Notes

Hydroxide Ion Initiated Reactions under Phase-Transfer Catalysis Conditions. 6. Dehydrobromination of (2-Bromoethyl)benzene via Slow Hydroxide Ion Extraction

Marc Halpern, Yoel Sasson,* and Mordecai Rabinovitz*

Department of Organic Chemistry and the Casali Institute of Applied Chemistry, Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received July 19, 1983

Two major mechanisms have been proposed that explain the behavior of most phase-transfer-catalyzed reactions initiated by the hydroxide ion (PTC/OH^- systems), the interfacial mechanism,[1] and the extraction mechanism.[2,3] Several PTC/OH^- reactions are believed to proceed through alternative mechanisms such as certain dehydrohalogenations[4a] and hydrolysis[4b] reactions. The extraction mechanism appears to be valid for dehydrohalogenations requiring stoichiometric quantities of tetrabutylammonium hydrogen sulfate[5,6] and in a case employing the very lipophilic tetraoctylammonium bromide (TOABr) as catalyst.[7] Dehmlow has suggested[4a] that the ion pair Q^+X^- (Q^+ = quaternary ammonium ion, "quat") may eliminate the halo acid from the substrate undergoing dehydrohalogenation, subsequently forming Q^+X^-HX, in cases where OH^- extraction is not plausible (e.g., ref 8). Elimination of HBr from (2-bromoethyl)benzene exhibits maximum reactivity with hexyltriethylammonium as the quat in the alkyltriethylammonium series,[9] but this result has not been reconciled in terms of mechanism. We report kinetic data of the dehydrobromination of (2-bromoethyl)benzene in the presence of the organophilic catalyst tetraoctylammonium bromide (TOABr). We show that this reaction represents a PTC/OH^- system in which the extraction of the hydroxide ion is a rate process and the determining step in the catalytic cycle.

The reactions and standard conditions are shown in eq 1. The reaction followed zero-order kinetics up to 1–4

$$\text{(1)}\quad PhCH_2CH_2Br \xrightarrow[\text{750° rpm (toluene)}]{\text{1 mol \% TOABr, 50\% NaOH}} PhCH{=}CH_2 + HBr$$

half-lives (50–94% conversion). The rate values are summarized in Table I. The energy of activation of the process as obtained from the Arrhenius plot is 8 kcal/mol. The proposed mechanism of the reaction is shown in Scheme I.

Two results are particularly striking. The independence of the reaction rate on the substrate concentration (zero-order kinetics) and the very low activation energy[10] indicate that the chemical reaction, i.e., step 2, is not the rate-determining step. On the other hand, these results are characteristic of diffusion control. At a given temperature, stirring speed, and shape of the reaction/mixing apparatus, there exists a definite rate of mass transfer between two phases in contact, which is also dependent on the catalyst concentration up to a certain value.[11] It can be seen from Table I that the dependence of the reaction rate on the concentration of the catalyst is stronger at the low concentrations and is weakly dependent at higher concentrations. In the concentration range examined, the dependence does not attain linearity. It may be concluded that a process involving catalyst diffusion occurs in this case and that the maximum rate of diffusion is being approached at the higher catalyst concentration of 5.0 mol %. At still higher concentrations the capacity of the system to accommodate diffusion of additional catalyst is smaller. This claim is also supported by the observed effect of stirring speed. At 1.0 mol % an increase in stirring speed from 750 to 1450 rpm doubles the reaction rate by facilitating mass transfer of the catalyst between the phases.[12] At 0.2 mol % a similar increase in stirring speed brings about an increase in reaction rate by only 30%. At the lower concentration, sufficient mass transfer of a large portion of the catalyst is attained at the lower stirring speed, and increasing the agitation does not result in as

Table I. Reaction Rates of the Dehydrobromination of (2-Bromoethyl)benzene in the Presence of TOA Br[a,e]

variable[b]	rate, M min^{-1}
5.0 mol %	6.2×10^{-2}
1.0 mol %	5.7×10^{-2}
0.2 mol %	4.6×10^{-2}
0.1 mol %	3.0×10^{-2}
1450 rpm	12×10^{-2}
1450 rpm (0.2 mol %)	6.0×10^{-2}
66 °C	4.8×10^{-2}
79 °C	7.3×10^{-2}
90 °C	9.9×10^{-2}
TEBABr[c]	9.1×10^{-4} M^{-1} min^{-1} [d]

[a] Standard reaction conditions are shown in eq 1. [b] The value of the variable only is noted. [c] Triethylbenzylammonium bromide. [d] Second-order rate constant. [e] The change of molar volume of the organic phase due to the conversion of the (2-bromoethyl)benzene to styrene was taken into account.

