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Both Oxidation and Reduction of Aromatic Hydrocarbons by an Electrolysis Cell Designed for Low-temperature ESR Studies

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A simple two-electrode cell for low-temperature electron spin resonance (ESR) measurements has been designed. A helical gold wire, the working electrode with large surface area (12 cm^2), generated *intra muros* enough positive or negative ions to measure the ESR spectra of unstable radical ions at low temperatures. To test the electrolysis conditions of the cell, the ESR spectra of about 20 aromatic compounds have been observed at temperatures as low as −90 °C. It has been shown that the cell can be applicable to the compounds with half-wave potential of 1.5 to −3.7 V SCE, provided that the ions produced are not reactive. The experimental conditions of the dimer cation generation have also been checked in polar or nonpolar solvents.

The electrochemical generation of organic radical ions for ESR studies has some advantages over the usual chemical methods.[1] The application of this method to the compounds with high ionization potential or with low electron affinity, however, has been severely limited by the following difficulties. One of the principal problems encountered in setting up an electrolysis cell inside the ESR cavity is the high dielectric loss caused by the large dielectric constants of the solvents commonly used in electrochemistry. This loss can have a very deleterious effect on the quality factor(Q) of the resonant cavity. Secondly, the conventional electrolysis cells so far used for ESR studies produced a large ohmic drop, which results in low electrolysis current. In 1975 Allendoerfer, Martinchek, and Bruckenstein[2] described a radically new design of a cell for simultaneous electrochemical-ESR(SEESR) measurements, based on a coaxial microwave cavity; this cell design has overcome the difficulties pointed out above. On the other hand, the use of low-temperature environments has proved to be of considerable value[3] for the observation of unstable species produced by electrochemical experiments. Modifying the cell developed by Allendoerfer *et al.*, Gerson, Ohya-Nishiguchi, and Wydler[4] have observed the ESR spectra of typical aromatic hydrocarbons at −90 °C to determine indirectly the half-wave reduction potentials ($E^{r}_{1/2}$) of benzene and paracyclophane, two compounds with low electron affinity. This modified cell was successfully used for the ESR measurements of the other compounds with high ionization potential or chemically unstable radical ions.[5] The purpose of this paper is to present a cell design which is useful for the low-temperature ESR measurements and to discuss its applicability according to the results obtained.

Cell Design

Optimum Conditions of Electrochemical ESR Measurements. We describe here the optimum conditions for electrochemical ESR measurements, assuming the linear diffusion model.[6] This assumption is not strictly applicable to our cell, but this model is adequate for qualitative understanding of the experimental conditions.

The radical concentration [R·] produced during a constant current electrolysis can be described simply by the rate equation:

$$\frac{d[R\cdot]}{dt} = \frac{i(T)}{VF} - k(T)[R\cdot] \tag{1}$$

where V is the effective volume of the diffusion layer of the radical ions produced, F the Faraday constants, and $k(T)$ and $i(T)$ are the decay constant of R· and the electric current producing R·, respectively, at temperature T. When $i(T)$ is assumed to be controlled by the linear diffusion process only, $i(T)$ can be derived from Fick's first law:

$$i(T) = \frac{D(T)A}{l(T)}nFC \tag{2}$$

where A is the surface area of the working electrode, C, $D(T)$, and $l(T)$ are the concentration, the diffusion coefficient, and the effective thickness of the diffusion layer, respectively, of parent molecules R, and n is the number of electrons involved in the electrode reaction. Hereafter n is assumed to be one, because ESR observation of the electrolysis means the one electron reaction on the electrode surface. Using the steady state condition $d[R\cdot]/dt=0$, and substituting Eq. 2 into Eq. 1, the radical concentration $[R\cdot]_s$ can be estimated from the next equation,

