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The Combined Field Emission-Spin Trapping Method for Studying Reactions of Electrons in Organic Solutions

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The reactions of electrons injected by field emission into solutions have been investigated. Free radicals generated by the dissociative electron attachment to chlorinated solutes in benzene solutions were detected by the spin trapping-ESR method, using pentamethylnitrosobenzene as a spin trapping agent. Nondissociative electron attachment to styrene caused by the field emission was also evidenced by detecting the α-methylbenzyl radical generated secondarily from the styrene radical anion. The electrons field-emitted into the solutions are captured almost quantitatively by the electron scavenging solutes. The field emission method has been found to be useful for generating authentically free radicals and for studying the anionic reaction induced by electrons without interference of countercations and of any reaction intermediates from solvent molecules. As an example of the chemical utilization of the field emission technique, the ESR parameters of the spin adducts of several hydrocarbon radicals have been collected by this technique.

The reactions of electrons in solutions have been a leading subject in a variety of fields in chemistry.1–3) The irradiation with ionizing radiations has been widely used to generate the electrons in solutions, though it simultaniously generates countercations which sometimes complicate the electron reactions to be studied. The photo-injection4–8) and the field emission8–10) of electrons from a metal cathode into liquids can also be used as electron sources. These methods generate the electrons in the solutions without accompanying countercations, but have been employed almost solely for studying the physical properties of the electrons in liquids, *i.e.*, electron mobility4,8,9) and quasifree electron energy.5–7,10) The field emission, emission of electrons from a sharp edge or a sharp tip of a metal cathode (emitter) at a high negative field, readily gives a current as high as 10^{-5} A.11) Nevertheless, the utilization of this method in chemical reaction study has been limited to the polymerization of styrene and α-methyl-styrene.11–13)

In order to exploit the chemical utilization of the field emission method, we have recently studied the dissociative and nondissociative attachments to organic solutes of the electrons field-emitted into benzene solutions. Free radicals, the short-lived intermediate products of the electron attachment reactions, have been detected by the spin trapping-ESR technique, in which the short-lived free radicals are transformed into stable nitroxyl radicals (to be detected readily by conventional ESR measurements) through the reactions with a proper nitroso compound or a nitrone compound (spin trap) coexisting in the solutions.14–17)

The present investigation will give several aspects of the electron attachment in solution for some model reaction systems studied by the combined field emission-spin trapping method, and will demonstrate the general prospect of the field emission method for chemical utilizations.

Experimental

A field emission cell was made of pyrex glass tubes equipped with an emitter (a razor blade of 0.7 cm length) and a collecting electrode (a brass rod, 1.0 cm diameter) facing each other at a distance of 0.1—0.2 cm, as shown in Fig. 1. The cell has a thin quartz tube (0.4 cm outer diameter) for ESR measurements. The emitter could be readily changed by disconnecting a part of the cell by means of a taper joint. The emitter and the collecting electrode could be completely covered with 3 ml of solution by turning the cell upside down. A high voltage, up to 15 kV, was applied by a stabilized high voltage supply. Typically *ca.* 5×10^{-5} F·dm^{-3} of electronic charge was field-emitted into a solution by generating for 1 h, a field emission current (monitored with an electronic microammeter) of 5 μA at a voltage of 5 to 6 kV applied to the emitter. Such a current induced a significant bulk flow of the solution, which was visible as a violent disturbance at the surface of the solution.

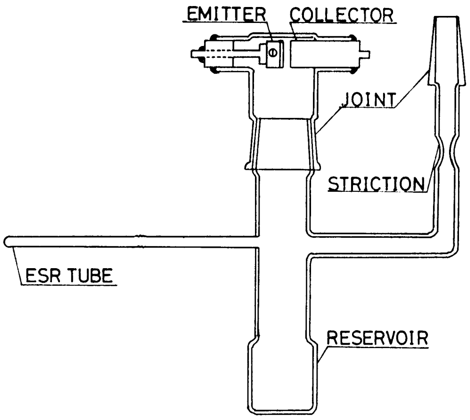

Fig. 1. Field emission cell.

Benzene, ethanol, and cyclohexane of spectrograde were used as received. All organic halides used as solutes were purified by vacuum distillation. Styrene was purified as described elsewhere.18) Pentamethylnitrosobenzene synthesized as described elsewhere19) was used as a spin trap. The solutions were degassed by repeated freeze-pump-thaw cycles, sealed in the cell, subjected to a high applied voltage for the field emission, and examined by a conventional ESR spectrometer with a 100 kHz magnetic field modulation. All the experiments were carried out at ambient temperature.

