Lawrence Berkeley National Laboratory

Recent Work

Title

THE REACTION OF SODIUM WITH UREA IN LIQUID AMMONIA. THE RATE CONSTANT OF THE REACTION OF THE AMMONIUM ION WITH THE AMMONIATED ELECTRON

Permalink

<https://escholarship.org/uc/item/0dt0d5tv>

Authors

Jolly, William L.
Prizant, Leonardo.

Publication Date

1968-07-01

eg. 2

University of California

Ernest O. Lawrence
Radiation Laboratory

RECEIVED
LAWRENCE
RADIATION LABORATORY

NOV 1 1968

LIBRARY AND
DOCUMENTS SECTION

THE REACTION OF SODIUM WITH UREA IN LIQUID AMMONIA.
THE RATE CONSTANT OF THE REACTION OF THE
AMMONIUM ION WITH THE AMMONIATED ELECTRON.

William L. Jolly and Leonardo Prizant

July, 1968

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

UCRL-18519
eg. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Chemical Communications

UCRL-18519
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE REACTION OF SODIUM WITH UREA IN LIQUID AMMONIA.

THE RATE CONSTANT OF THE REACTION OF THE
AMMONIUM ION WITH THE AMMONIATED ELECTRON.

William L. Jolly and Leonardo Prizant

July, 1968

The Reaction of Sodium with Urea in Liquid
Ammonia. The Rate Constant of the Reaction
of the Ammonium Ion with the Ammoniated
Electron.

By William L. Jolly* and Leonardo Prizant

(Department of Chemistry, University of California, and
Inorganic Materials Research Division,
Lawrence Radiation Laboratory, Berkeley, California, 94720)

Kinetic studies of the reactions of alcohols^{1,2} and water² with sodium
in liquid ammonia have been interpreted^{2,3} in terms of the following
mechanism

where HA represents an alcohol or water molecule. The kinetic data
are consistent with a low steady-state concentration of ammonium
ion and the corresponding rate law

$$-\frac{d(e^-)}{dt} = \frac{k_1(\text{HA})(e^-)}{(k_2/k_3)(\text{A}^-) + (e^-)}$$

Evaluation of the rate constants from the data is very difficult
because of the very strong complexing of the alkoxide ion by
dissolved alcohol³ (probably to form species of the type $\text{OR}(\text{HOR})_n^-$)
and of the hydroxide ion by dissolved water⁴ (probably to form species
of the type $\text{OH}(\text{H}_2\text{O})_n^-$). However, we have found that the same type
rate law (and presumably the same mechanism) applies to the reaction of

sodium with urea, in which complex-formation of this type is absent. In this case the rate constants may be evaluated relatively unambiguously. It seems possible that the above mechanism, characterized by the lack of a direct reaction between the electron and the species HA, is fairly general for the reaction of metal-ammonia solutions with protonic acids.

We followed the course of the urea-sodium reaction by measuring the electrical conductivity of the solution as a function of time at -45° . The measured conductivity at any given time was assumed to be the sum of the conductivity of a sodium solution[†] of concentration (e^-) and the conductivity of an NaNCONH_2 solution[†] of concentration $(e^-)_0 - (e^-)$, where $(e^-)_0$ is the initial concentration of sodium metal. A least-squares fitting of the experimental data for a given run to the rate law was accomplished with the aid of a computer, which calculated values of k_1 and k_2/k_3 and plotted the theoretical curve (based on these values of k_1 and k_2/k_3) of conductivity against time along with the experimental points. Several runs, with initial urea:sodium ratios ranging from 1.5:1 to 10:1, yielded the values $k_1 = 3.6 \times 10^{-4} \text{ sec}^{-1}$ and $k_2/k_3 = 0.30$. The computer plot of conductivity against time for a run with an initial urea:sodium ratio of 5:1 is given in Fig. 1.

