Reaction of Nitrous Oxide with Solvated Electrons in Mixtures of Water and Dimethyl Sulphoxide

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Summary The rate constant of the reaction between electrons and N_2O in mixtures of H_2O–Me_2SO increases rapidly at concentrations of Me_2SO above 0·66 mole fraction suggesting that the degree of solvation of the electron diminishes markedly in these solutions.

ORGANIC chemists use the properties of dimethyl sulphoxide (DMSO) to increase the rates of some S_N2 or S_E1 anionic reactions. The explanation given for this action is that reduced solvation of anions in the presence of DMSO makes them more reactive.

Thus, particularly since DMSO solvates small anions less strongly than large ones, some reactions of the hydrated electron in aqueous solutions of DMSO should be accelerated due to partial dehydration of the electron. This binary solvent mixture may therefore provide a simple means for studying the reactions of e^-_{aq} in different states of solvation.

N_2O was chosen as solute to avoid ionic strength effects and the concentration of DMSO was varied from 0 to 100%. The experiments were carried out with a Febetron delivering 10 ns pulses (base) of 1·8 MeV electrons. The rate of disappearance of the hydrated electrons formed by the pulse was measured by direct observation of the decay of their absorption at 900 nm. N_2O 99·99% pure (Air Liquide) was used as supplied: saturated solutions were prepared by bubbling the gas through the solution. The concentration of N_2O in the mixtures was determined by gas chromatography: it varied non linearly from $2·5 \times 10^{-2}$ M in pure water to $7·88 \times 10^{-2}$ M in pure DMSO at 23°C.[1] DMSO (Merck) was redistilled before use. 2×10^{-2} M KBr was added to the solution to avoid interference by the spectrum of the radical formed from $DMSO^+$.[2]

We first of all determined the value of the rate constant $k(e^-_s + \text{DMSO})$ as a function of the DMSO concentration. The reaction is pseudo-first order and the results obtained were in good agreement with those of Cooper *et al.*[3] In particular we confirmed the increase of k in going from 66 to 80% volume DMSO.

In the presence of N_2O the reaction is always more rapid but still of pseudo-first order so the values of $k(e_s^- + N_2O)$ may be calculated as a function of the DMSO concentration. These are shown in the Figure together with calculated values which correspond to $k(e_s^- + N_2O)$ in water (8×10^9 l mol^{-1} s^{-1}) corrected for the varying viscosity of the medium. In fact the reaction in water is diffusion controlled and the diffusion coefficient D of the electron is related to the viscosity η of the medium by the Stokes–Einstein law $D = kT/6\pi r\eta$ where k is Boltzman's constant, T the temperature and r the ionic radius. This theoretical curve passes through a minimum since the viscosity of the medium passes through a maximum.[4]

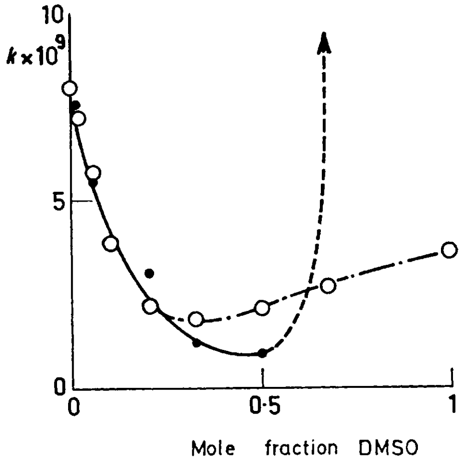

FIGURE. Rate constant for the reaction of the electron with nitrous oxide in mixtures of water-dimethylsulphoxide, ● experimental values, ○ values calculated on the basis of the rate constant in water corrected for the viscosity of the medium – – – experimental rate constant greater than 9×10^9 mol^{-1} s^{-1}.

Three zones may be distinguished in the curves. (a) Up to 50% volume DMSO (0·21 mole fraction) the two curves are identical suggesting that the electron is solvated only by water. (b) Above 90% DMSO (0·68 mole fraction) the experimental rate constant increases too rapidly to be measured. The electron formed under these conditions is extremely reactive and may be considered as "dry," a conclusion which is borne out by the displacement of the absorption spectrum maximum from 730 nm to above 1500 nm.[3] (c) Between 50 and 90% DMSO the measured rate constant is lower than that indicated by the theoretical curve. In this range and particularly around 66% DMSO (0·33 mole fraction) the mixture is known to be especially strongly structured by hydrogen bonding and under these conditions one would expect that the electron, solvated by such bonded molecules, would be less reactive than the simple hydrated electron in the same medium.

These results are in good agreement with those of Morel[6] who studied ionic conductivity in such media and found a similar pattern, especially for the ion Cl$^-$ which exhibits the same zones of variation of conductivity as a function of its solvation.

This influence of the structure of the medium on the solvation of the electron due to short range interaction has been previously invoked by several authors[7] in contrast to long range interactions which depend mainly on the dielectric constant of the medium. It appears that the former may become preponderant in certain cases.[7c]

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