$$[R\cdot]_s = \frac{D(T)}{Vl(T)}\cdot\frac{AC}{k(T)} \tag{3}$$

In order to obtain high concentrations of $[R\cdot]_s$, A has to be made as large as possible without any appreciable disturbance of the microwave mode inside the cavity. Allendoerfer *et al.* succeeded in obtaining large A values by using a finely wound shallow pitched helix as a working electrode. Secondly, it can be deduced from Eq. 3 that a high concentration of the parent compound is desirable to increase $[R\cdot]_s$. High resolution ESR spectroscopy in solution requires usually a concentration not higher than 1 mmol dm^{-3}, because in the high concentration range the electron transfer effect on the ESR line width becomes predominant, in addition to the problem of the inhomogeneity of the solution.[7] Such effect, however, can be safely suppressed if the temperature of the solution is lowered below about −60 °C to the region where the electron transfer effect becomes negligible. Thirdly, Eq. 3 shows also the necessity of low temperature measurements to suppress mainly the radical decay. Strictly speaking, Eq. 3 has a maximum at a temperature (T_m) slightly higher than freezing point of the solution,

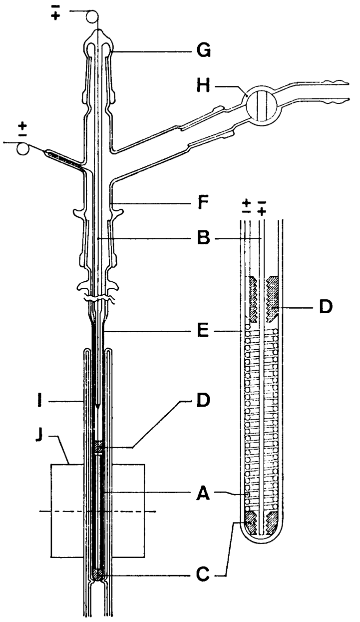

Fig. 1. Schematical diagram of the electrolysis cell mounted in a TE_{011} cylindrical cavity (J) with a temperature control dewar (I). See text about the other notations.

because of the rapid increase of viscosity and solution resistance near the melting point. This requires the development of pertinent solvent-supporting electrolyte systems possessing reasonably high conductivity over a wide low temperature range.[3] Taking such conditions into account a simple cell for the low-temperature ESR study has been designed.

Apparatus. Figure 1 shows a schematic diagram of the electrolysis cell mounted in a TE_{011} cylindrical cavity (J) with a temperature control dewar (I). The cell consists of four parts, (E) to (H): (E) contains a helical electrode wound of a 0.5 mm diameter gold wire (A) and a straight platinum wire of a 0.5 mm diameter (B) supported by two Teflon holders (C) and (D) along the tube axis. By changing the polarity of these electrodes either cations or anions can be produced on the working electrode. (F) and (G) hold the terminals for (A) and (B), respectively, which are connected to a potentiostat with a sensitive current meter. (A) is wound to fit against the inner wall of the 3.5 mm i. d. pyrex tube (E), its length and surface area being about 50 mm with 80 turns and 12 cm^2, respectively. The mercury amalgamation of (A) was carried out as required in the case of the anions. It should be noted in this figure that no reference electrode was used in order to simplify the electrolysis apparatus. If necessary one can estimates $E_{1/2}$ from a linear relationship between $E_{1/2}$ and the minimum voltages applied between two electrodes, V_a, at which the ESR spectra of the radicals appear during the electrolysis.[4]

Procedure

Each solution prepared under a nitrogen atmosphere was degassed by the freeze-pump-thaw cycles three or four times. After the cell was pumped and flushed with dry nitrogen through the stop cock in Fig. 1, the solution of about 0.7 ml was transferred into (E) through (F) with a pipette under the dry nitrogen atmosphere. Then the cell containing the solution was inserted into the cavity. After the solution temperature was decreased, the voltage was applied between two electrodes and gradually increased until ESR signals could be observed. The observation of the ESR signals was carried out with the field modulation of 1.0×10^{-4} T, which was appropriate to observe the appearance of the signals. As the voltage applied reached V_a, the electric current of the circuit also increased appreciably, its amount depending on the temperature, solvent used, and the concentration of the substrates (see Eq. 2). Several solvents were tested for the generation of both radical cations and anions. 1,2-dimethoxyethane(DME) with 0.1 mol tetrabutylammonium perchlorate (TBAP) is recommended for anions, and dichloromethane(CH_2Cl_2) including 10% trifluoroacetic acid (TFAc) and 10% trifluoroacetic anhydride(TFAn) with or without 0.01 mol TBAP[8] are recommended for cations. It should be noted in the latter case that the pertinent ratios of these solvents depend on the stability of the parent compound to be oxidized and solubility of the radical cations produced in the solvent, as will be discussed in the following section.

