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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 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 electrochemical cell described in ref. 1 was modified to allow reactants to be introduced by adding a glass tube, sealed with a rubber, through which they could be injected. Benzene (Merck) was purified by distillation over sodium and injected into the electrochemical cell without being exposed to air. Distilled

water from which the oxygen had been removed by means of argon gas was used in the experiment.

The glassy carbon–glassy carbon rotating ring–disk electrode (C_g – C_g 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 $N_t = 0.358$.

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:

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_m will decrease. Alber and Bruckenstein [2] developed a theory in which

* Dedicated to Professor Jan Sluyters on the occasion of his 65th birthday.

they concluded that N_m must be a function of λ , r_1 , r_2 and r_3 , where

$$\lambda = (k_1/\omega)^{1/2}(\nu/D)^{1/6}(0.51)^{-1/3} \quad (4)$$

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

$$N_m = 1.75\lambda^{-3} \exp[4\lambda^3(r_2 - r_1)/r_3] \quad (5)$$

In this case, the method can be applied to values of k_1 between 10 and 10^3 s^{-1} . For small values of λ , an improved expression for thin gap–thin ring electrodes was given:

$$N_t/N_m = 1 + 1.28(\nu/D)^{1/3}(k_1/\omega) \quad (6)$$

If $1/N_m$ is plotted against $1/\omega$, the intercept gives N_t and the slope gives k_1 . Using this equation, reaction rate constant values from 4×10^{-2} to 13 s^{-1} can be measured. Since

$$k_1 = k_2[C] \quad (7)$$

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 λ 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_g – C_g 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 τ (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

must take place. A value of $16 \text{ M}^{-1} \text{ s}^{-1}$ 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

Fig. 1. E_D vs. time at $[\text{H}_2\text{O}] = 1.5 \text{ M}$ in 0.3 M LiBr + HMPA solution: $E_R = 0 \text{ V}$; $I_D = -2 \text{ mA}$; $\omega = 94.1 \text{ rad s}^{-1}$; $T = 0^\circ\text{C}$.

LiOH onto the disk and ring electrodes [1]. After about 10 min, the resistance of this layer is approximately 500Ω .

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_g – C_g RRDE and oxidized at the ring electrode. No change was observed in N_m , τ or the transient of τ . 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. 2. I_R vs. I_D in 0.3 M LiBr + HMPA solution: $[\text{benzene}] = 1.4 \times 10^{-2} \text{ M}$; $E_R = 0 \text{ V}$; $\omega = 94.3 \text{ rad s}^{-1}$; $T = 0^\circ\text{C}$.

Fig. 3. Possible equilibrium between e_s^- and benzene.

zene. 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_g - C_g 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

Fig. 5. Collection efficiency vs. rotation frequency: +[benzene] = 0.28×10^{-2} M; Δ [benzene] = 1.4×10^{-2} M. $[H_2O] = 1.38 \times 10^{-2}$ M; $T = 0^\circ\text{C}$, $I_D = -2$ mA; $E_R = 0$ V.

proton donor water. Figure 4 shows N_m versus benzene concentration at a water concentration of 1.38×10^{-2} M.

It was found experimentally that the decrease in N_m is independent of water concentration between 1.38×10^{-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 ω , suggesting a kinetically controlled reaction. A diffusion-controlled reaction would result in a decrease in N_m with increasing ω . The reaction of e_s^- with benzene in LiBr + HMPA + H_2O 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. benzene concentration: $[H_2O] = 1.38 \times 10^{-2}$ 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.

Fig. 7. $1/N_m$ vs. $1/\omega$ for different benzene concentrations: $\circ$ 0 M; Δ 0.28×10^{-2} M; $\circ$ 0.56×10^{-2} M; $+$ 0.84×10^{-2} M; $\blacktriangle$ 1.12×10^{-2} M; $\bullet$ 1.4×10^{-2} M. $[H_2O] = 1.38 \times 10^{-2}$ M; $I_D = -1.25$ mA; $E_R = 0$ V; $T = 0^\circ\text{C}$.

“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 λ . In this case eqn. (6), derived by Alberly 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 $k_2[\text{benzene}]$. Figures 7

Fig. 8. $1/N_m$ vs. $[\text{benzene}]/\omega$; $[H_2O] = 1.38 \times 10^{-2}$ M; $I_D = -1.25$ mA; $E_R = 0$ V; $T = 0^\circ\text{C}$.

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 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, V vs. Ag wire
E_R	ring potential, V vs. Ag wire
I_D	disk current, mA
I_R	ring current, mA
k_1	(pseudo) first-order reaction rate constant, 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, $^\circ\text{C}$
λ	Alberly–Bruckenstein variable
ν	kinematic viscosity, $\text{cm}^2 \text{ s}^{-1}$
τ	transit time, s
ω	rotation frequency, rad s^{-1}

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