Scheme I

Step 1:

$$Q^+Br^-_{org} + Na^+OH^-_{aq} \xrightarrow{\text{slow}} Q^+OH^-_{org} + Na^+Br^-_{aq}$$

Step 2:

$$Q^+OH^-_{org} + PhCH_2CH_2Br_{org} \longrightarrow PhCH{=}CH_{2\ org} + Q^+Br^-_{aq} + H_2O$$

(1) Makosza, M. *Pure Appl. Chem.* **1975**, *43*, 439.
(2) Starks, C. *J. Am. Chem. Soc.* **1971**, *93*, 195.
(3) Halpern, M.; Sasson, Y.; Rabinovitz, M. *J. Org. Chem.* **1983**, *48*, 1022.
(4) Dehmlow, E.; Dehmlow, S. "Phase Transfer Catalysis"; Verlag-Chemie: Weinheim, 1980; (a) p 35, 153–154; (b) p 36–7, 154.
(5) Gorgues, A.; Le Coq, A. *Tetrahedron Lett.* **1976**, 4723.
(6) Mizuno, K.; Kimura, Y.; Otsuji, Y. *Synthesis* **1979**, 688.
(7) Dehmlow, E.; Lissel, M. *Tetrahedron* **1981**, *37*, 1653.
(8) Herriott, A.; Picker, D. *Tetrahedron Lett.* **1972**, 4521.
(9) Dockx, J. *Synthesis* **1973**, 441.
(10) E_a = 0–10 kcal/mol for diffusion-controlled processes and usually over 15 kcal/mol for chemical reaction control: Levenspiel, O. "Chemical Reaction Engineering"; Wiley: New York, 1972; Chapter 14.
(11) Y. Sasson, unpublished results.
(12) One of the phases is the organic phase. Various theories exist as to the nature of the second phase, though it is believed to be a thin film existing between the two bulk phases: McCabe, W.; Smith, J. "Unit Operations of Chemical Engineering"; McGraw-Hill, Tokyo, 1976; Chapter 22.

0022-3263/84/1949-2011$01.50/0

dramatic an increase in the efficiency of mass transfer as is observed for the higher concentration of 1.0 mol %.

Addition of 1.00 equiv of NaBr relative to NaOH to the initial reaction mixture greatly inhibits the rate although the reaction profile suggests autocatalysis (e.g., at 30 min is obtained 3% conversion; 80 min, 17%; 170 min, 62%; 280 min, 98%). It may be concluded therefore that the bromide ion is not the base but competes with the base for extraction. We have shown that the hydroxide ion may be extracted into the organic phase by TOA in the presence of bromide[3] and can catalyse the isomerization of allylbenzene. In that system an induction period is observed which is necessary to attain a steady-state concentration of $[Q^+OH^-]$ in the organic phase. In dehydrobromination, bromide ions are continuously released and $Q^+OH^-_{org}$ must be regenerated by a diffusion-extraction process (most likely at the interface for TOA[13]) that, as we see in both systems, may delay the chemical reaction. The apparent autocatalysis observed is probably due to catalysis of the dehydrobromination by trioctylamine obtained by Hoffmann decomposition of the catalyst with time in the warm basic system.[14] However, the presence of trioctylamine has not been evidenced.

PTC reactions proceeding through the extraction mechanism are characterized by the greater efficiency of organophilic quats.[3,13,15,16] A comparison of TOABr and TEBABr reveals that the organophilic quat induces a higher reactivity. In the presence of TEBABr the reaction follows second-order kinetics for $1^1/_2$ half-lives, and the second-order rate constant is reported in Table I. The mechanism in the presence of TEBA appears to be complicated and is being investigated further.

In conclusion, we have presented and characterized a PTC reaction proceeding via the extraction mechanism and that is diffusion controlled.

Experimental Section

The standard reaction procedure consisted of reacting a solution of 12.30 g of (2-bromoethyl)benzene and 840 mg of toluene (as internal GC standard—total volume 10.00 mL) with 35.0 mL of 50% NaOH in the presence of 364 mg (0.665 mmol) of TOABr and sampling for GC at regular intervals. The reaction was performed in a 100-mL three-necked round-bottomed flask equipped with a mechanical stirrer (Teflon blade), thermometer, and sampling port. The flask was immersed in a stirred thermoregulated (contact thermometer) oil bath ±0.5 °C. Each reaction mixture was stirred 15 min in the absence of catalyst and checked for zero conversion, and then catalyst was added and time taken. Every run was analyzed by at least 12 points determined after conducting a suitable GC calibration graph and correcting concentrations for changes in the volume of the organic phase. The GC was run on a 2-m column 15% SE-30 on Chromosorb operating at 150 °C and a He flow of 2 mL/s. The retention times of toluene, styrene, and (2-bromoethyl)benzene were 1.1, 1.5, and 4.9 min, respectively.

