

Solvated-Electron Reaction Rates in Amines

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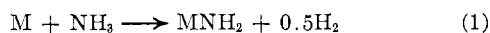
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Solutions of the alkali and alkaline earth metals in ammonia, which produce solvated electrons, have been studied for more than a century.^{1,2} However, the generality of electron trapping by polar liquids was not fully appreciated until the beginning of this decade, when radiation chemists found that electrons produced by ionizing radiation are trapped by most liquids and live long enough to exhibit characteristic physical and chemical properties.³⁻⁵ Since 1962 many investigations have been made of the optical properties and reactions of solvated electrons produced by radiolysis or photolysis. In fact, kinetic investigations of the hydrated electron alone have resulted in the determination of over 600 rate constants for its reaction with a variety of organic and inorganic compounds, more than for any other single species.⁶

The intensity of recent research on the properties and reactions of solvated electrons produced by ionizing radiation has stimulated increased interest in the properties of "stable" solutions of solvated electrons. These solutions can be produced by dissolving active metals in polar solvents which are resistant to reduction. Solvated electrons in the presence of a variety of nonreactive ions can also be produced by electrolytic reduction.^{7,8}

In view of the importance of metal-ammonia reductions in synthetic chemistry, surprisingly few kinetic studies have been made using these solutions. Undoubtedly, problems arising from the decomposition reaction shown in eq 1 have hindered such studies.



However, it is now possible to prepare stable solutions in which this decomposition reaction is very slow⁹⁻¹¹ so

that we can expect an increase in the number of reliable studies in the future.

Since the alkali metals also dissolve in other solvents such as amines and ethers, rate studies using the solvated electron in these solvents are also feasible and have formed the basis for a number of studies in our laboratory. However, complications arise, not only because of the decomposition reaction but also because of the slight solubility of the metals and the formation of other reducing species. This article reviews briefly some of the properties and reactions of metal solutions in ammonia and amines. The reaction with water has been chosen to exemplify the methods used to study reaction rates.

The Nature of Isolated Solvated Electrons

Of continued lively interest is the nature of electron trapping by polar liquids. It is easy enough to describe electron capture by aromatic molecules having low-lying unfilled molecular orbitals since a single anionic species can be formed. With molecules such as water and ammonia, however, the vacant orbitals lie at such high energies that the electron must be delocalized over a number of solvent molecules in order to be stabilized. Orientation of solvent dipoles appears to be an important factor in such stabilization, while short-range repulsive forces can lead to the formation of a cavity in the solvent. The original cavity model of Ogg¹² has been refined by a number of workers, the most comprehensive treatments being those of Jortner and coworkers.^{13,14} Recently Land and O'Reilly¹⁵ have considered the nature of electron and electron-pair trapping in liquid ammonia. Using volume expansion data for metal-ammonia solutions to estimate the cavity size, Jortner obtained satisfactory agreement with the absorption spectrum and heat of solution of the ammoniated electron. To describe the temperature dependence of the absorption band position, it was necessary to use the coefficient of thermal expansion of the cavity as an adjustable parameter. For calculations involving the hydrated electron, the cavity radius can also be used as an adjustable parameter, but even with this added degree of freedom the discrepancy between the calculated and experimental absorption band positions is appreciable. The lack of quantitative agreement between theory and experiment is not surprising in view of the relatively small net bind-

(1) For more information about the properties of metal-ammonia solutions see "Metal-Ammonia Solutions," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964.

(2) A recent review article on the subject which contains references to previous work is J. C. Thompson in "Chemistry of Non-Aqueous Solvents," Vol. II, J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1967, Chapter 6, pp 265-315.

(3) For more information about the properties of solvated electrons see "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1964, especially the papers by L. M. Dorfman (p 36), M. S. Matheson (p 45), and M. Anbar (p 55).

(4) L. M. Dorfman and M. S. Matheson, *Progr. Reaction Kinetics*, **3**, 239 (1965).

(5) A description of the steps which led to the identification of the hydrated electron is given by E. J. Hart, *Science*, **146**, 19 (1964).

(6) M. Anbar and P. Neta, *Intern. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(7) H. P. Cady, *J. Phys. Chem.*, **1**, 707 (1897).

(8) R. K. Quinn and J. J. Lagowski, *ibid.*, **72**, 1374 (1968).

(9) D. Y. P. Chou, M. J. Pribble, D. C. Jackman, and C. W. Keenan, *J. Am. Chem. Soc.*, **85**, 3530 (1963).

(10) D. F. Burrow and J. J. Lagowski, ref 3, pp 125-137.

(11) R. R. Dewald and R. V. Tsina, *Chem. Commun.*, 647 (1968).

