Kinetics of the Sodium–Ammonia Reduction of 3-Octyne

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Abstract: The reduction of 3-octyne by sodium in liquid ammonia was studied kinetically with use of conventional conductometric techniques. The reaction was found to obey the second-order differential rate law $-d[e_{am}^-]/dt = 2k[e_{am}^-][3\text{-octyne}]$. An activation energy of 3.8 ± 0.9 kcal/mol was calculated. The presence of a weak acid (H_2O) markedly increased the reaction rate. A mechanism in which protonation of the radical anion is the rate-determining step is suggested.

The reduction of disubstituted acetylenes by sodium in liquid ammonia is a well-established synthetic route to high-purity *trans*-olefins.[1] Two different mechanisms have been proposed for this reaction. Greenlee and Fernelius[2] suggested that the stereochemistry of this reduction can be explained by a mechanism involving the formation of a dianion resulting from a stepwise addition of two electrons. The dianion will assume the trans geometry in order to minimize electrostatic repulsion between two unshared electron pairs. Moreover, the mechanistic scheme suggested by Greenlee and Fernelius would be expected to exhibit a rate law that would have a second-order dependence with respect to the ammoniated electron concentration.

On the other hand, House and Kinloch[3] argued that dianion formation is difficult to reconcile with polarographic studies of the electrochemical reduction of acetylenes. Consistent with the observations of other investigators,[4] House and Kinloch[3] reported that no reduction waves other than the reduction of the supporting electrolyte were observed when a number of nonconjugated acetylenes were examined either by conventional polarography or by cyclic voltammetry. Therefore, House suggested that the radical anion that is formed by addition of an electron to the triple bond is rapidly protonated to form a *trans*-vinyl radical. The *trans*-vinyl radical is then reduced and protonated at a rate faster than inversion of the radical, thus retaining the trans stereochemistry. The mechanism suggested by House would be expected to be consistent with a first-order rate expression with respect to the ammoniated electron.

We have undertaken the present study of the sodium–ammonia reduction of 3-octyne in hopes of attaining the experimental rate law which will be useful in elucidating the mechanism of reduction of dialkyl acetylenes.

Experimental Section

All work was done with high vacuum techniques (ca. 5 × 10^{-6} Torr). Ammonia (Matheson) and sodium (United Mineral) were purified by the methods described elsewhere.[5] Sodium chloride (Fisher Scientific) and 2,2,2-cryptand (MCB Reagents) were used as received. Tared samples were prepared by placing a known amount of the reagent in a tared fragile glass ampule or break-seal tube, evacuating, and sealing off under vacuum. Details of this procedure have been described elsewhere.[6] 3-Octyne (Chemical Procurement Laboratories, Inc.) was purifed by first drying over calcium hydride and then degassing by repeated freeze–pump–thaw cycles. The 3-octyne was then distilled under high vacuum onto a sodium mirror and then into break-seal tubes for storage. The contents of these break-seal tubes were subsequently distilled into tared fragile glass ampules for further use.[6]

Table I. Kinetic Data for the Reaction of 3-Octyne with Sodium in Liquid Ammonia

T, °C	[sodium], 10^3 M	[3-octyne], 10^2 M	10^2k, M^{-1} s^{-1}
−34	3.86	0.594	4.6
−34	1.68	0.404	5.8
			av 5.2 ± 0.6
−45	1.53	1.57	4.2
−45	4.21	0.972	3.9
−45	3.23	0.891	3.8
−45	2.31	0.942	3.7[a]
−45	2.88	1.88	5.3
−45	9.21	2.82	4.9[a]
			av 4.3 ± 0.5
−65	2.23	0.588	2.3
−65	2.05	1.30	1.9
−65	5.74	1.44	2.1
−65	2.75	0.352	2.6
−65	1.46	1.81	1.7
−65	3.10	3.77	1.7[a]
−65	2.01	2.72	2.4[b]
−65	1.02	0.800	1.5[c]
			av 2.0 ± 0.3
−75	5.06	2.88	1.3
−75	6.31	2.48	1.1
			av 1.2 ± 0.1

[a] NaCl added (2.9 to 5.8 × 10^{-3} M). [b] Cryptand added (4.95 × 10^{-3} M). [c] Sodium amide added (4.5 × 10^{-3} M).

