EQUILIBRIUM IN HEXAMETHYLPHOSPHOROTRIAMIDE BETWEEN SOLVATED ELECTRONS AND DIELECTRONS STABILIZED BY REACTION WITH CATIONS

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UDC 541.135

In electrochemical generation of electrons in a solution of NaBr in hexamethylphosphorotriamide (HMPA, an equilibrium is established in the bulk of the solution between solvated electrons (e_s^-) and electron-cation complexes. On the basis of the data on the destruction of radiochemically generated e_s^- [1], comparison of the ESR results [2,3], optical absorption spectra [4], dynamics of polarization of solvent protons [5], and the influence of irradiation on the ESR spectra in the case of electrochemical generation [6], it has been proposed [1-6] that the composition of these complexes corresponds to the formula Na^+, e_2^{2-}.

The question of the nature of the products of reaction of e_s^- with itself and also with the cations of alkali metals (M^+) has been widely discussed in the literature. While in systems where e_s^- has a short lifespan the existence of similar particles, particularly the dielectron e_2^{2-}, is purely hypothetical [7,8], in amines and esters in solutions of alkali metals under stationary conditions it is possible to record the optical absorption spectra of particles which are the reaction products of e_s^- with M^+. However, there are no unambiguous data regarding the nature of these particles. In particular, there has been investigation of the possibility of existence of ionic vapors of M^+, e^- [9-12], of so-called monomers [13, 14], i.e., electrons in remote orbitals of M^+, of simple metal atoms M^0 [12, 15], and also of anions of alkali metals M^- [16-18] and complexes M^+, e_2^{2-}, and M_2^{2+}, e_2^{2-} [9] or M_2 molecules [7, 15]. As a rule, it is not possible to determine the stoichiometric composition of the reaction products of electrons with cations to which a definite spectral absorption is assigned. This is because of the fact that in these systems the electrons exist basically in complexes with metal cations and the composition of the complexes is judged from the kinetic measurements of the fall in absorption of e_s^- generated by photolysis of the complexes. Until now it has appeared that the only system in which it is possible to study the equilibrium between e_s^- and its complexes with M^+ is a metal-ammonium solution. However, for these solutions there is no direct spectroscopic evidence of the existence of other reducing particles besides e_s^- [19].

A solution of 0.2 M NaBr in HMPA in which e_s^- exists under stationary conditions in equilibrium with alkali metal-electron complexes makes it possible to carry out a similar investigation using the spectrophotometric method with electrochemical generation of electrons. On dissolving alkali metals it is only possible to carry out qualitative observations [20, 21]. The measuring electrochemical cell had a cathode compartment for generation of electrons consisting of a quartz vessel with plane-parallel optical windows [4]. The optical path length l was 0.3 cm. The measurements were carried out on an apparatus consisting of the optical system, a DKSSh-1000 lamp, a ZMR-3 monochromator with slit widths of 0.3 mm, and an FÉU-28 photomultiplier. Measurements on the stationary processes were carried out with an M-28 galvanometer, the fast processes being recorded on an S1-42 oscillograph. After generation of considerable concentration of electrons the solution was mixed to give uniform coloration and the spectrophotometric measurements were carried out in the e_s^- absorption region (980 nm) and at the maximum absorption of the complex (750 nm). The chosen wavelength corresponded to the absorption of individual particles since in the transition from 980 to 750 nm, a sharp minimum in the optical density D was observed at around 850 nm. The different nature of the particles responsible for absorption at 980 and 750 nm also follows from the kinetic measurements on the reaction with radicals, as will be demonstrated later.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 10, No. 5, pp. 830-834, May, 1974. Original article submitted August 30, 1973.