(12) R. A. Ogg, Jr., *Phys. Rev.*, **69**, 668 (1946).

(13) J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

(14) J. Jortner, S. A. Rice, and E. G. Wilson, ref 1, pp 222-276.

(15) R. H. Land and D. E. O'Reilly, *J. Chem. Phys.*, **46**, 4496 (1967).

ing energy of the electron and the complexities of liquid structures, especially when strong hydrogen bonding is present.

A characteristic feature of solvated electrons, common also to excess electrons trapped in crystals (F centers) and in glassy solids, is an intense, broad, optical absorption band showing marked asymmetry on the high-energy side. In the model of Jortner, which uses a hydrogen-like wave function, this absorption is assigned to a $2p \leftarrow 1s$ transition. The asymmetry could arise from unresolved transitions to higher levels, but it has also been attributed to a distribution of cavity sizes.¹⁶

In dilute solutions of metals in ammonia, the electrons are far enough apart to exhibit the spin paramagnetism expected for free spins. The epr spectrum consists of a single narrow line with the electron relaxation dominated by modulation of the hyperfine coupling to nitrogen nuclei.

Although the electron is attracted to a rather large polarization center, its mobility exceeds that of ordinary ions in the same solvent, but not by a large factor. For example, in liquid ammonia the mobility of the solvated electron is about eight times that of a sodium ion,^{17,18} while in water¹⁹ it is less than four times that of a sodium ion. The observed mobility is much smaller than would be expected for a free electron, but it is high enough to require an electron-jump mechanism rather than migration of the entire cavity.

Aggregation of Solvated Electrons

"Normal" electrolytes in ammonia and amines, because of the low dielectric constant of the solvent, form ion pairs as the solution is concentrated. Any model for metal solutions must allow for such an interaction between the cation and the solvated electron to form a species of stoichiometry M . Conductivity studies^{17,18} indicate that this species is nonconducting and yield association constants for reaction 2 not greatly dif-



ferent from those for other ionic solutes in ammonia. Over the same region of concentration (10^{-4} to $10^{-2} M$) the optical absorption spectrum shows little change in either position or intensity of the band. Although a model for this species based on a centrosymmetric "monomer" has been developed,²⁰ it seems more likely that M is merely an ion pair, M^+e^- , between a solvated electron and a solvated cation in which each species retains its essential characteristics.²¹ The formation of a centrosymmetric monomer would require

loss of solvation energy. That the energy balance is a delicate one, however, is shown by the fact that a monomer with considerable charge density on the alkali nucleus (as shown by epr measurements) is indeed formed as a minor constituent in certain metal-ammine solutions.^{22,23}

Another kind of aggregation which is not expected on the basis of a simple ionic model occurs in metal-ammonia solutions. The spin paramagnetism decreases markedly with increasing concentration;^{24,25} this can only be explained by the formation of diamagnetic species involving electron spin pairing. A model in which two electrons occupy the same cavity to form e_2^{2-} has been proposed.¹² Again, however, simple electrostatic arguments would require ion pairing so that practically all of the diamagnetic species would have the stoichiometry M^- or M_2 . Indeed, one of the models for such solutions²⁶ is based upon the formation of alkali metal anions. The absence of a significant volume effect and the virtually unchanged optical spectrum once again argue in favor of an "ion triple" $e^-M^+e^-$,²⁷ although in this case "hard-sphere" electrostatic forces alone are not enough to give the requisite stability. Possible sources of extra stabilization are additional long-range solvent polarization energy and the singlet-triplet splitting resulting from electron-electron interactions.²⁸ To complete the picture in dilute metal-ammonia solutions it is only necessary to include the ion pair M^+M^- formed by normal electrostatic interactions.

Although the situation in ammonia is complicated enough, it is worse in the amines! In addition to the solvated electron and the "loosely bound" ionic aggregates discussed above for the ammonia case, new species are formed in amines which involve the alkali metal in a more active role than simply as the counterion of an ion pair. This conclusion is based upon optical and epr spectra. In all cases (except for sodium solutions in some amines) a broad optical absorption band, independent of the metal used, is observed in the infrared at 1300–1500 $m\mu$. Based upon the independence of band shape and position on metal, correlation with conductance data and solubilities,²⁹ and the absorption spectrum obtained by the pulse radiolysis of amines,^{30,31} this band has been assigned to the solvated electron and its "ammonia-like" aggregates.

(22) K. D. Vos and J. L. Dye, *J. Chem. Phys.*, **38**, 2033 (1963).

(23) K. Bar-Eli and T. R. Tuttle, Jr., *Bull. Am. Phys. Soc.*, **8**, 352 (1963); *J. Chem. Phys.*, **44**, 114 (1966).