Acknowledgment. A grant from the National Council for Research and Development, Ministry of Science, is gratefully acknowledged.

Registry No. Br^-, 24959-67-9; OH^-, 14280-30-9; TOABr, 14866-33-2; NaOH, 1310-73-2; $PhCH_2CH_2Br$, 103-63-9; $PhCH{=}CH_2$, 100-42-5.

(13) Landini, D.; Maia, A.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1977**, 112.
(14) March, J. "Advanced Organic Chemistry"; McGraw Hill: New York, 1977; p 935.
(15) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796.
(16) Herriott, A.; Picker, D. *J. Am. Chem. Soc.* **1975**, *97*, 2345.

Synthesis of Bicyclo[*n*.2.1] Bridgehead Alkenes Acetoxy Substituted at the Opposite Bridgehead Position

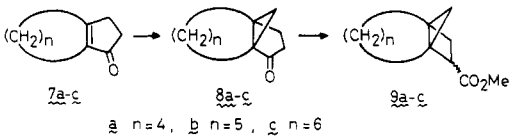
Yoshito Tobe,* Yasushi Fukuda, Kiyomi Kakiuchi, and Yoshinobu Odaira

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received October 12, 1983

Bridgehead alkenes containing a functional group at the opposite bridgehead position are of considerable interest from theoretical and synthetic points of view as models for examination of the effect of the substituents on the properties of the strained double bond[1] and as synthetic precursors of more strained bridgehead dienes.[2] Concerning bicyclo[*n*.2.1] bridgehead alkenes, only the parent hydrocarbons of the bicyclo[4.2.1] system have been synthesized,[3] while little is known for those functionalized at the opposite bridgehead position.[4] In this paper, we report on the synthesis of a series of bicyclo[*n*.2.1] bridgehead alkenes **2a–c** (*n* = 4–6) substituted at the opposite bridgehead position with an acetoxyl group based on the methodology that was successfully employed in the synthesis of bicyclo[*n*.2.2] bridgehead alkenes,[1] i.e., oxidative decarboxylation of [*n*.2.1]propellanecarboxylic acids **1a–c**[5] with lead tetraacetate. But, in applying this methodology to the [*n*.2.1] case unlike the [*n*.2.2] case, it is anticipated that oxidative cleavage of the central bond of **1a–c** would take place to afford bridgehead diacetates **3a–c** after decarboxylation (path B) in competition with the desirable oxidative decarboxylation (path A) as shown in Scheme I, because it has been well-known that strained cyclopropane derivatives suffer from oxidative cleavage of the σ bond by lead tetraacetate.[2b,7] This problem, however, could be readily solved by converting **3a–c** to **2a–c** by hydrogenation followed by elimination of 1 mol of acetic acid (path C). Furthermore, as a preliminary study on the synthesis of bicyclo[*n*.2.1] bridgehead dienes from **2a–c** by elimination of acetic acid, we also report here on the synthesis of bicyclo[6.2.1] bridgehead diene **6a** means of vapor-phase pyrolysis of **2c**.

(1) Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474.
(2) (a) Warner, P.; Boulanger, W. *Tetrahedron Lett.* **1980**, *21*, 123. (b) Scott, L. T.; Brunvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216. (c) Tobe, Y.; Ueda, Y.; Matsumoto, M.; Sakai, Y.; Odaira, Y. *Tetrahedron Lett.* **1982**, *23*, 537. (d) Tobe, Y.; Kishimura, T.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1983**, *48*, 551.
(3) (a) Wiseman, J. R.; Chan, H. F.; Ahola, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 2812. (b) Becker, K. B.; Pfluger, R. W. *Tetrahedron Lett.* **1979**, *3713*.
(4) (a) Carruthers, W.; Qureshi, M. I. *J. Chem. Soc. C* **1970**, 2230. See also: (b) Warner, P. M.; LaRose, R. C.; Palmer, R. F.; Lee, C.; Ross, D. O.; Clardy, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5507.
(5) Acids **1a–c** were prepared by alkaline hydrolysis of the corresponding methyl esters **9a–c**, which were derived by cyclopropanation of bicyclic enones **7a–c** with dimethylsulfoxonium methylide[6] followed by ring contraction[1] of [*n*.3.1]propellanones **8a–c** (see Experimental Section).



7a-c 8a-c 9a-c

a n=4, b n=5, c n=6

(6) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(7) For example: (a) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 414. (b) Ouellette, R. J.; South, A., Jr.; Shaw, D. L. *J. Am. Chem. Soc.* **1965**, *87*, 2602. (c) Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanishi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318. (d) Sakai, Y.; Terashima, K.; Tobe, Y.; Odaira, Y. *Ibid.* **1981**, *54*, 2229.

0022-3263/84/1949-2012$01.50/0