$$H_2C{=}C{=}O \xrightarrow{H^+} CH_3C^+{=}O \qquad (6)$$

$$H_2C{=}C{=}O \xrightarrow{H^+} CH_2{=}C^+OH \qquad (7)$$

A mechanism according to eq 6 or 7 was suggested to occur in the hydration of di-*tert*-butylketene in aqueous solution.[10] Since we found no influence of pH on the rate of acetic acid formation from unsubstituted ketene, reactions 6 and 7 are not considered to be the rate-determining steps for this case in the pH range studied. Because of the expected high rates for the irreversible reaction of water with the cations formed in eq 6 and 7, the latter reactions are not assumed to be the first steps in the hydrolysis.

The second possibility for the first step of the hydrolysis is the uncatalyzed nucleophilic addition of water to ketene, whereby a ketene hydrate may be formed as an intermediate. In the case of the unsubstituted ketene, this spontaneous hydrolysis takes place with a rate constant of 0.79 $M^{-1}\ s^{-1}$. Comparatively, Tidwell and co-workers found a rate constant of less than $10^{-6}\ M^{-1}\ s^{-1}$ for the uncatalized hydrolysis of di-*tert*-butylketene. This at least 10^6-fold decrease in the rate constant of the neutral hydrolysis is surprisingly large and is explained to be due to steric and to electronic factors introduced by the two *tert*-butyl groups. This low rate constant for the neutral hydrolysis renders the proton-catalyzed hydrolysis of di-*tert*-butylketene observable.[10] It is expected that, above and below the pH range studied in the present work, proton- or base-catalyzed hydrolysis appears also with the unsubstituted ketene. Because of the limitation of the conductivity method, these pH values were not accessible.

For the 4-substituted phenylketenes the reaction rate constants were correlated with the $\sigma_p{}^n$ values of the substituents leading to $\rho = +1.2$. This result as well as the independence of the hydrolysis rate constants from pH suggest a nucleophilic addition of water to be the primary step in the hydrolysis also with these ketenes.[9]

The results of the experiments with dioxane/water and acetonitrile/water mixtures as solvents show that no specific solvent effect is contributing to hydration of the unsubstituted ketene, since the first-order rate constant of the reaction was approximately proportional to water concentration in the mixture. A strongly polar transition state has been proposed for the spontaneous hydrolysis of acetyl fluoride[16] and acetic anhydride,[17] whereas less polar cyclic transition states have been suggested for the spontaneous hydrolysis of dimethylketene.[7,8] The size of the observed solvent kinetic isotope effect for ketene is in the range reported for neutral hydrolysis of various compounds.[18]

Acknowledgment. We thank Professor Dr. C. v. Sonntag, Dr. S. Steenken, and Dr. G. Koltzenburg for valuable discussions.

References and Notes

(1) R. N. Lacey in "Chemistry of the Alkenes", S. Patai, Ed., Wiley, New York, 1964, p 1161.
(2) E. Schaumann, *Chem. Ber.*, **109**, 906 (1976).
(3) N. J. Turro, M.-F. Chow, and Y. Ito, *J. Am. Chem. Soc.*, **100**, 5580 (1978).
(4) W. E. Truce and P. S. Bailey, Jr., *J. Org. Chem.*, **34**, 1341 (1969).
(5) A. Kivinen in "The Chemistry of Acyl Halides", S. Patai, Ed., Wiley, New York, 1972, p 177.
(6) N. F. Yaggi and K. T. Douglas, *J. Am. Chem. Soc.*, **99**, 4844 (1977).
(7) P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. B*, 889 (1968).
(8) D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.*, **4**, 231 (1975).
(9) E. Bothe, H. Meier, D. Schulte-Frohlinde, and C. von Sonntag, *Angew. Chem., Int. Ed. Engl.*, **15**, 380 (1976).
(10) Shaik Habibul Kabir, Hani R. Saikaly, and Thomas T. Tidwell, *J. Am. Chem. Soc.*, **101**, 1059 (1979).
(11) E. Bothe, Dissertation, Ruhr-Universität Bochum, 1976.
(12) R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).
(13) T. Howard McGee, *J. Phys. Chem.*, **72**, 1621 (1968).
(14) G. P. Laroff and H. Fischer, *Helv. Chim. Acta*, **56**, 2011 (1973).
(15) E. Bothe and D. Schulte-Frohlinde, submitted for publication. The elimination rate constant of $HO_2\cdot$ from $CH_3CH(OH_4)\dot{O}_2$ aqueous solution is increased by a factor of $\geq 10^4$ if the CH_3 group is replaced by an OH group.
(16) C. A. Burton and J. H. Fendler, *J. Org. Chem.*, **31**, 2307 (1966).
(17) A. R. Butler and V. Gold, *J. Chem. Soc.*, 2305 (1961).
(18) P. M. Laughton and R. E. Robertson in "Solute–Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, p 399.