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(26) S. Golden, C. Guttman, and T. R. Tuttle, Jr., *J. Am. Chem. Soc.*, **87**, 135 (1965); *J. Chem. Phys.*, **44**, 3791 (1965).

(27) See discussion in ref 1, p 144.

(28) H. Tsujikawa, K. Fueki, and Z. Kuri, *Bull. Chem. Soc. Japan*, **39**, 406 (1966).

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(17) C. A. Kraus, *J. Am. Chem. Soc.*, **36**, 864 (1914).

(18) Recently the limiting mobility of the electron has been shown to be about 11% higher than the value obtained by Kraus (R. R. Dewald, private communication, to be published).

(19) K. H. Schmidt and W. L. Buck, *Science*, **151**, 70 (1966).

(20) E. Becker, R. M. Lindquist, and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

(21) M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2264 (1962).

Because of the lower dielectric constant, the formation of ion pairs is more pronounced in the amines than in ammonia.

New optical bands appear in metal-amine solutions which are absent in metal-ammonia solutions. Two additional absorption bands have been observed in potassium-amine solutions and occasionally in rubidium and cesium solutions as well. The shape and position of the band at highest energy (V band) are independent of the metal used. This band has been observed for all of the alkali metals under some conditions. When sodium can be dissolved in the amines at all, it gives only the V band, with at most a very small infrared absorption. Potassium, rubidium, and cesium show an additional band at intermediate wavelengths (R band) whose position is strongly dependent on the metal. Figure 1 gives absorption spectra for metal-ethylenediamine solutions which are typical of those generally found in metal-amine solutions. At lower concentrations, the infrared absorption of both K and Rb, which is only a shoulder in Figure 1, becomes a maximum.

In spite of the observation of three bands by a number of investigators, there has been a disconcerting lack of agreement among various laboratories about the relative intensities and decomposition rates of the various bands.^{32,33} Recently, Hurley, *et al.*,³⁴ demonstrated the absence of a V band in potassium solutions prepared in fused silica vessels and the presence of sodium in solutions which had a V band. They contend that potassium solutions release sodium from Pyrex and that the sodium is actually responsible for the V band. Although a number of results are not readily explained by this mechanism, it appears that their basic conclusion is correct. We have found the following, using ethylenediamine as the solvent. (1) Sodium bromide reacted very rapidly with solutions containing R and/or IR bands to produce a V band.³⁵ (2) In agreement with the results of Hurley, *et al.*,³⁴ potassium solutions prepared in fused silica vessels showed only the R band. When a V band was present, as always occurred in Pyrex, analysis showed the presence of a high enough sodium ion concentration to have been responsible for this band.³⁶

It appears, then, that only two types of optical absorption bands need be considered in metal-amine solutions. One of these (IR band) is in the infrared at approximately $1300\text{ m}\mu$ and is nearly independent of metal in both shape and position. The other band (R band) occurs at higher energies with the position of the maximum dependent upon the metal used. In ethylenediamine at 25° this band occurs at $660, 850, 890,$ and $1020\text{ m}\mu$ for Na, K, Rb, and Cs, respectively.

While assignment of the IR band to the solvated

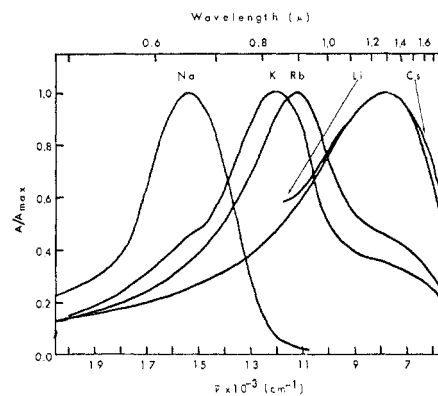


Figure 1. Optical spectra of the alkali metals in ethylenediamine at 25° .²⁹

electron and "loosely bound aggregates" appears to be satisfactory, the species responsible for the R band has not been identified. The intensity relative to the IR band decreases as the solution is diluted. This, and the dependence of band position on the metal used, suggest a metal-containing species which can dissociate upon dilution. The absorption has been attributed to solvated alkali dimers similar to those found in the gas phase but with enough interaction between the valence electrons and the solvent to shift the absorption bands to the red compared with those in the gas phase.³⁷ Another possibility is that the absorption arises from the anionic species M^- , although the dependence on metal shows that this is probably not just an ion pair.

From epr studies we can unambiguously conclude that a monomer species, M , exists in some metal-amine solutions,^{22,23} usually as a minor constituent. The hyperfine splitting at high temperatures is so large that it seems reasonable to conclude that the high temperature limit is a solvated atom. The marked decrease in hyperfine splitting with a decrease in temperature is unmatched by any other system and requires either that the electron density on solvent molecules in the neighborhood of the alkali metal nucleus be strongly temperature dependent²³ or else that one or more species of low hyperfine splitting be in equilibrium with the solvated atom^{33,38} with very rapid rates of interconversion.

