was ruled out by control experiments. No reaction was detected after 20 h of stirring in the absence of catalyst or in the presence of 5 mol % tri-*n*-octylamine. Likewise, no reaction was observed without the initial presence of aqueous NaOH.

Discussion

Two major mechanisms have been proposed for PTC reactions, the Starks extraction mechanism[3] and the Makosza interfacial mechanism.[6] Reactions believed to proceed through the extraction mechanism are characterized by (1) increased reaction rate with increased organophilicity or with larger symmetrical tetraalkyl ammonium ions,[1,11,12] (2) independence of reaction rate on stirring speed above a certain value,[1,4,12] and (3) linear dependence of reaction rate on catalyst concentration.[1,4,12] In contrast, reactions believed to proceed via the Makosza interfacial mechanism are characterized by (1) maximum reactivity with relatively hydrophilic quats, usually alkyltriethylammonium quats,[9,13,14] (2) increased reaction rate with increased stirring speed, even up to 1950 rpm,[8] and (3) fractional kinetic order with respect to catalyst[8] (when interfacial steps are at least partially rate limiting).

The dependency of the rate of isomerization of allylbenzene on quat structure, stirring speed, and catalyst concentration is consistent with that found for the extraction mechanism. The detailed mechanism proposed is represented in Scheme I.

Scheme I. Mechanism of Isomerization of Allylbenzene under PTC Conditions

step 1: $Q^+Br^-(org) + OH^-(aq) \rightleftharpoons Q^+OH^-(org) + Br^-(aq)$

step 2: $Q^+OH^-(org) + PhCH_2CH{=}CH_2(org) \xrightarrow{k} Q^+[Ph{-}CH{-}\dot{C}H{-}CH_2]^-(org) + H_2O$

step 3: $Q^+[Ph{-}CH{\cdots}\dot{C}H{\cdots}CH_2]^- + H_2O \xrightarrow{\text{fast}} 2 + 3 + Q^+OH^-$

$$\text{rate} = k[Q^+OH^-]_{org}[\text{allylbenzene}]_{org} \qquad (3a)$$

$$k[Q^+OH^-]_{org} = k_{obsd} \qquad (3b)$$

Step 1 involves the extraction of the hydroxide ion into the organic phase by the quat through an equilibrium process. The extraction of the very hydrophilic hydroxide ion into such a nonpolar phase as toluene is expected to be difficult, especially in the presence of the bromide ion. Dehmlow has reported an extraction constant of about unity for tetraheptylammonium in the presence of chloride.[5] In the presence of bromide the extraction constant of hydroxide should decrease by about 1–2 orders of magnitude.[15] The low extraction constant is partially offset by a large aqueous hydroxide ion concentration. As expected, it was difficult to quantitatively determine $[Q^+OH^-]_{org}$ when exchanging OH^- for Br^-. Qualitatively, aliquots taken from the organic phase in a Q^+Br^-/toluene/50% NaOH system (Q^+ = tetraoctyl-, tetrahexyl-, tetrabutylammonium) turned a yellow solution of 2,4-dinitroaniline indicator red, indicating the presence of base. Tri-*n*-butylamine and tri-*n*-octylamine under the same conditions did not cause a color change in the yellow indicator solution. It is concluded that the hydroxide ion is transferred into the organic phase.

The induction periods observed most likely result from the need for $[Q^+OH^-]_{org}$ to reach a steady-state concentration. This is supported by the dependence of induction period on stirring speed (Figure 2) and temperature (Figure 6). In all cases, a time interval is needed to reach the steady-state concentration. Increasing the stirring speed facilitates mass transfer up to a certain point. Over 550 rpm the induction period levels off at about 8 min. An increase in temperature also facilitates mass transfer, and again the induction period decreases.

Deprotonation of allylbenzene by Q^+OH^-(org) in step 2 is the rate-determing step as can be concluded from the first-order dependence of allylbenzene and of the catalyst. Once the equilibrium of step 1 is reached, the concentration of Q^+OH^-(org) is constant and enters the pseudo-first-order rate constant, k_{obsd}. The monotonic increase in k_{obsd} with increasing organophilicity between tetrabutylammonium and tetraoctylammonium reflects the corresponding shift of the equilibrium of step 1, yielding higher steady-state Q^+OH^-(org) concentrations for the larger quats. Dehmlow has found a leveling off of hydroxide ion extraction at tetrahexylammonium in the equilibration of Q^+Cl^- in benzene with 50% NaOH.[5] In contrast, it may be concluded from Figure 1 that in the presence of the more lipophilic bromide ion, hydroxide ion extraction into toluene continues to increase with increasing size of the quat at least until tetraoctylammonium.