Experimental

DME was refluxed with $LiAlH_4$ for two days, followed by distillation onto the Na–K alloy. Dry DME was distilled into a bottle with 0.1 mol supporting reagent, and flushed with dry nitrogen gas. Spectrograde CH_2Cl_2, TFAc, and TFAn were used without further purification. ESR spectra were measured with a Varian E-9 spectrometer.

Results and Discussion

Effects of the Cell on the Cavity Properties. When this cell was inserted into the cavity, the resonance frequency became only 0.22 GHz higher than that without the cell (9.07 GHz). Such a small shift means that the cell can be treated in a similar manner to the usual sample tube containing the solution for the ESR measurements. The Q factor, on the other hand, depended on the solution to be electrolyzed as well as on the design of working electrode. Tight fitting of the helix electrode to the inner wall of (E) in Fig. 1 was most important to maintain the high Q. The loaded Q in the case of polar solvents, *i.e.* H_2SO_4, H_2O, and *N,N*-dimethylformamide(DMF), were measured as 2200, 2500, and 3200, respectively. Even in the case of H_2SO_4, Q was high enough to measure the ESR spectra.

Oxidation of Some Aromatic Hydrocarbons. The electrolytic oxidation of aromatic hydrocarbons was more difficult than the electrolytic reduction was, mainly because in nonpolar solvents the cations produced deposited on the surface of the electrode, while in polar solvent such as CF_3COOH, on the other hand, substrates sometimes decomposed. The most