The kinetic experiments were performed in a silicone convection fluid test chamber (Harris Manufacturing Co.). Conductivity was measured with a Wayne Kerr Universal Conductance Bridge Model B 221A. Sodium concentrations were determined from published conductivity data.[5] The apparatus and experimental procedure have been described previously by Dewald and Jones.[6] The experiments were run at four different temperatures, −34, −45, −65, and −75 °C. The concentration of sodium at −75 °C was determined by measuring the conductivity at −65 °C and then lowering the temperature to −75 °C and calculating the sodium concentration with use of published density values of liquid ammonia.

Results and Discussion

The linearity of the second-order plots[7] and the consistency of the second-order rate constants at each temperature investigated indicate that the reaction of the ammoniated electron with 3-octyne is first order with respect to each reactant and second order overall. The second-order plots were linear for the experiments at −65 and −75 °C over the entire concentration range monitored which was typically until 90% of the original sodium had reacted. For the higher temperature where reaction between metal and solvent would be expected to be more extensive, the second-order plots were linear in all cases until at least 60% of the original sodium had reacted. The corresponding rate law is

$$-\frac{1}{2}\frac{d(e_{am}^-)}{dt} = k[e_{am}^-][3\text{-octyne}] \qquad (1)$$

Table I gives a summary of the kinetic data. It should be noted

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[1] For reviews and references, see: (a) Smith, M. *Reductions*; Augustine, R. L., Ed.; Marcel Deckker: New York, 1968; p 116. (b) Smith, H. *Organic Reactions in Liquid Ammonia*; Wiley-Interscience: New York, 1963; Vol. 1, Part 2, pp 213–216. (c) Birch, A. J; Rao, G. S. *Adv. Org. Chem.* **1972**, *8*, 38. (d) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 205–209.

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(Table I) that the sodium cation concentration, as demonstrated by addition of either NaCl or 2,2,2-cryptand, had no observable effect on the rate. Addition of sodium amide also resulted in no observable change in the rate constant. However, addition of water (4.7×10^{-3} to 2.1×10^{-2} M) to the reaction mixture accelerated the rate to such an extent that the reaction progress was too fast to monitor by our conventional technique.

Our observations are consistent with a mechanism which is similar to that proposed by House[3] for the reactions of sodium with dialkyl acetylenes in liquid ammonia. Therefore, a modification of the House mechanism is suggested to interpret the results of the present study. We view the initial electron transfer as a reversible step rather than an irreversible process suggested by House.[3] The protonation step (eq 3) is assumed to be the rate-determining step in the following sequence of reactions

$$e_{am}^{-} + R'C{\equiv}CR \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R'C{=}CR^{\bullet -} \text{ (fast)} \qquad (2)$$

$$R'C{=}CR^{\bullet -} + NH_3 \xrightarrow{k_3} R'CH{=}CR^{\bullet} + NH_2^{-} \text{ (slow)} \qquad (3)$$

$$R'CH{=}CR^{\bullet} + e_{am}^{-} \rightarrow R'CH{=}CR^{-} \text{ (fast)} \qquad (4)$$

$$R'CH{=}CR^{-} + NH_3 \rightarrow NH_3 \rightarrow R'CH{=}CHR + NH_2^{-} \text{ (fast)} \qquad (5)$$

where $R'C{\equiv}CR$ is 3-octyne. The above mechanism yields the following rate law

$$-\frac{1}{2}\frac{d[e_{am}^{-}]}{dt} = \frac{k_2k_3}{k_{-2}}[e_{am}^{-}][\text{3-octyne}] \qquad (6)$$

The acceleration of the rate by addition of water (a proton source more acidic than ammonia) is consistent with the above mechanism. The reaction of water with the ammoniated electron (eq 7) must also be considered.[8] The extent of reaction 7 can be

$$e_{am}^{-} + H_2O \rightarrow 0.5H_2 + OH^{-} \qquad (7)$$

determined by measurement of the amount of evolved hydrogen. In one experiment with added water the evolved hydrogen gas measured after completion of the reaction accounted for only 22% of the initial amount of sodium. Therefore, it can be concluded that reaction 7, which is known to be slow,[8] does not compete extensively with the protonation step (eq 3 and 5) in the suggested mechanism. Since our results suggested that the initial protonation step was rate determining, we were discouraged from investigating the inductive effect of different alkyl substituents upon the rate.