The data presented in Table I demonstrate the competition between the hydroxide ion and the catalyst counterion for extraction into toluene. In the presence of 40% NaOH more TBA^+OH^- is extracted into toluene on employing $TBA^+HSO_4^-$ than on employing TBA^+Br^-, despite the much greater solubility of TBA^+Br^- in toluene. The order of lipophilicity $HSO_4^- < Cl^- < Br^-$ also determines the ease of achieving the steady-state concentration of Q^+OH^-(org) as can be seen from the corresponding induction times.

The great sensitivity of the reactivity of the system toward the aqueous NaOH concentration (Figure 7) may be explained by a combination of several major factors, the mass law, the salting out effect, and the basicity of the hydrated hydroxide ion. We have demonstrated the importance of water molecules accompanying the quat–anion ion pair in benzene, even in the presence of concentrated aqueous NaOH.[16] At lower NaOH concentrations more water molecules are available for concurrent transfer with the hydroxide ion into the organic phase. Varying extents of hydroxide ion hydration in the organic phase may significantly alter the basicity of the hydroxide ion. Employment of powdered NaOH afforded a lower reaction rate than expected for such an increase in $[OH^-]$. This may be due to the relative shortage of available water molecules in the organic phase for reprotonation in step 3.

We submit that a hydroxide ion extraction mechanism is possible for PTC/OH^- reactions. Due to the relative hydrophilicity of the hydroxide ion, hydroxide ion extraction cannot compete with a parallel reaction involving softer anions. Thus, deprotonated substrates such as RO^-, PhS^-, or $PhCHCN^-$, deprotonated either in the aqueous phase or at the interface, will preferably associate with the quat in the organic phase and will undergo subsequent reaction. When such reactions are not possible, extraction of the hydroxide ion into as nonpolar a phase as toluene is possible, even in the presence of bromide, and may initiate further reaction.

Experimental Section

All materials were commercially available at >99% purity. Analytical purity of the toluene and allylbenzene were confirmed by GC analysis. GC determinations were performed on a GOW-Mac gas chromatograph (TC detector) equipped with a 2-m 15% DEGS on Chromosorb P column operating at 95 °C. Clear resolution of the peaks was obtained at a flow rate of 1 cm^3/s with

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retention times of 155, 270, and 195 s for compounds **1**–**3**, respectively. The trans (**2**) to cis (**3**) ratio is about 11:1.

In a typical reaction, a 50-cm^3 round-bottomed flask with a side arm for sampling was charged with 243 mg (0.755 mmol) tetrabutylammonium bromide and with a 15.1 mmol allylbenzene in 8.00 cm^3 of toluene solution (1.42 M at 75 °C). The mixture was heated to 75 °C and 5.00 mL of aqueous 50% NaOH preheated to 75 °C was added, stirring was commenced, and the time was taken. At regular intervals, 5.0-μL samples of the upper organic layer were taken and immediately injected into the gas chromatograph. Phase separation was almost immediate after stopping the stirring. No less than nine samples were taken per run. The temperature was maintained ±0.4 °C by a Fried thermoregulator, electric relay, and thermostated bath. Stirring was provided by a Heidolph mechanical stirrer with appropriate gears attached to a flat-bladed Teflon paddle. The stirring speed was determined by a Jaquet tachometer to ±10 rpm.

Registry No. 1, 300-57-2; TBA-HSO4, 32503-27-8; TBA-Cl, 1112-67-0; Bu_4NBr, 1643-19-2; Pnt_4NBr, 866-97-7; Hex_4NBr, 4328-13-6; Hep_4NBr, 4368-51-8; Oct_4NBr, 14866-33-2; Dec_4NBr, 14937-42-9; $Dodec_4NBr$, 14866-34-3.