In summary, metal-amine solutions are complex mixtures of solvated electrons, ion pairs and other loosely bound aggregates, metal-containing diamagnetic species such as M_2 or M^- , and one or more monomeric species, M . Recently, studies of dilute solutions of the alkali metals in hexamethyl phosphoric triamide,^{39,40} $[(CH_3)_2N]_3PO$, a liquid of fairly high dielectric constant, have indicated that these systems may be nearly as "simple" as metal-ammonia solu-

(32) M. Ottolenghi, K. Bar-Eli, H. Linschitz, and T. R. Tuttle, Jr., *J. Chem. Phys.*, **40**, 3729 (1964).

(33) L. R. Dalton, J. D. Rynbrandt, E. M. Hansen, and J. L. Dye, *ibid.*, **44**, 3969 (1966).

(34) I. Hurley, T. R. Tuttle, Jr., and S. Golden, *ibid.*, **48**, 2818 (1968).

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(36) M. G. DeBacker, unpublished results, this laboratory.

(37) J. L. Dye and R. R. Dewald, *J. Phys. Chem.*, **68**, 135 (1964).

(38) J. L. Dye and L. R. Dalton, *ibid.*, **71**, 184 (1967).

(39) T. Cuvigny, J. Normant, and H. Normant, *Compt. Rend., Ser. C*, **258**, 3503 (1964).

(40) R. Catterall, L. P. Stodulski, and M. C. R. Symons, *J. Chem. Soc., A*, 437 (1968).

tions⁴¹ with an infrared band at 2250 $m\mu$, presumably arising from the solvated electron and loosely bound aggregates. Except for sodium, the bands at higher energies are either weak or absent in dilute solutions. Similarly, dilute solutions of cesium in ethylenediamine show only the IR band and are therefore believed to be similar to metal-ammonia solutions.

Reactions of Isolated Solvated Electrons

The preceding discussion of the complexity of metal solutions shows that one must be cautious in assigning reactions to isolated solvated electrons. Only in dilute metal-ammonia solutions and in solutions prepared by the radiolysis of liquids can one be reasonably certain that reactions attributed to the solvated electron are not actually reactions of other reducing species in the solution. Even in these cases, the reaction ostensibly being studied can easily be interfered with by reactions with impurities. Most reactions of the solvated electron studied to date by the methods of pulse radiolysis have had second-order rate constants larger than $10^5 M^{-1} \text{ sec}^{-1}$. To study slower reactions requires extremely pure solvents and a way to remove the oxidizing species produced by the radiation. In spite of these difficulties, an impressive number of reactions of solvated electrons have been studied using radiolysis techniques. It is also possible to study sufficiently slow reactions of solvated electrons using metal-ammonia or metal-amine solutions. However, flow techniques are limited to rate constants smaller than about $10^7 M^{-1} \text{ sec}^{-1}$, so that only slight overlap with the presently available data from radiolysis is possible. When the reaction being studied by radiolysis involves the solvent itself, however, dilution in a nonreacting solvent can slow the reaction enough to permit its study by flow techniques.

It is with this in mind that we began the study of reactions between cesium and water in ethylenediamine. We reasoned that if this reaction were demonstrably slow in ethylenediamine, then electrons should be stabilized in pure water long enough to be observed. Before completion of these studies,⁴² which showed that the reaction of electrons with water in ethylenediamine is relatively slow, the spectrum of the hydrated electron in pure water had already been measured,⁴³ showing the hydrated electron to be a relatively long-lived species. It was at first presumed⁴⁴ that the reaction between the solvated electron and water in ethylenediamine proceeded as in pure water, to produce H and OH^- . However, thermodynamic arguments show that this reaction, although feasible in water because of the extra stabilization of OH^- in this solvent, cannot occur to an appreciable extent in am-

monia. The standard free energy change is about +30 kcal/mol⁴⁵ and can hardly be in error by more than 5 kcal. Therefore the reaction between metal-ammonia (and probably also metal-amine) solutions and water cannot proceed *via* H and OH^- .

The reaction between metal-ammonia solutions and ethanol in liquid ammonia has been studied by Eastham and coworkers,⁴⁶ who followed the evolution of hydrogen as the reaction proceeded. After an initial rapid reaction, the rate decreased markedly and the solutions remained blue for hours. A mechanism to describe this behavior has been proposed by Jolly.⁴⁷ This mechanism assumes that the reaction proceeds through NH_4^+ , produced by proton transfer from ethanol to ammonia. Recently, Dewald and Tsina¹¹ examined the reaction of metal-ammonia solutions with water and with alcohols in ammonia. Their results are in general agreement with the assumption of Jolly that the reaction proceeds through NH_4^+ and show that the direct reaction of the solvated electron with water and with alcohols in ammonia is *very slow*.