Hydrogen Production from the Reaction of Solvated Electrons with Benzene in Water–Ammonia Mixtures

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Product analysis data for the reaction of the ammoniated electron with benzene–water mixtures in liquid ammonia show that the dominant product is evolved hydrogen and not 1,4-cyclohexadiene.

The hydrogenation reactions of unsaturated systems with metal–ammonia reagents (Birch reductions) are of considerable synthetic utility.[1–3] However, surprisingly little is quantitatively known about the mechanism of the Birch reductions.[4] The first reported kinetic studies of the hydrogenation reactions were for the reduction of benzene to 1,4-cyclohexadiene by alkali metals and alcohols in liquid ammonia.[5] The overall reaction is

$$C_6H_6 + 2e_{am}^- + 2ROH \rightarrow C_6H_8 + 2RO^- \qquad (1)$$

where R = H or C_2H_5. The mechanism originally suggested by Birch[6] appeared to be in agreement with the kinetic data reported by Krapcho and Bothner-By.[5] However, in a later report, Eastham and co-workers[7] give strong experimental evidence that the reaction of the metal (or solvated electron) with the weak acid (alcohol in their experiments) competes with the benzene reduction. The competing reaction is

$$2e_{am}^- + 2ROH \rightarrow 2RO^- + H_2 \qquad (2)$$

0022-3654/80/2084-3272$01.00/0

TABLE I: Results of Product Analysis for the Reaction of the Ammoniated Electron with Benzene-Water Mixtures in Liquid Ammonia at −34 °C

expt no.	NH_3, mol	10^3(initial concn of Na metal), M	initial H_2O, mmol	mole fraction H_2O	initial benzene, mmol	initial sodium, mmol	hydrogen collected, mmol	hydrogen recovery,[a] %	C_6H_8, by GC,[b] %
SJ1-20	2.35	1.90	275.9	0.105	3.55	0.222	0.108	97	*c*
SJ1-29	2.42	1.63	8.63	3.55×10^{-3}	6.33	0.984	0.482	98	*c*
SJ1-30	2.18	41.6	20.0	9.12×10^{-3}	1.55	2.36	1.20	102	2.0
SJ1-31	2.48	1.76	50.2	1.99×10^{-2}	4.44	0.110	0.0556	101	0.0
BS1-51	2.25	38.1	21.8	9.58×10^{-3}	6.97	2.14	*c*	*c*	4.3
BS1-56	2.20	4.42	33.7	1.51×10^{-3}	5.21	0.122	0.0593	97	0.0

[a] Based on initial sodium. [b] Estimated uncertainty of 2%. [c] Not determined.

In fact, the latter authors state "that any kinetic analysis of reaction 1 that fails to take into account reaction 2 is unwarrantable". Recently, Gordon et al.[8] suggested that the reaction of solvated electrons with benzene in water is consistent with the scheme