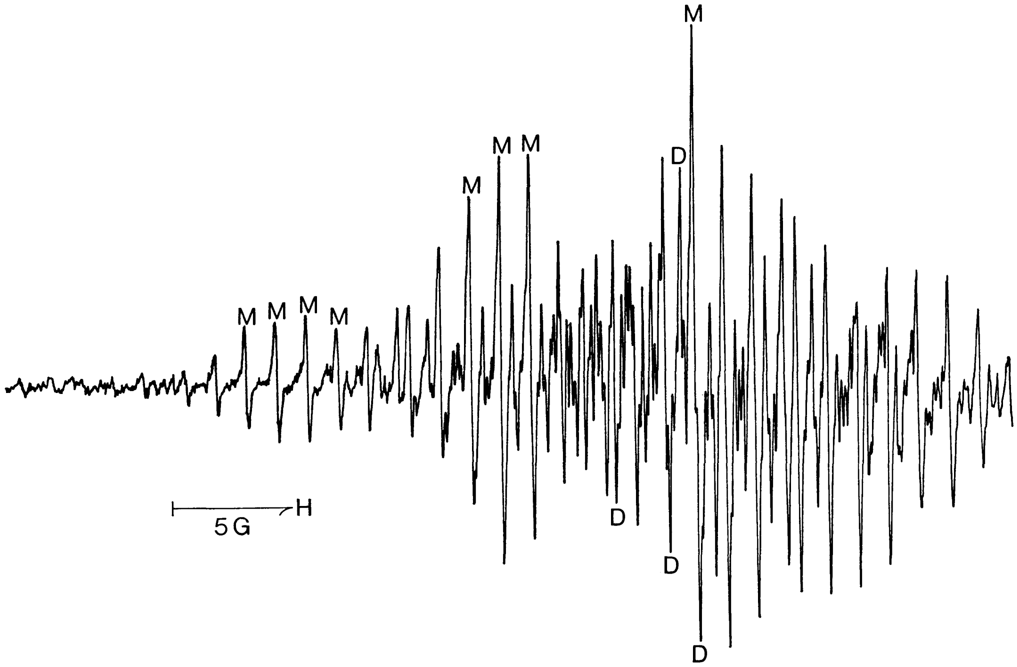

Fig. 2. The ESR observation after partial electrolytic oxidation of 3 mM 9,10-dimethylanthracene in CH_2Cl_2 with 10% CF_3COOH and 10% $(CF_3CO)_2O$ at −80 °C. Supporting reagent: Tetrabutylammonium perchlorate, field modulation: 0.1 G. M and D in the figure correspond to the representative lines due to the monomer and the dimer cation radicals, respectively. The ratio of $[DMA^{\dot{+}}]$ to $[(DMA)_2^{\dot{+}}]$ is about 1 : 6. Slight difference of their *g*-values leads to an asymmetric ESR spectrum.

effective solvent for electro-oxidation of aromatic hydrocarbons was the mixture CH_3NO_2 or CH_2Cl_2/TFAc/TFAn, with TBAP as a supporting reagent. The ratios of these reagents were changed, corresponding to the stability of the parent molecules and cation radicals produced. The compounds with oxidation potential ($E^\circ_{1/2}$) lower than *ca.* 0.9 V SCE, hereafter called Category I, were oxidized partially when dissolved in the solvent mixture (ratios: 10/(1—10)/1/0) without any application of voltage. When the voltage larger than $E^\circ_{1/2}$ was applied, the ESR signals increased substantially, and sometimes became highly resolved. Secondly, the compounds with $E^\circ_{1/2}$ between 0.9 and 1.3 V SCE (Category II) could be oxidized at temperatures as low as −60 °C in the solvent with ratios of 10/1/1/0. V_a roughly corresponded to $E^\circ_{1/2}$. Thirdly, the compounds of Category III having $E^\circ_{1/2}$ higher than *ca.* 1.3 V SCE gave the spectra at −70 to −90 °C (ratios: 10/1/1/0.01 mol dm^{-3}). Durene was the compound with the highest $E^\circ_{1/2}$ of all the compounds which successfully gave the resoved ESR spectra. This means that the ESR spectra of the compounds with $E^\circ_{1/2}$ lower than 1.5 V SCE can be observed provided that no chemical reactions of the cation produced occur. It should be pointed out here that the ESR spectra of the dimer radical cations can also be observed under the conditions a) high concentration, b) low temperature, c) nonpolar solvents, d) low voltage available, and e) the beginning of electrolysis, unlike the situation of monomer production. In some cases, i.e. pyrene, acenaphthene, and tetramethylparacyclophane, the ESR spectra due to monomer cations could not be observed even if the conditions mentioned above were changed. This means that in CH_2Cl_2, nonpolar solvent, the dimer configuration is quite stable compared with the corresponding monomer cations. The ESR observation after the oxidation of 9,10-dimethylanthracene(DMA), a typical example, showed clearly the existence of the dimer species in addition to that of the monomer under the conditions mentioned above: a) to e) (see Fig. 2). It should be noted that Van Duyne and Reilley[3] also measured the steady-state cyclic voltammograms of DMA on a platinum electrode at low temperatures. From these results they postulated an equilibrium between monomer and dimer cations of DMA:

$$DMA^{\dot{+}} + DMA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (DMA)_2^{\dot{+}} \tag{4}$$

which is in good agreement with our results. In Table 1 the coupling constants of the monomer and dimer cations of typical aromatic compounds are summarized, with some experimental conditions. From this table one can say roughly that V_a corresponds to $E^\circ_{1/2}$ in the range of the error +0.2 V, in spite of different conditions. On oxidations of benzene and naphthalene a broad line with the line width of 5 to 6 G has been observed.

