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Studies of solvated electrons in LiBr + HMPA solutions using the rotating ring–disk electrode technique *

Part 2. The reaction of benzene with solvated electrons

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Abstract
By means of a rotating ring–disk electrode (RRDE) it was found that in LiBr + hexamethylphosphoramide (HMPA) solutions solvated electrons react very slowly with water, even at concentrations higher than 1 M. The reaction of benzene with solvated electrons in LiBr + HMPA solutions takes place only in the presence of a proton donor such as water. A second-order reaction rate constant was determined for this reaction and was found to be $0.26 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at a disk current of $-1.25 \text{ mA}$.

1. Introduction
Solvated electrons $e^-_s$ are chemically stable in proton-donor-free LiBr + hexamethylphosphoramide (HMPA) solutions. Thus this medium is suitable for the study of the reaction of solvated electrons with compounds such as water and benzene. These reactions are studied using the rotating ring–disk electrode technique.

2. Experimental
2.1. Solution preparation, cell design and measuring devices
The preparation of the solution and the measuring devices used have been described in detail elsewhere [1].

The glassy carbon–glassy carbon rotating ring–disk electrode (Gg-Gg RRDE) used in this work had the following dimensions: $r_1 = 0.350 \text{ cm}$, $r_2 = 0.464 \text{ cm}$ and $r_3 = 0.599 \text{ cm}$, with $N_1 = 0.358$.

3. Theory
The RRDE has great potential as a technique for studying the kinetics of homogeneous reactions in solution. We consider the case where a reactant $B$, generated at the disk electrode, diffuses into the solution where it reacts with a substrate $C$:

\begin{align*}
\text{disk} \quad & A \longrightarrow B \\
\text{solution} \quad & B + C \longrightarrow \text{product} \\
\text{ring} \quad & B \longrightarrow A
\end{align*}

Second-order rate constants can be obtained if $B$ is destroyed in the bulk by a (pseudo) first-order reaction or undergoes a second-order reaction with another species $C$.

Because of the chemical reaction in the bulk, the measured collection efficiency $N_{1u}$ will decrease. Albery and Bruckenstein [2] developed a theory in which...
they concluded that $N_m$ must be a function of $\lambda$, $r_1$, $r_2$ and $r_3$, where

$$\lambda = (k_i/\omega)^{1/2}(v/D)^{1/6} (0.51)^{-1/3}$$  \hspace{1cm} (4)

For a particular electrode, systems with equal values of $\lambda$ will give equal values of $N_m$. If $\lambda$ is large, $N_m$ is given by

$$N_m = 1.75\lambda^{-3} \exp\left[4\lambda^3(r_2 - r_1)/r_3\right]$$  \hspace{1cm} (5)

In this case, the method can be applied to values of $k_i$ between 10 and $10^3$ s$^{-1}$. For small values of $\lambda$, an improved expression for thin gap–thin ring electrodes was given:

$$N_i/N_m = 1 + 1.28(v/D)^{1/3}(k_i/\omega)$$  \hspace{1cm} (6)

If $1/N_m$ is plotted against $1/\omega$, the intercept gives $N_i$ and the slope gives $k_i$. Using this equation, reaction rate constant values from $4 \times 10^{-2}$ to $13$ s$^{-1}$ can be measured. Since

$$k_i = k_2[C]$$  \hspace{1cm} (7)

second-order reaction rate constants can be obtained.

In practice thin gap–thin ring electrodes are difficult to construct, and so the variation of $N_m$ with $\lambda$ can best be determined empirically using known reaction rate constants.

4. Results and discussion

4.1. Solvated electrons in the presence of water

Water was added to a LiBr + HMPA solution in which solvated electrons were electrochemically generated at the disk electrode of a C$_x$–C$_y$ RRDE and oxidized at the ring electrode. The addition of water up to 1 M did not affect the collection efficiency $N_m$, reflecting the oxidation of solvated electrons at the ring electrode, nor did it affect the potential at which the solvated electrons were galvanostatically generated. This means that during the time that the electron travels from the disk to the ring electrode, i.e. the transit time $\tau$ (ca. 0.4 s), no measurable reaction with water occurs. Even after 5 min the system remained unchanged, indicating that no measurable reaction leading to LiOH precipitation onto the electrodes occurs in the bulk. At water concentrations higher than 1 M, the disk potential $E_D$ increases and $N_m$ decreases slowly with time. This is shown in Fig. 1. The transit time also increased. Thus the reaction

$$2e^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (8)

must take place. A value of $16$ M$^{-1}$ s$^{-1}$ has been reported for the reaction rate constant [3]. The slow change of $E_D$ and $N_m$ with time at higher water concentrations is caused by the visible precipitation of LiOH onto the disk and ring electrodes [1]. After about 10 min, the resistance of this layer is approximately 500 $\Omega$.

4.2. Solvated electrons in the presence of benzene

Benzene up to a concentration of 0.07 M was added to an LiBr + HMPA solution in the absence of water. Solvated electrons were galvanostatically generated at the disk of a C$_x$–C$_y$ RRDE and oxidized at the ring electrode. No change was observed in $N_m$, $\tau$ or the transient of $\tau$. Figure 2 shows $I_R$ versus $I_D$ at a benzene concentration of 0.014 M; the collection efficiency was 0.38. It is known that benzene does not react with solvated electrons in Li salt + HMPA solutions in the absence of a proton donor. Various conclusions can be drawn from the observation that neither $N_m$ nor the transit time transient changed upon addition of ben-
Fig. 3. Possible equilibrium between $e^-_s$ and benzene.