A dianion mechanism would be more consistent with a rate expression that is second order with respect to the ammoniated electron. Moreover, extensive ion-pairing[9] between the sodium cation and the dianion would be expected. Since no effect on the reaction rate was observed in the presence of added NaCl or 2,2,2-cryptand, we conclude that there is no cation dependence in the rate expression. The observance of first-order dependence with respect to the ammoniated electron on the rate and the absence of a cation dependence lead us to rule out a dianion mechanism at this time.

Figure 1 gives an Arrhenius plot of the observed second-order rate constants for the reaction of 3-octyne with sodium in liquid ammonia. An activation energy, E_a, of 3.8 ± 0.9 kcal/mol was determined from the slope of the Arrhenius plot, and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at −34 °C were determined to be 3.3 ± 0.9 kcal/mol and -50.0 ± 10.0 cal/(mol·K), respectively. The values of E_a and $\Delta H^{\ddagger}$ are exceptionally small when compared to normal Arrhenius-type reactions. This fact appears to be a characteristic feature of solvated electron reactions.[6,10]

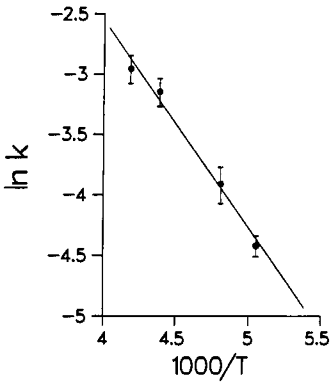

Figure 1. Arrhenius plots of ln k versus $1/T$ for the reaction of 3-octyne with sodium in liquid ammonia.

The observed activation energy can be expressed as a sum of two terms

$$E_a(\text{obsd}) = E_{a_3} + \Delta H^{\circ}_2 \qquad (8)$$

E_{a_3} is the activation energy associated with step 2 (eq 3) of the proposed mechanism, and ΔH°_2 is the enthalpy for the formation of the radical anion (step 1, eq 2). ΔH°_2 should be negative since the radical anion would be expected to be more stable at lower temperatures.[11] In other words, the small observed activation energy can be explained in terms of step 1 being exothermic. The observed entropy of activation can also be expressed as the sum of two terms

$$\Delta S^{\ddagger}_{\text{obsd}} = \Delta S^{\ddagger}_3 + \Delta S_2 \qquad (9)$$

The large negative $\Delta S^{\ddagger}_{\text{obsd}}$ is due to a large negative ΔS_2 which in turn is due the large positive entropy of the solvated electron in liquid ammonia.[12] The large negative $\Delta S^{\ddagger}_{\text{obsd}}$ value is also consistent with other ammoniated electron reactions.[6,9,10] These large negative $\Delta S^{\ddagger}$ values have been attributed to the freezing out of ammonia molecules by the activated complex and/or the collapse of the cavity of the ammoniated electron.[13]

Since the rate was found to be first order with respect to each reactant with no sodium cation dependence, the initial step (eq 2) can be viewed as the conversion of the 3-octyne to the nonlinear radical anion. The radical anion, being a carbanion, would be highly basic and should be rapidly protonated by ammonia to yield a *trans*-vinyl radical (eq 3). Moreover, steric effects such as the observed slow reduction rate of di-*tert*-butylacetylene reported by House and Kinloch[3] are consistent with the initial protonation step being rate determining as suggested in our mechanism.

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Registry No. 3-Octyne, 15232-76-5; Na, 7440-23-5.

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