$$e_{aq}^- + C_6H_6 \xrightarrow{k_1} C_6H_6^{-}\cdot \qquad (3)$$

$$C_6H_6^{-}\cdot + H_2O \xrightarrow{k_2} C_6H_7\cdot + OH^- \qquad (4)$$

where the protonation step (eq 4) occurs so rapidly that the benzene radical anion $C_6H_6^{\cdot}$ cannot be observed. Unfortunately, these authors did not identify the reaction products, so that it is not possible to determine whether net reaction 1 or net reaction 2 occurred. Using laser-flash photolysis, Schindewolf and Neumann[9] extended the work of Gordon et al. and found that the observed second-order rate constant for the disappearance of solvated electrons in H_2O–NH_3 mixtures decreases by more than seven orders of magnitude with decreasing water content. Again, the results of these authors do not allow one to decide between net reaction 1 or net reaction 2. Therefore, we exposed solvated electrons produced by the dissolution of sodium in liquid ammonia to benzene–water mixtures in liquid ammonia to determine the extent of reaction 2. In our experiments, ammonia and sodium were purified by following procedures reported elsewhere.[10] Weighed samples of water and benzene were prepared by high-vacuum distillation into tared fragile glass ampules or break-seal tubes. The reaction cell used in this study was designed to permit independent preparation of the sodium–benzene–ammonia and the water–ammonia solutions such that the two homogeneous solutions could be mixed to initiate the reaction. No measurable extent of reaction was observed when benzene was added to the sodium–ammonia solution as indicated by conductance measurements. A detailed description of the equipment and procedures used has been given elsewhere.[10,11] When the reaction of the ammoniated electron in the presence of H_2O was complete (bleaching of the blue color), the hydrogen evolved from reaction 2 was quantitatively collected or the amount of 1,4-cyclohexadiene formed via reaction 1 was determined by GC. In some experiments, the quantities of both hydrogen and C_6H_8 were determined. Table I gives a summary of the results of this study. Examination of Table I clearly shows that, under the experimental conditions of this present work, reaction 2 must be considered the dominant reaction. We also did a few preliminary experiments (not under high-vacuum conditions) in which concentrations were ~0.5, 0.5, and 0.25 M in sodium, ethanol, and benzene, respectively. The yield of C_6H_8 was between 40 and 60% (based on sodium) and in agreement with reports by other investigators.[5,12] Moreover, Eastham and Larkin[13] have shown that the alkoxide ion has a profound effect on the rate of hydrogen liberation and that reaction 2 could be virtually brought to a halt if sufficient alkoxide ion is present. In fact, this observation is in agreement with a kinetic analysis[4] of reaction 2. The results of the present study plus those reported by Eastham and co-workers[7] do indeed show that reaction 2 is the dominant process but give limited insight concerning the mechanism of reaction 2. Since added base was reported to have a pronounced effect on the rate of reaction 2, a mechanism involving ammonium ions seems to be implicated. In water–ammonia mixtures, the equilibrium given by eq 5 must be present. The evolved hydrogen can then

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (5)$$

result from reaction of the solvated electron with NH_4^+.[14] We, therefore, conclude that the scheme described by Schindewolf and Neuman[9] cannot be a major pathway for the disappearance of relatively high concentrations of solvated electrons in benzene–water–ammonia mixtures.

References and Notes

(1) M. Smith in "Reduction", R. L. Augustine, Ed., Marcel Dekker, New York, 1968, p 95.
(2) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, New York, 1963.
(3) H. Smith, "Organic Reactions in Liquid Ammonia", Wiley, New York, 1963.
(4) R. R. Dewald, *J. Phys Chem.*, **79**, 3044 (1975).
(5) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).
(6) A. J. Birch, *Q. Rev., Chem. Soc.*, **5**, 69 (1950); **12**, 17 (1958).
(7) J. F. Eastham, C. W. Keenan, and H. V. Secor, *J. Am. Chem. Soc.*, **81**, 6523 (1959).
(8) S. Gordon, K. H. Schmidt, and E. J. Hart, *J. Phys. Chem.*, **81**, 104 (1977).
(9) V. Schindewolf and B. Neumann, *J. Phys. Chem.*, **83**, 423 (1979).
(10) C. A. Young and R. R. Dewald, *J. Am. Chem. Soc.*, **101**, 2884 (1979).
(11) R. L. Jones and R. R. Dewald, *J. Am. Chem. Soc.*, **96**, 2315 (1974).
(12) C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937).
(13) J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **81**, 3652 (1959).
(14) J. M. Brooks and R. R. Dewald, *J. Phys. Chem.*, **75**, 968 (1971).