Urea is one of the few acids whose ionization constants in ammonia are known. Herlem⁵ has determined that $K_a = 1.25 \times 10^{-13}$ for urea at -60° . By neglecting the difference in K_a between -60° and -45° , we may take $K_a = k_1/k_2 \approx 1.25 \times 10^{-13}$ at 45° , the temperature of our kinetic runs. By combining this value with our value for k_1 , we obtain

$k_2 \approx 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The magnitude of this rate constant appears reasonable when compared with the rate constants for the reactions of the ammonium ion with the hydroxide ion and ammonia in aqueous solution (3.4×10^{10} and $1.06 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, respectively)⁶ and with the rate constant for the transfer of a proton from the ammonium ion to ammonia in liquid ammonia ($2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°).⁷ Apparently the transfer of a proton from an ammonium ion to the anion of urea is essentially a diffusion-controlled reaction.

From the values for k_2 and k_2/k_3 we calculate $k_3 \approx 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. This value again corresponds to a diffusion-controlled reaction having a low activation energy, and it is interesting to note that the value is considerably greater than that of the rate constant for the reaction of the aqueous ammonium ion with the aqueous electron,⁸ $1.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. There is reason to question whether the rate-determining step for the liquid ammonia reaction can be formulated as it has been for the aqueous reaction:

The heats of formation in liquid ammonia for the first three species in this equation are known,³ and that for atomic hydrogen may be estimated (probably with an accuracy of ± 3 kcal./mole) by assuming zero heat of solution. Thus we calculate $\Delta H^\circ = 15 \pm 3$ kcal./mole for the liquid ammonia reaction. Now if this process is the rate-determining step, then $\Delta H^\ddagger$ must be at least 15 ± 3 kcal./mole, corresponding to a slow reaction. Thus the formation of atomic hydrogen is inconsistent with the rate constant in liquid ammonia. Perhaps the rate-determining process is better

represented by the equation

The ammonium radical might be expected to react further, as in either of the following sequences.

It should be pointed out that if, as expected for a variety of weak acids, k_2 always has a value near $10^9 \text{ M}^{-1} \text{ sec}^{-1}$, then the kinetic determination of k_1 is in effect a determination of k_1/k_2 or K_a . In some cases the kinetic measurement may be more easily accomplished than the equilibrium measurement.

This work was supported by the U.S. Atomic Energy Commission.

Footnotes and References

[†] In a separate set of experiments, the conductivity of a series of sodium solutions was determined. The data were expressed as a polynomial which was used in the computer calculations.

[‡] At the end of each run, the conductivity of the solution was that of an NaNHCONH_2 solution of concentration $(e^-)_0$.

¹ E. J. Kelly, H. V. Secor, C. W. Keenan and J. F. Eastham, J. Am. Chem. Soc., 1962, 84, 3611.

² R. R. Dewald and R. V. Tsina, Chem. Commun., 1967, 647; R. R. Dewald and R. V. Tsina, Paper presented before the Division of Physical Chemistry at the National A.C.S. Meeting in Chicago, Ill., Sept., 1967.

³ W. L. Jolly, in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D.C., 1965, p. 27; W. L. Jolly and C. J. Hallada, Chapter 1 in "Non-Aqueous Solvent Systems," T. C. Waddington, ed., Academic Press, London, 1965, p. 1.

⁴ W. L. Jolly, J. Chem. Education, 1967, 44, 304; J. Phys. Chem., 1954, 58, 250.

⁵ M. Herlem, Bull. Soc. Chim. France, 1967, 1687.

⁶ H. Strehlow, in "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd ed., S. L. Friess, E. S. Lewis and A. Weissberger, ed., Interscience, 1963, p. 865; M. Eigen and L. deMaeyer, ibid., p. 895.

⁷ D. R. Clutter and T. J. Swift, J. Am. Chem. Soc., 1968, 90, 601.

⁸ J. Rabani, in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D.C., 1965, p. 242.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.