Reaction Rates in Ethylenediamine

It is of interest to ask whether this mechanism can also explain the result in ethylenediamine. A number of factors indicate that another mechanism must be operative. Conductivity studies⁴⁸ show that water in ethylenediamine is such a weak acid that even if the reverse of reaction 3 were diffusion controlled, the



forward rate constant would be only about $10^{-1} M^{-1} \text{ sec}^{-1}$. Combination of this with the solubility of cesium hydroxide in wet ethylenediamine⁴⁹ shows that the mechanism of Jolly predicts a reaction rate several orders of magnitude slower than that observed. In ethylenediamine, then, the reaction between the alkali metals and water does not seem to proceed through either direct formation of H atoms or by reaction with ethylenediammonium ion formed as an intermediate. In attempting to interpret the results in ethylenediamine we must keep in mind the greater complexity of metal solutions in this solvent as well as the availability of α -hydrogen atoms on the solvent molecules which might be involved in the reaction.

Since the initial studies of the reaction between cesium and water in ethylenediamine by the stopped-flow method,⁴² a number of other metals and several other oxidizing agents have been used. It soon became apparent that the decay of absorbance could not be

(45) Based upon the free energies of formation of $e_{\text{NH}_3}^-$ from two sources: (a) J. L. Dye, ref 1, pp 137-145; (b) E. J. Kirschke and W. L. Jolly, *Inorg. Chem.*, **6**, 855 (1967).

(46) J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **81**, 3652 (1959); C. W. Keenan, H. V. Secor, E. J. Kelly, and J. F. Eastham, *ibid.*, **82**, 1831 (1960); E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastham, *ibid.*, **84**, 3611 (1962).

(47) W. L. Jolly, ref 3, pp 27-35.

(48) K. Keskey, S. Spleet, and J. L. Dye, unpublished results, this laboratory.

(49) E. M. Hansen, unpublished results, this laboratory.

(41) J. M. Brooks and R. R. Dewald, *J. Phys. Chem.*, **72**, 2655 (1968).

(42) R. R. Dewald, J. L. Dye, M. Eigen, and L. deMaeyer, *J. Chem. Phys.*, **39**, 2388 (1963).

(43) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(44) L. H. Feldman, R. R. Dewald, and J. L. Dye, ref 3, pp 163-172.

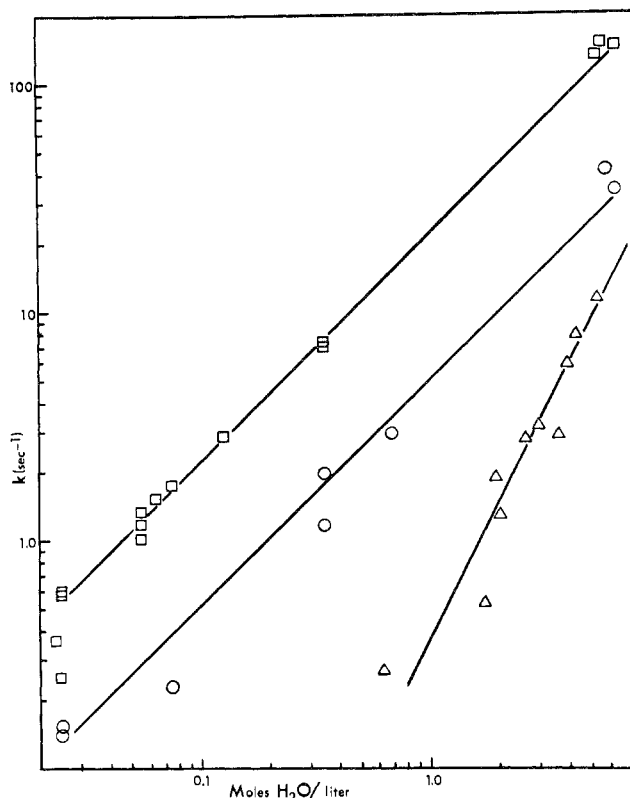
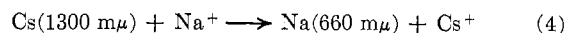


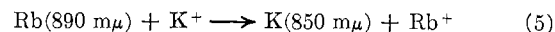
Figure 2. Pseudo-first-order rate constants for the reaction of cesium (circles and squares) and of sodium (triangles) with water, *vs.* water concentration (log-log scales). The straight lines have slopes of 1 and 2.