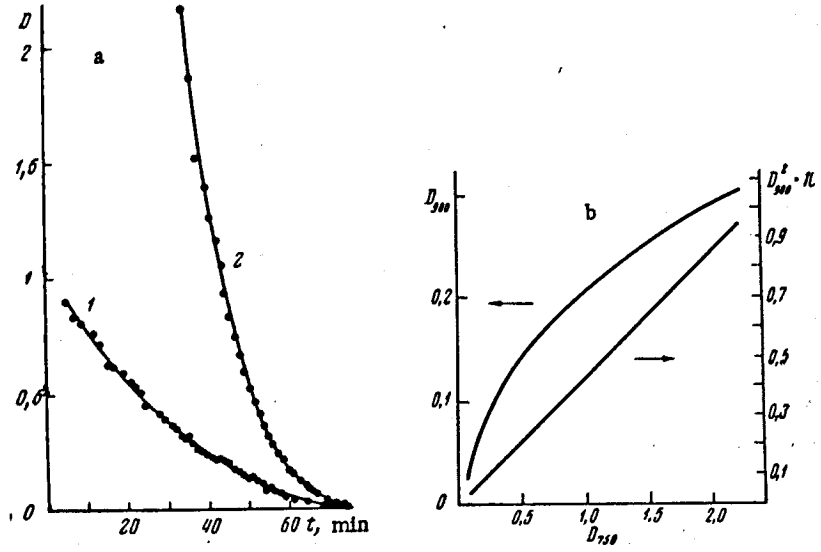

Fig. 1. a) Kinetics of the change in optical density of solvated electrons D_{980} (1) and complexes D_{750} (2); b) variation of D_{980} with D_{750}.

Figure 1a shows the kinetics of the change in optical density of e_S^- (D_{980}) and of the complexes (D_{750}). The optical densities were calculated from the FÉU current, $D = \log (I_0/I)$, where I_0 is the FEU current for complete clearing of the solution. It may be seen that the curves for variation of D_{980} and D_{750} differ sharply. The fall in optical density is connected with the disappearance of electrons by reaction with the acceptors present in the system and, to a certain extent, with the molecules of HMPA. Different experiments show different kinetics of variation of optical density; however, the ratio D_{750}/D_{980}^2 always remains constant and equal to 54.5. This indicates that the equilibrium between e_S^- and the complexes is established in a time which is considerably less than the time for recording the kinetic curves. The variation of D_{980} with D_{750} is shown in Fig. 1b. As we see, two electrons take part in formation of the complex and this provides direct confirmation of the earlier assumption [1-6] regarding its composition, namely that of a dielectron (or simply two electrons) bound to a Na^+ cation – Na^+, e_2^{2-}. In principle it is possible to have $2Na^+$, e_2^{2-} but the literature contains no data indicating that a similar particle must have an absorption band with a considerable extinction coefficient. Na_2 molecules and the Na^0 atom must have absorption bands which are so narrow that their spectrophotometric detection will be difficult [12].

It is known that in the presence of cations in HMPA, e_S^- forms noncontact ions of Na^+, e vapor; this is shown by shift of the e_S^- spectrum to the short wavelength region in the presence of Na^+ [4]. With considerable excess of Na^+, the basic fraction of e_S^- must be bound in ionic vapor [22]. The simplest mechanism of complex formation in excess of Na^+ which explains the observed spectral and paramagnetic [2,3] properties of the systems studied is as follows:

$$e_s^- + e_s^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} e_2^{2-}, \quad K = \frac{[e_2^{-2}]}{[e_s^-]^2} = \frac{k_1}{k_2}; \tag{1}$$

in this case e_S^- denotes the noncontact vapor ion and e_2^{2-} denotes two electrons bound to the Na^+ cation. The existence of a dielectron in the form of an Na^+ complex is the most probable since in pure HMPA the corresponding absorption band is absent [1] and in a solution of Li^+ salt it is only possible to observe it at low temperatures [4, 21].

In order to evaluate K it is necessary to change from optical densities to concentrations: $D = \varepsilon [x] l$, where ε is the extinction coefficient. Evaluation of ε_{980} and ε_{750} for e_S^- and the complex may be carried out from the data of impulse radiolysis of HMPA. The calculation is carried out as follows. The variation of the extinction coefficient of e_S^- with wavelength is obtained in impulse radiolysis of pure HMPA; at 980 nm it is $1 \cdot 10^3$ $M^{-1}cm^{-1}$. In the presence of 0.2 M NaBr the e_S^- spectrum is shifted to the short wavelength region [4]. The form of the absorption band in this case does not change and its half width, both in pure HMPA and in a 0.2 M solution of NaBr, remains constant and equal to 0.45 eV. This makes it possible to calculate the value of ε_{980} in 0.2 M solution of NaBr in HMPA; $\varepsilon_{980} = 2 \cdot 10^{-3}$ $M^{-1}cm^{-1}$. Using the complete yield of electrons in irradiation of solutions of HMPA obtained by acceptance of electrons by anthracene [1] and also the spectral variation of the extinction coefficient of e_S^-, the radiochemical yields of e_S^- and complexes were calculated and the extinction coefficient of the complexes $\varepsilon_{750} = 4 \cdot 10^3$ $M^{-1}cm^{-1}$. Then, using the data of Fig. 1,