Results and Discussion

Dissociative Electron Attachment. The dependence of the field emission current on the applied voltage is shown in Fig. 2, for the benzene solution of benzyl chloride (0.04 mol·dm^{-3}) and spin traps

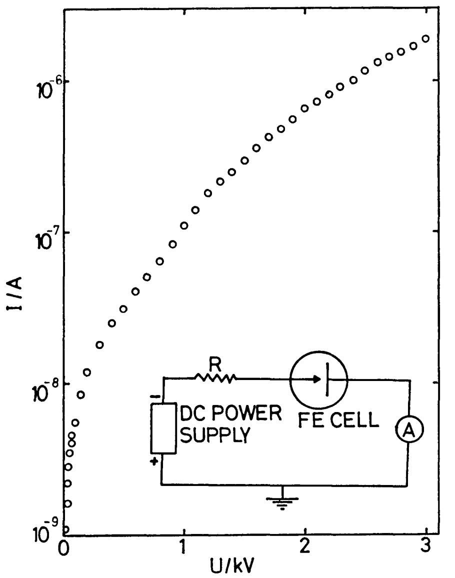

Fig. 2. Emission current-voltage curve for the benzene solution of benzyl chloride (0.04 mol·dm^{-3}) and the spin trap (0.002 mol·dm^{-3}). The electric circuit for the field emission experiment is also shown in the figure.

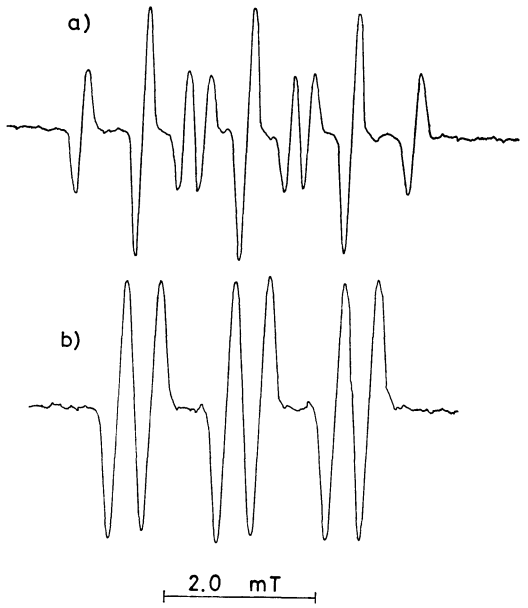

Fig. 3. ESR spectra of the spin-adduct radicals observed in a) the benzene solution of benzyl chloride (0.04 mol·dm^{-3}) and in b) the benzene solution of styrene (0.1 mol·dm^{-3}) and ethanol (0.2 mol·dm^{-3}). The concentration of the spin trap is 0.002 mol·dm^{-3} in both solutions.

(0.002 mol·dm^{-3}). The current increases with the applied voltage sharply in the low voltage region and then slowly in the higher region. The steep increase in the current indicates the onset of the field emission. The onset occurs at a high applied voltage for cyclohexane solutions. The characteristics of the current-voltage curve have been studied in detail for several liquids,¹⁰⁾ and the onset of the field emission has been found to depend on the quasifree electron energy in the liquids.

Spin adduct radicals were found by ESR to be generated in the solution to which electrons had been field-emitted (Fig. 3A). The spin adduct radicals indicated by hyperfine splitting due to a nitrogen nucleus (0.14 mT) and two equivalent protons (0.084 mT) have been identified to be the nitroxide radicals generated by the reaction between the spin trap and benzyl radical.¹⁹⁾ The latter are unquestionably the products of the dissociative electron attachment to benzyl chloride. The yield of the adduct radicals (5×10^{-5} mol·dm^{-3}) was very close to the field-emitted charge (2×10^{-7} F, or *ca.* 7×10^{-5} F·dm^{-3}). This indicates that 0.04 mol·dm^{-3} of benzyl chloride effectively scavenges all the emitted electrons. The spin trap can act as an electron scavenger.¹⁴⁾ In the present experiments, however, the concentration of electron-scavenging solutes is higher than that of the spin trap by one to three orders of magnitude, so that the solutes preferentially compete with the spin trap in reacting with the field-emitted electron. The field emission appears to provide a method to study selectively and quantitatively the electron reactions with the solutions.