Reduction of Aromatic Hydrocarbons. In order to check the applicability of the cell, the reduction of aromatic hydrocarbons, whose $E^r_{1/2}$ values were known by the polarographic measurements, was carried out under the same conditions (C: 5 mmol, DME/0.1 mol TBAP, −90 °C), followed by the observation of both V_a and its high-resolution ESR spectrum. The proton hyperfine coupling constants which were used for the

Table 1. The electrolysis conditions and the hyperfine coupling constants of some aromatic hydrocarbon radical cations

Substance	Voltage applied (V)	Temperature (°C)	Hyperfine coupling constants (G)[a]					
			Monomer			Dimer		
Category I								
Naphthacene	0.5	≤ 25	5.09 (4)	1.68 (4)	1.04 (4)			
Perylene	0.9	≤ 25	4.08 (4)	3.07 (4)	0.44 (4)	1.96 (8)	1.53 (8)	0.22 (8)
9,10-Dimethyl-anthracene	0.9	≤ 0	8.08 (6)	2.48 (4)	1.24 (4)	3.51 (12)	1.22 (8)	0.66 (8)
Anthracenophane	0.5	≤ 25	1.10 (8)	0.95 (8)	0.64 (8)			
Category II								
Biphenylene	1.15	≤ -20	3.55 (4)	0.20 (4)		1.75 (8)	0.15 (8)	
Indeno[1,2,3-*cd*]-fluoranthene	1.20	$-10 \leq T \leq +10$	2.01 (4)	0.71 (4)	0.19 (4)			
Chrysene	1.30	≤ -30	5.56 (2)	2.65 (2)	1.81 (2)			
			1.40 (2)	0.70 (2)				
Pyrene	1.25	≤ -30				2.68 (8)	1.03 (8)	0.54 (4)
Anthracene	1.35	≤ -30	6.61 (2)	3.05 (4)	1.40 (4)	3.24 (4)	1.45 (8)	0.71 (8)
Category III								
Coronene	1.3	≤ 25	1.50 (12)			0.77 (24)		
Hexamethylbenzene	1.55	≤ -40	6.50 (18)			3.25 (36)		
Acenaphthene	1.6	≤ -60				9.10 (8)	2.38 (4)	0.88 (4)
						0.70 (4)		
Tetramethyl-paracyclophane	1.7	≤ -70				2.23 (24)	1.67 (8)	0.372 (8)
						0.186 (8)		
Durene	1.8	≤ -90				5.0 (24)	0.2 (4)	

a) $G = 10^{-4}$ T. Numbers of equivalent protons giving rise to the coupling constants are indicated in parentheses.

Table 2. Appearance voltages and estimated reduction potentials of aromatic hydrocarbons with low electron affinities

Compounds	$-V_a$(V)	$-E^r_{1/2}$ *vs.* SCE(V)
Biphenyl	5.02 ± 0.05	2.57
[2.2]Paracyclophane	5.85 ± 0.05	3.05
Benzene	6.35 ± 0.05	3.31
Toluene	7.0 ± 0.1	3.7
m-Xylene	7.0 ± 0.2	3.7

identification of the anion produced, coincided with those previously published, within the range of experimental errors. In the previous paper[4)] we described the relationship between V_a and $E^r_{1/2}$. The pertinent regression line has an equation

$$V_a = (1.92 \pm 0.06) E^r_{1/2} \tag{5}$$

with a correlation coefficient of 0.991 and a deviation from the origin (0.007). V_a defined above can be alternatively described as the voltage at which $[R\cdot]$ reaches the minimum radical concentration detectable. If the radical decay becomes appreciably larger, i.e. irreversible in terms of cyclic voltammetry, one has to apply a voltage lower than the real one, which causes a deviation from the linear relationship of Eq. 5. Such a good relationship as in Eq. 5, therefore, has two significant meanings: One is a good correspondence of V_a and $E^r_{1/2}$, which was successfully applied to the indirect determination of $E^r_{1/2}$ of benzene and other aromatic hydrocarbons with low electron affinity (Table 2). The other is that if $E^r_{1/2}$ of a compound is higher than that of *p*-xylene (-3.7 V SCE), it is possible to observe the ESR spectrum by applying V_a corresponding to its $E^r_{1/2}$ given by Eq. 5. This is in contrast with the cell used by Levy and Myers,[9)] who applied voltage as large as 110 V to reduce the pyridines and diazines.

It should be mentioned finally that DMF with 0.1 mol tetraethylammonium perchlorate(TEAP) was also a good solvent for chemically unstable radicals, because the electrolysis current is *ca.* 10 times larger than that in DME at the same temperature, although its freezing point (-60 °C) is a little high.

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