described by a single pseudo-first-order process at all metal and water concentrations. The reaction between cesium and water for a number of initial metal concentrations appeared to involve two pseudo-first-order processes.⁴⁴ Two second-order rate constants were determined based upon the assumption that parallel pseudo-first-order reactions were responsible for the decay. In Figure 2 these pseudo-first-order rate constants are plotted *vs.* the water concentration using log-log scales. (Also shown in this figure is a similar graph for sodium solutions to be considered later.) Of course this does *not* require the presence of parallel first-order processes. It does show, however, that the function which describes the rate has a form which depends upon the first power of the water concentration. Separation of the rate into two processes yields, of course, greater uncertainty in the values of the individual rate constants than is the case when only one rate constant is involved. Values of 20 ± 5 and $7 \pm 2 M^{-1}$ (average deviations given) were obtained in this way for the decay of absorbance of cesium in ethylenediamine at water concentrations from 0.023 to 6.11 *M*. At the time, all measurement had been made at a pre-set wavelength so that examination of the spectrum during the reaction was impossible. It was conjectured⁴⁴ that the fast process might be associated with the reaction of the solvated electron and its loosely bound aggregates, in which case the slower process could be the independent reaction of Cs_2 dimers. However, interconversion of

the various species in metal solutions appears to be rapid.⁵⁰ We have recently studied reactions such as



and



using the stopped-flow apparatus. These reactions also occur very rapidly ($k > 10^5 M^{-1} sec^{-1}$). Earlier reports of slow interconversions²⁹ in the lithium-ethylenediamine system are not valid if the band at 660 *mμ* is indeed due to the presence of sodium ions, as recently reported.³⁴

The use of a scanning monochromator with the flow system has permitted us to study both the wavelength- and time-dependence of spectra during reaction. Since publication of the description of this apparatus⁵¹ we have expanded its usefulness by converting the analog signal recorded by an FM tape recorder into digital form using a Varian C-1024 time averaging computer. By advancing the address of this computer externally with a controlled number of pulses, the absorbance of any desired portion of the spectrum can be converted into digital form. From the C-1024 computer, the digital data are entered into punched cards for processing by a CDC-3600 computer and can also be displayed *via* an X-Y recorder. It is also possible to use the C-1024 computer to subtract the background spectrum and to increase the signal-to-noise ratio (for nonreacting systems) by accumulating data. This method of data collection also permits us to use neutral density filters to automatically correct for deviation of the apparent absorbance from linearity because of light scattering and other instrumental errors.

Using these techniques, it has been possible to examine the shape of the absorbance curve as a function of wavelength under various conditions. Dilute cesium solutions, which show only an infrared absorption,²⁹ yield no detectable change in the shape of the absorption band up to 1100 *mμ* during reaction with water. This is illustrated in Figure 3 in which the absorption spectra, normalized to nearly the same value at 1100 *mμ*, are shown for three widely differing conditions during reaction with water.

In spite of this insensitivity of band shape to reaction conditions, the decay of absorbance is not simply first or second order. This is not surprising, since a comparison with metal-ammonia solutions as well as available conductance and magnetic data on metal-amine solutions indicate the presence of several species, even when only a single infrared band is observed. These "loosely bound" species probably result from ion-pair and electron-pair interactions and have the *stoichiometry* e^- , M , M^- , and M_2 . The decay of absorbance upon reaction with water is, of course, complicated by interconversion of these species during reaction. Since it appears that such interconversions

(50) M. Ottolenghi, K. Bar-Eli, and H. Linschitz, *J. Chem. Phys.*, **43**, 206 (1965).

(51) J. L. Dye and L. H. Feldman, *Rev. Sci. Instr.*, **37**, 154 (1966).

are rapid compared to the rate of reaction with water, we expect the rate of disappearance of the various species to decrease in the order: $M_2 > M^- > M > e^-$. If the concentration of M^+ were constant, the order would be: $M_2 = M^- > M = e^-$. In this case, if the rate-determining step is first order in water, the overall rate of reaction would be first order in water as observed. Also, a plot of log absorbance *vs.* time would show deviations from linearity in the direction observed. Data for the reaction of cesium with water are compatible with this mechanism, but it will be necessary to reinforce the rate studies with quantitative equilibrium studies to verify the mechanism.