Tweleve free radicals were generated from the corresponding chlorinated compounds in benzene and studied by the combined field emission-spin trapping method. The ESR parameters of the spin adduct of these free radicals are summarized in Table 1, where some other spin adducts generated by other means¹⁹⁾ are also included for comparison. The spin-trapped free radicals were, in almost all the cases, those generated by the dissociative electron attachment (by the rupture of the C–Cl bond) to the solutes. No free radical from solvents was generated by field emission into benzene and cyclohexane solutions of the chlorinated compounds, whereas in γ-radiolysis the solvent radicals were also generated and spin-trapped. Field emission is a useful method to generate authentically free radicals. From *o*- and *p*-chlorotoluenes, both *o*- and *p*-chlorobenzyl radicals and *o*- and *p*-methylphenyl radicals were generated and spin-trapped. The former radicals may have been formed secondarily by the hydrogen abstraction of the latter.

Nondissociative Electron Attachment. When the benzene solution of styrene (0.1 mol·dm^{-3}), ethanol (0.2 mol·dm^{-3}), and the spin traps (0.002 mol·dm^{-3}) were subjected to the field emission, the α-methylbenzyl radical was identified by observing the ESR spectrum of its spin adduct (see Fig. 3B), which contained the hyperfine splitting due to a nitrogen nucleus (0.144 mT) and a proton (0.044 mT).¹⁹⁾ However, no ESR spectrum was observed in the absence of ethanol under the same conditions of measurement. Ethanol takes an essential role in the formation of α-methylbenzyl radical, which very probably results from the proton transfer from ethanol to a styrene radical anion generated by the nondissociative electron attachment to styrene. The presence of styryl radical was confirmed in the benzene–ethanol solution of phenyl acetylene. Its formation can be interpreted, in the same way, by the nondissociative electron attachment followed by the proton transfer. ESR parameters of these free radicals are also included in Table 1.

TABLE 1. HYPERFINE SPLITTING CONSTANTS AND *g*-VALUES FOR SPIN ADDUCTS (NITROXIDES) FORMED FROM PENTAMETHYLNITROSOBENZENE AS A SPIN TRAP IN BENZENE AT ROOM TEMPERATURE

Trapped radical	Radical sourse	*g*-value	a_N/mT	$a_{\beta H}$/mT
$\cdot CH_3$[a]	$CH_3I + (n\text{-}C_4H_9)_3SnH$	2.0058	1.38	1.23
$\cdot CH_2CH_3$	$CH_3CH_2Br + FE$	2.0062	1.40	1.16
$\cdot CH_2CH_2CH_3$[a]	$n\text{-}C_3H_7Cl + \gamma$	2.0058	1.42	1.12
$\cdot CH(CH_3)_2$[a]	$CHCl(CH_3)_2 + \gamma$	2.0059	1.39	0.77
$\cdot CH(CH_3)CH_2CH_3$[a]	$CHCl(CH_3)C_2H_5 + \gamma$	2.0058	1.37	0.78
$\cdot C(CH_3)_3$	$t\text{-}C_4H_9Cl + FE$	2.0060	1.35	—
$\cdot C(CH_3)_2CH_2C(CH_3)_3$	C_8H_{18}[b]	2.0060	1.35	—
$\cdot cyclo\text{-}C_6H_{11}$[a]	$cyclo\text{-}C_6H_{12} + \gamma$	2.0058	1.40	0.76
$\cdot CH_2C_6H_5$	$C_6H_5CH_2Cl + FE$	2.0062	1.40	0.84
$\cdot CH_2C_6H_4(o\text{-}Cl)$	$o\text{-}ClC_6H_4CH_3 + FE$	2.0061	1.40	0.88
$\cdot CH_2C_6H_4(p\text{-}Cl)$	$p\text{-}ClC_6H_4CH_3 + FE$	2.0062	1.40	0.84
$\cdot CH(CH_3)C_6H_5$	$CH_3CHClC_6H_5 + FE$	2.0060	1.44	0.44
$\cdot CH(C_6H_5)_2$	$(C_6H_5)_2CHCl + FE$	2.0061	1.42	<0.24
$\cdot C_6H_5$	$C_6H_5Br + FE$	2.0058	1.03	0.28(*o*, *p*-) 0.10(*m*-)
$\cdot CH{=}CHC_6H_5$	$C_6H_5CH{=}CHBr + FE$	2.0063	1.34	0.40
$\cdot CH_2\text{-}C(Cl){=}CH_2$	$CH_2{=}C(Cl)CH_2Cl + FE$	2.0060	1.36	0.88
$\cdot C(CH_3){=}CHCH_3$	$CH_3C(Cl){=}CHCH_3 + FE$	2.0061	1.37	—
$\cdot CH(CH_3)CH{=}CH_2$	$CH_3CH(Cl)CH{=}CH_2 + FE$	2.0061	1.34	0.80
$\cdot CH(CH_3)OC_2H_5$[a]	$(C_2H_5)_2O + \gamma$	2.0058	1.40	0.46
$\cdot CH(CH_3)C({=}O)CH_3$	$CH_3CHClC({=}O)CH_3 + FE$	2.0060	1.36	0.41
$\cdot C(CH_3)O$[a]	$(CH_3CO)_2 + h\nu$	2.0058	1.32	—
$\cdot C(CN)(CH_3)_2$[a]	$((CH_3)_2C(CN)N{:})_2 + h\nu$	2.0063	1.30	—
$\cdot CH_2Si(CH_3)_3$[a]	$Si(CH_3)_4 + \gamma$	2.0060	1.38	1.58