A change in the transit time transient would indicate the presence of an oxidizable benzene intermediate because, since the kinematic viscosity remains constant, any change can only be caused by a change in the diffusion coefficient $D$, reflecting a different species (a decrease of $D$ by an order of magnitude corresponds to an increase of a factor of 4 in the transit time). A decrease in $D$ also causes change in the ring current, since this current is controlled by the Levich equation (a decrease of $D$ by an order of magnitude produces a decrease of one-third in the original ring current).

In the benzene system described above it is reasonable to assume that the equilibrium shown in Fig. 3 is established. The benzene radical anion will have a $D$ that is at least an order of magnitude less than the $D$ of $e^-_s$. Therefore the absence of any change in the transit time transient and $N_m$ indicates the absence of any detectable Li-benzene radical anion complex and shows that the equilibrium lies on the benzene side.

4.3. Solvated electrons in the presence of water and benzene

Benzene was added to a 0.3 M LiBr + HMPA solution containing water. Solvated electrons were galvanostatically generated at the disk electrode of a $C_6^+ - C_6^-$ RRDE and were oxidized at the ring electrode. Upon addition of benzene up to 0.014 M, $N_m$ decreased as a result of its reaction with $e^-_s$ in the presence of the proton donor water. Figure 4 shows $N_m$ versus benzene concentration at a water concentration of $1.38 \times 10^{-2}$ M.

It was found experimentally that the decrease in $N_m$ is independent of water concentration between $1.38 \times 10^{-2}$ M and 0.2 M. This indicates that the first electron addition is probably the rate-determining step.

At a constant benzene concentration, $N_m$ depends on the frequency of rotation. This is shown in Fig. 5 for two different benzene concentrations and a water concentration of 0.014 M. $N_m$ increases with increasing $\omega$, suggesting a kinetically controlled reaction. A diffusion-controlled reaction would result in a decrease in $N_m$ with increasing $\omega$. The reaction of $e^-_s$ with benzene in LiBr + HMPA + H$_2$O is complex [4–6]. Several products are formed (Fig. 6): cyclohexadiene, cyclohexene and cyclohexane. These products are not oxidized at the ring electrode, unlike some intermediates such as radicals, anions and radical anions. Therefore the decrease in $N_m$ is the result of the decrease of $e^-_s$ corrected for the oxidation of oxidizable intermediates. Since their concentration will be low and, moreover, their diffusion coefficients are much smaller than that of $e^-_s$, their contribution to the ring current was neglected. The reduction reaction was considered as a

Fig. 4. Collection efficiency vs. rotation frequency: +[benzene] = 0.28 \times 10^{-2} M; $\Delta$ [benzene] = 1.4 \times 10^{-2} M; $[\text{H}_2\text{O}]$ = 1.38 \times 10^{-2} M; $T = 0^\circ\text{C}$; $I_D = -2$ mA; $E_R = 0$ V.

Fig. 5. Collection efficiency vs. benzene concentration: $[\text{H}_2\text{O}] = 1.38 \times 10^{-2}$ M; $I_D = -2$ mA; $\omega = 64.7$ rad s$^{-1}$; $T = 0^\circ\text{C}$; $E_R = 0$ V.

Fig. 6. Reaction mechanism for the reduction of benzene in LiBr + HMPA solution in the presence of a proton donor.
"black box" and a second-order reaction rate constant for the \( e^-_s \) decay was derived. As noted earlier, the equation used to determine \( k_1 \) depends on the value of \( k_1 \), reflected in \( \lambda \). In this case eqn. (6), derived by Albery and Bruckenstein [2] for the determination of \( k_1 \), was used.

Second-order reaction rate constants can be obtained when \( k_1 \) is replaced by \( k_2 \) (benzene). Figures 7 and 8 show plots of \( 1/N_m \) versus \( 1/\omega \) and \([\text{benzene}]/\omega \) respectively. The intercept on the ordinate corresponds to the collection efficiency \( N_t \) without any reactant. A second-order reaction rate constant can be obtained from these data and is found to be \( 0.26 \times 10^3 \text{ M}^{-1} \text{s}^{-1} \) at a disk current of \(-1.25 \text{ mA}\). It was found experimentally that \( k_2 \) depends on the disk current. This dependence requires further investigation.

Nomenclature

- \( C_g \): glassy carbon
- \( D \): diffusion coefficient, \( \text{cm}^2 \text{s}^{-1} \)
- \( e^-_s \): solvated electron
- \( E_D \): disk potential, \( \text{V vs. Ag wire} \)
- \( E_R \): ring potential, \( \text{V vs. Ag wire} \)
- \( I_D \): disk current, mA
- \( I_R \): ring current, mA
- \( k_1 \): (pseudo) first-order reaction rate constant, \( \text{s}^{-1} \)
- \( k_2 \): second-order reaction rate constant, \( \text{M}^{-1} \text{s}^{-1} \)
- \( N_m \): measured collection efficiency
- \( N_t \): theoretical collection efficiency
- \( r_1 \): disk radius, cm
- \( r_2 \): inner ring radius, cm
- \( r_3 \): outer ring radius, cm
- \( T \): temperature, \( ^\circ\text{C} \)
- \( \lambda \): Albery–Bruckenstein variable
- \( \nu \): kinematic viscosity, \( \text{cm}^2 \text{s}^{-1} \)
- \( \tau \): transit time, s
- \( \omega \): rotation frequency, \( \text{rad s}^{-1} \)

References