Solutions of sodium in ethylenediamine show only a single band at 650–700 $m\mu$ with very little, if any, infrared absorption.²⁹ This affords us the opportunity to study the kinetics of reaction of a different reducing species with water. Except when the reaction rate is very slow, so that competition from decomposition catalyzed by reaction products or impurities becomes important, the disappearance of this band is nearly first order in absorbance. The decay was initially thought to be strictly first order under these conditions. Use of the scanning system and data transfer described above, however, shows systematic deviations from first-order behavior. Although for cesium solutions the reaction is first order in water, sodium solutions give an order higher than unity and a much slower reaction rate for intermediate and low water concentrations. Using only data with half-lives less than 3 sec to minimize problems arising from catalyzed decomposition, the order in water appears to be two. This is shown in Figure 2 in which the pseudo-first-order rate constant is plotted *vs.* the water concentration on a log-log scale. The solid line through the data for sodium has a slope of two. Scanning the spectrum during reaction shows neither new absorption bands nor a change in the shape

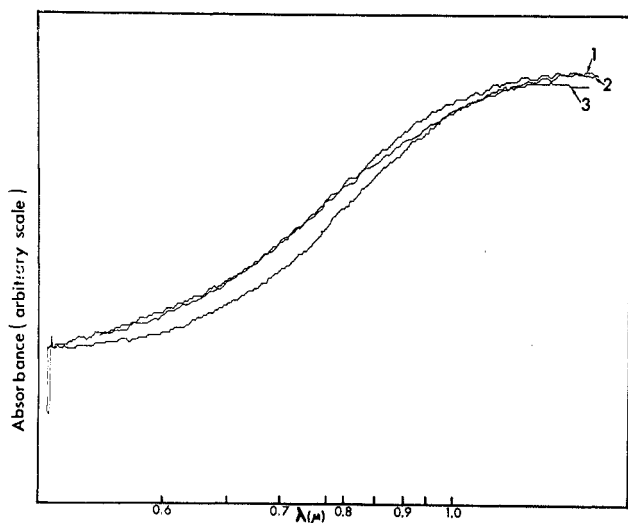


Figure 3. Spectra of cesium solutions in ethylenediamine during reaction with water: (1) during flow, water concentration 0.037 M ; (2) same push as curve 1 but after about 50% reaction; (3) during flow, water concentration 3.2 M . The signal intensities were adjusted so as to be equal at the end of the scan (about 1100 $m\mu$).

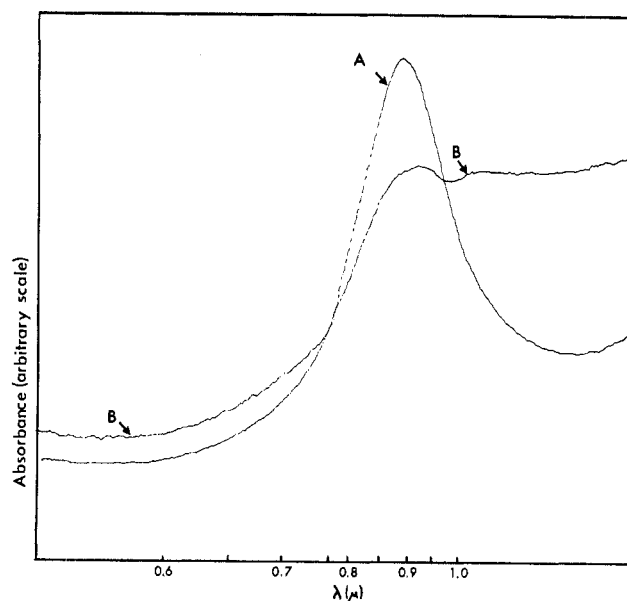


Figure 4. Spectra of rubidium solutions in ethylenediamine during reaction with water: (A) during flow, water concentration 0.122 M ; (B) same push as curve A at twice the sensitivity after about 60% reaction. The minimum in curve A is at the scan reversal point and corresponds to about 1100 $m\mu$.

or position of the principal band. The slow decay at low water concentrations is zero order in the absorbance.

Examination of the maximum ratio of infrared to visible absorption for sodium solutions and the rate of reaction of the IR species (cesium solutions) with water leads to the conclusion that the species responsible for the 660- $m\mu$ absorption in sodium solutions cannot react at the observed rate through conversion to the IR species. Therefore, the reaction with water probably involves the principal species directly, leading to second-order dependence on water concentration. Conversely, even if the species responsible for the R band in potassium and rubidium solutions were to react directly with water at the same rate as sodium, this process would be too slow to compete with a pathway involving conversion of the R species to the IR species. Therefore, the second-order dependence upon water is unique to the sodium system because of the very low concentration of IR species in sodium solutions.

Potassium and rubidium solutions in ethylenediamine show both R and IR bands so that the features prominent separately in sodium and cesium solutions are present together in these systems. Although a number of runs have been made using potassium, it appears that sodium contamination from the Pyrex vessels always gave a small but detectable sodium band. Because of this complication, we will consider rubidium solutions, which show no band due to sodium but otherwise behave in a similar fashion to potassium solutions.