a) Ref. 19. b) 2,2,4-Trimethylpentane.

Schnabel and Schmidt[12] have studied the field emission into bulk styrene and found no indication of its anionic polymerization. They suggested that the electron attachment to styrene does not occur because it possesses a negative electron affinity in the gas phase. In this connection, Horloyd[20] has demonstrated that an electron can be localized on a single styrene molecule in liquid hydrocarbons, whereas Shinsaka and Freeman[21] have inferred that an electron cannot be localized on a single molecule in bulk aromatic compounds, but rather moves freely and is delocalized. The present result indicates that the field-emmitted electron in the benzene solution can be localized on a styrene molecule or a phenylacetyrene molecule to form the corresponding radical anion.

Based on the possible electron localization on a styrene molecule, we attempted the anionic polymerization of styrene by the field emission method in benzene, as well as in cyclohexane and in diethyl ether, all carefully purified and dried by the standard methods in polymer chemistry.[22] A small amount of polymer was actually obtained in benzene and cyclohexane with a field-emitted charge of *ca.* 10^{-5} F, but not in diethyl ether. The polymerization was inhibited by adding triethylamine, an inhibitor for the cationic polymerization, into the benzene and the cyclohexane solutions. In addition, nitroethylene could not be polymerized by the field emission in toluene or in diethyl ether. It is a monomer polymerizable exclusively by the anionic mechanism.[23] These results seems to indicate that the radical anions generated by the field emission have a lifetime too short to grow sufficiently long polymer chains before being neutralized at the collecting electrode.

Ionization by the Injected Electrons. The field emission into the benzene solution of 0.2 mol·dm^{-3} ethanol and 0.02 mol·dm^{-3} spin traps generated the spin adduct of the phenyl radical, while no ESR spectrum was observed without ethanol. The phenyl radical adduct formation was efficiently suppressed by an electron scavenger, such a *t*-butyl chloride or styrene. The phenyl radical formation from benzene cannot be interpreted by anionic reactions initiated by the field-emitted electron, but it tentatively attributed to the cationic mechanism: the ionization of benzene by an energetic electron giving a benzene radical cation, which transfers a proton to ethanol and transforms to a phenyl radical. The emitted electron can be accelerated by a locally high electric field near the sharp edge of the emitter. Since the initial kinetic energy of the field-emitted electron is 4 to 5 eV[24] and the local electric field is thought to be 10^7—10^8 V/cm, it is probable that the electron attains a kinetic energy of *ca.* 10 eV.

The ionization energy of a molecule in condensed media is generally less than that in the gas phase by the sum of the polarization energy of a resultant positive ion, P_t, and the quasifree electron energy in the media, V_0.[25] For benzene, the gas phase ionization energy is 9.6 eV,[26] and P_t and V_0 are roughly estimated to be -2 eV[25] and -0.1 eV[27] in liquid phase. Thus, the ionization energy is expected to be about 7.5 eV for liquid benzene, which can be ionized by the field-emitted electron after being accelerated. Such an ionization process has been demonstrated by Schnabel and Schmidt[12] for the field emission into liquid styrene.

In the presence of an electron scavenger, the emitted electrons are scavenged before being accelerated to a significant kinetic energy. This is the reason why the anionic reactions occur only in the presence of the electron scavenger.

Conclusions. The field emission into liquid solutions is a promising technique to study dissociative and nondissociative electron attachment reactions in the solutions. This is superior to the radiation chemical techniques in that the anionic reactions exclusively occur in the solutions without being interferred with the reactive intermediate coming from solvent molecules. The field emission has been used, as an example of its chemical utilization, for the authentic generation of several free radicals, whose spin adducts were examined by the ESR method. The ESR parameters of the spin adducts thus determined (Table 1) will be helpful for the spin trapping studies using pentamethylnitrosobenzene as the spin trap.

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