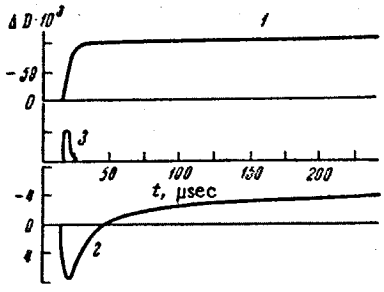

Fig. 2. Kinetics of establishment of equilibrium in the solvated electron-complex system: 1) ΔD_{750}; 2) ΔD_{980}; 3) shape of impulse of high-energy electrons.

$$K = \frac{D_{750} \times \varepsilon_{980} \times l}{D_{980}^2 \times \varepsilon_{750}} = (7 \pm 3.5) \times 10^3\ M^{-1}.$$

For confirmation of the proposed mechanism we carried out experiments on the kinetics of establishment of equilibrium. A convenient method is irradiation of HMPA solutions containing equilibrium concentrations of e_S^- and complexes by impulses of high-energy (4 MeV) electrons of duration about 3 μsec and recording of the change in optical density ΔD, which in this case is determined from $\Delta D = -\log(1 - I_{\sim}/I)$, where $I_{\sim}$ is the alternating component of the FÉU current. This is a combination of the methods of impulse radiolysis [1] and electrochemical generation of e_S^- [2, 3]. Figure 2 shows the oscillograms of the change in optical density ΔD_{750} and ΔD_{980}. The equilibrium concentrations after electrochemical generation were $[e_S^-]_e = 3.6 \cdot 10^{-4}$ M, $[Na^+, e_2^{2-}]_e = 8.5 \cdot 10^{-4}$ M. With the action of high-energy electrons on HMPA there is additional formation of e_S^- (positive ΔD_{980}) and the complexes disappear through reaction with the radical products of radiolysis of HMPA (clearing of the system at 750 nm, negative ΔD_{750}). The changes in concentration are, respectively, $+2.3 \cdot 10^{-5}$ and $-8.5 \cdot 10^{-5}$ M. The predominant reaction of radicals with complexes as compared to e_S^- is connected both with the high equilibrium concentration of the former and with the fact that the radius and, consequently, the rate constant is greater for the complex as compared with e_S^-. The kinetics of establishment of equilibrium are shown by curve 2 in Fig. 2. The kinetic characteristics of the reversible reactions have been extensively studied in the literature [23]. To a high degree of accuracy the shape of the experimental curve agrees with the theoretical variation describing the process of establishment of equilibrium by scheme (1):

$$\lg\left[\frac{\Delta[e_s^-]_e}{a}\left(\frac{a-\Delta[e_s^-]}{\Delta[e_s^-]_e-\Delta[e_s^-]}\right)\right] = 1.72(a-\Delta[e_s^-]_e)k_1 t$$

with $k_1 = (1.1 \pm 0.5) \cdot 10^8\ M^{-1}sec^{-1}$, where $\Delta[e_S^-]$ is the change in concentration of e_S^- after breakdown of equilibrium as a result of the action of high-energy electrons (curve 2, Fig. 2) and $\Delta[e_S^-]_e$ is the change in concentration before establishment of the new equilibrium value

$$a = \frac{4K([e_s^-]_e + 2.3 \cdot 10^{-5}) + 1}{4K} - \Delta[e_s^-]_e .$$

After the action of an impulse of radiation, the new equilibrium concentration of e_S^- and complex are $3.35 \cdot 10^{-4}$ and $7.9 \cdot 10^{-4}$ M, respectively. Having determined k_1 it is possible, using the value of K, to find that $k_2 = (1.6 \pm 0.8) \cdot 10^4\ sec^{-1}$, and that the lifespan of the complex $\tau = 6 \cdot 10^{-5}$ sec. The estimates presented indicate that reaction rate constant for the interaction of two electrons is approximately a factor of 10 less than the diffusion value. Similar measurements in solutions of Li^+ salt showed no difference in behavior at 750 and 980 nm. This is in agreement with the propositions [4, 21] regarding the absence of complexes at room temperature in this case. Thus, it is possible to explain all the experimentally observed effects without invoking hypothetical reaction products of the electrons with alkali metal cations which are not detected in the optical or ESR spectra. For the first time we have direct demonstration of the existence of equilibrium between complexes containing the dielectron and solvated electrons. We have thereby provided unambiguous determination of the stoichiometry of the complex with respect to electrons. It should, however, be noted that in principle it is also possible to have formation of e_2^{2-} by parallel multistage paths including other intermediate products existing in very low concentration. In evaluation of the equilibrium constant we consider that this will have no effect although the kinetic constants will be different. For this reason the proposed mechanism of complex formation between electrons and cations and also their composition require additional measurements on the kinetics of interconversion of solvated electrons and complexes, in particular, at different Na^+ ion concentrations.

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