Mass Spectrometric Analysis of the Isotopomeric Species in the Solvolysis of 1,2-Diphenyl-2-[$^2H_5$]phenyl[2-^{13}C]vinyl Bromide in 70% HOAc–30% H_2O

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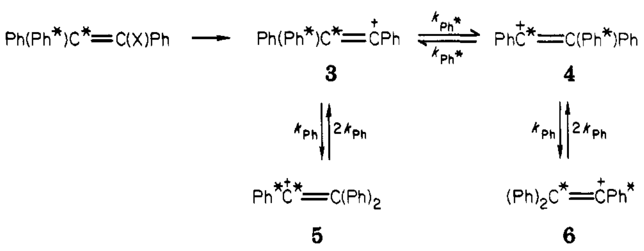
The distributions of products from four possible isotopomeric triphenylvinyl cations derived from solvolyses in 70% HOAc–30% H_2O of the doubly labeled 1,2-diphenyl-2-[$^2H_5$]phenyl[2-^{13}C]vinyl bromide (**1**-Br-2-^{13}*C*-2-*Ph*-d_5) were determined by mass spectrometry. The electron-impact spectra of the reaction products, the various labeled 1,2,2-triphenylethanones derived from the four isotopomeric cations, did not give consistent or reproducible results probably because of complications by multiple fragmentation. After degradation of the reaction products to give $(C_6H_5)_2CO$, $(C_6H_5)_2{}^{13}CO$, $C_6H_5(C_6D_5)CO$, and $C_6H_5(C_6D_5){}^{13}CO$, the chemical ionization spectra of these isotopomeric benzophenones gave, for each solvolysis reaction, the relative amounts of the four isotopomers and hence the distribution of products derived from the four isotopomeric triphenylvinyl cations. The results obtained showed agreements between the mass spectrometric data and previous ^{14}C scrambling data or the ^{13}C scrambling data obtained in the present work by ^{13}C NMR, with the ^{14}C or ^{13}C scrambling data showing greater precision. For example, the scrambling of the ^{13}C label from C-2 to C-1 as determined by ^{13}C NMR for the solvolysis of **1**-Br-2-^{13}*C*-2-*Ph*-d_5 in 70% HOAc in the presence of various amounts of added NaOAc was found to be 15.2 ± 0.5%, while the analogous value derived from the CI spectral analysis was 13.9 ± 2.2%. The observed formation of the various possible isotopomeric products also demonstrated definitely the occurrence of successive 1,2-phenyl shifts in the triphenylvinyl cation, and this would not have been detected with the use of only a singly labeled substrate.

Degenerate rearrangements arising from 1,2 phenyl shifts in the triphenylvinyl cation were first observed in 1974 in the solvolysis of triphenyl[2-^{14}C]vinyl triflate (**1**-OTf-2-^{14}*C*) in HOAc, HCOOH, or CF_3COOH.[2] Subsequently, extensive isotopic scrambling studies on a variety of singly labeled triarylvinyl cationic systems have been carried out, and the results have been summarized in a recent book on vinyl cations[3] as well as in a recent review.[4] It is anticipated that in a triarylvinyl cation, repeated cycles of 1,2 aryl shifts may be possible. In the acetolysis of trianisyl[2-^{14}C]vinyl bromide (**2**-Br-2-^{14}*C*), for example, scrambling of the label from C-2 to C-1 was observed in both reaction product and recovered, unconsumed reactant.[5] In the later stages of reaction, the scrambling in the recovered reactant was found to be even higher than that in the corresponding product, thus indicating the occurrence of many cycles of ionization, 1,2 shift, and return to covalent bonding, leading to the accumulation of large amounts of scrambled reactant.[5] In the case of triphenyl[2-^{14}C]vinyl bromide (**1**-Br-2-^{14}*C*), however, solvolysis in HOAc was too slow, and in reactions in 70% HOAc–30% H_2O (70% HOAc), no significant extent of scrambling was observed in the recovered, unconsumed reactant.[6]

Scheme I



A more definitive measure of successive 1,2 shifts could be obtained from studies with doubly labeled substrates. With a single isotopic label such as **1**-Br-2-^{14}*C* or **2**-Br-2-^{14}*C*, 1,2 aryl shifts could only give rise to two different isotopomers with the label at C-2 or C-1. With a doubly labeled substrate, as illustrated in Scheme I for a triphenylvinyl system labeled at C-2 and at one of the C-2 phenyl groups, four isotopomeric cations (**3**–**6**) would be detectable.

It should be pointed out, however, that labeling with a radioisotope would involve only a tracer amount of the

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