It is clear, as shown in Figure 4, that the R band disappears before the IR band when rubidium solutions are allowed to react with water. This figure shows the absorption spectrum just after mixing compared with the spectrum after the absorbance had decreased by a

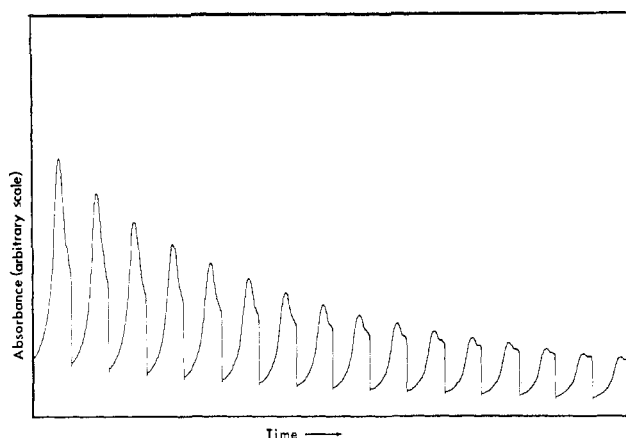


Figure 5. Decay of absorbance of rubidium in ethylenediamine during reaction with 0.122 *M* water. The duration of each spectrum sample was 16 msec, while the time between successive scans was 67 msec.

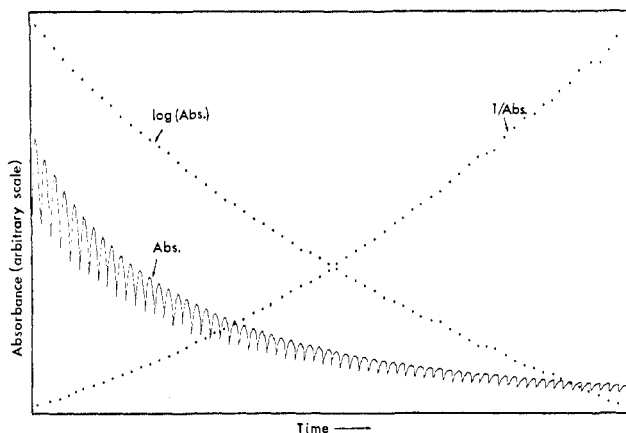


Figure 6. Decay of absorbance of rubidium in ethylenediamine during reaction with 0.122 *M* water. The duration of each spectrum sample was 4.2 msec, while the time between successive scans was 67 msec. Also shown are first- and second-order graphs of these data.

factor of about three. The decay of the absorption is also evident in Figure 5, in which the rapid decrease in absorption of the R band can be contrasted with the slower decrease of the IR band. A typical use of the C-1024 time-averaging computer is illustrated in Figure 6, in which the decay of absorbance at the maximum is shown. Deviation from simple first- or second-order kinetics is also shown by the curvature of logarithmic and inverse graphs.

While the kinetics have not yet been analyzed in

detail, they seem to be consistent with a mechanism in which equilibrium among the reducing species is maintained during the reaction with water. The relative intensity of the R band decreases upon dilution, indicating less dissociation than for the IR species. Therefore the absorbance decrease of the R band during reaction would be faster than the IR band.

Although we have discussed only reactions of the alkali metals with water in ethylenediamine, similar reactions with methanol and ethanol have also been studied using stopped-flow techniques. The results indicate at least two modes of reaction. A fast initial reaction is followed by a slower process. The fast reaction is considerably faster than the reaction with water while the slower reaction has a rate comparable to that observed with water.

In summary, metal solutions in ethylenediamine are complex. This complexity extends to the rate of reduction of water and other species. However, the reaction of cesium with water in ethylenediamine shows, as is true also in other solvents, that the reaction of the solvated electron with water is relatively slow—indeed, reaction may proceed through an associated species such as M^- , M , or M_2 rather than with e^- directly. When the solvated electron concentration is very low, as with sodium in ethylenediamine, the reaction mechanism apparently changes and the order in water approaches two. When several absorption bands are present, as with potassium and rubidium, the higher energy band decays more rapidly than the IR band, probably in accord with the stoichiometric requirements of equilibrium among reducing species.

The studies of fast reactions in solutions containing solvated electrons and other reactive reducing agents have opened a promising field of research. The use of both pulse-radiolysis and flow methods permits a wide range of reaction rates to be studied. The complexity and instability of metal solutions and the time and effort required to purify liter amounts of solvents such as ethylenediamine have made progress much slower than we would like. However, the ability to scan the spectrum during reaction and to digitize the data for computer calculations promises to compensate, at least in part, for these difficulties.

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