

RESONANCE RAMAN SPECTROSCOPIC DETECTION OF ELECTROCHEMICALLY
GENERATED DIANION OF NAPHTHACENE

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Resonance Raman and visible absorption spectra of the naphthacene dianion generated by electrolytic reduction from the naphthacene anion radical were measured in tetrahydrofuran in the absence of any supporting electrolyte. The resonance Raman scattering from the dianion located near a cathode was successfully observed when the intensity of laser light as an exciting source was reduced to prevent the convection of the dianion by thermal effect.

Raman spectroscopy has been applied for the determination of electrolytic products¹⁻⁴⁾. Hendra et al. measured the Raman spectra of mercury compounds such as Hg_2Cl_2 , Hg_2Br_2 , and HgO electrodeposited on mercury anodes¹⁾ and two adsorption types of pyridine on a silver electrode²⁾. The Raman scattering is too weak as an analytical method for a solution of concentration lower than 0.01 M.

Recently Van Duyne et al. reported to utilize the resonance Raman effect which shows very strong intensity by the factor of 10^3 - 10^5 comparing with Raman scattering to detect the tetracyanoethylene anion radical³⁾ and the tetracyanoquinodimethane anion radical (TCNQ^-)⁴⁾ generated by electroreduction and also the TCNQ^--O_2 decay product⁴⁾ in solution. Fujihira et al. obtained the resonance Raman spectra of methylene blue adsorbed on an optically transparent SnO_2 electrode by an internal reflection method⁵⁾.

Dianions generated by electroreduction of aromatic hydrocarbons such as anthracene have not been directly identified yet by any spectroscopic technique, though aromatic hydrocarbons are electrochemically reduced to anion radicals and dianions, which are stable during the time scale of the slow cyclic voltammetry⁶⁾. Those anion radicals and dianions should have the strong resonance Raman effect⁷⁾. In a tetrahydrofuran (THF) solution without any supporting electrolyte the naphthacene dianion has been generated by electroreduction from the naphthacene anion radical which was prepared by lithium metal reduction. This letter describes the resonance Raman and visible absorption spectroscopic detection of the dianion and an electrochemical behavior of the naphthacene anion radical in the absence of any supporting electrolyte. In THF solutions containing lithium perchlorate or tetrabutylammonium perchlorate as a supporting electrolyte no resonance Raman spectra of dianions derived from corresponding aromatic hydrocarbons such as anthracene, naphthacene, p-terphenyl, and quarterphenyl have been obtained⁸⁾.

Experimental

A THF solution of naphthacene anion radical prepared by lithium metal reduction was electrolyzed at 1 μ A in an H-type cell with a glass filter diaphragm. Platinum cathode and anode were placed at bottoms of 2.5 ml optical cells.

Cyclic voltammetry was performed at a platinum micro electrode in the cathode compartment. The electrode potential was measured as the potential against a platinum wire placed near the working electrode.

The concentrations of reactants and products were determined from their absorbances and their Raman scattering intensities.

Absorption spectra were measured using the pyrex optical cells which had 2 mm optical path length. Naphthacene anion radical and the dianion prepared by lithium metal reduction and the parent molecule, naphthacene, had absorption peaks at 716, 618, and 476 nm where the molar absorption coefficients were respectively 1.4×10^4 , and 4.3×10^4 , and $9.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, which are somewhat different from the coefficients appeared in the literature⁹⁾.

The Raman scattering was measured with a JEOL JRS-S1 type laser Raman spectrophotometer by focusing a 30 mW He-Ne laser beam (632.8 nm).

Results and Discussions

The sweep voltammogram and resonance Raman spectrum of 0.4 mM naphthacene anion radical in THF solution containing 0.04 mM naphthacene are shown in figs. 1a and 2a. After electrolyzing this solution for 24 hr the resonance Raman spectrum of the electrogenerated dianion and the sweep voltammogram were obtained as shown in figs. 2c and 1b. Absorption and resonance Raman spectra of the electrogenerated anion radical and dianion are coincident to the spectra of those prepared by lithium metal reduction.

In fig. 1, when the direction of potential sweep was changed after a reduction peak (R_2), oxidation peaks O_1 and O_2 were observed. When the direction of sweep was changed at the potential between peak R_1 and peak R_2 , peak O_1 was observed but peak O_2 was not observed. Therefore peak O_1 corresponds to the reverse reaction of peak R_1 which is the peak for reduction of naphthacene, and peak O_2 corresponds to the reverse reaction of peak R_2 for reduction of the anion radical. A peak O_3 is considered to be the peak for oxidation of electrodeposited lithium. A peak O' was observed in the catholyte where the dianion was present, namely in the solution before electrolysis the peak was not observed. Under the condition where peak O' appeared an absorption band was observed at 470 nm in THF. This peak O' is assigned to the peak for oxidation of the carbanion (MH^-) produced from the dianion by protonation, because the oxidation peak potential of the carbanion is 0.5 V more positive than the oxidation peak of the anion radical in dimethylformamide¹⁰⁾ and the carbanion has the absorption peak at 485 nm in 1,2-dimethoxyethane¹¹⁾. As any supporting electrolyte such as lithium perchlorate was not used in this experiment, potential differences between reduction peak and oxidation peak were not 60 mV and peak height of O_1 and R_1 were not equal to those of O_2 and R_2 ; potential differences of reduction and oxidation peaks were observed to be 0.4-0.7 V because of ohmic drop by high resistance in solution. The peak height of O_1 corresponding to the oxidation of the anion radical was higher than the peak height of O_2 , because the anion radical migrates toward the working electrode but the dianion which forms an ion pair $\text{M}^{=}\text{2Li}^+$ ¹²⁾ does not.

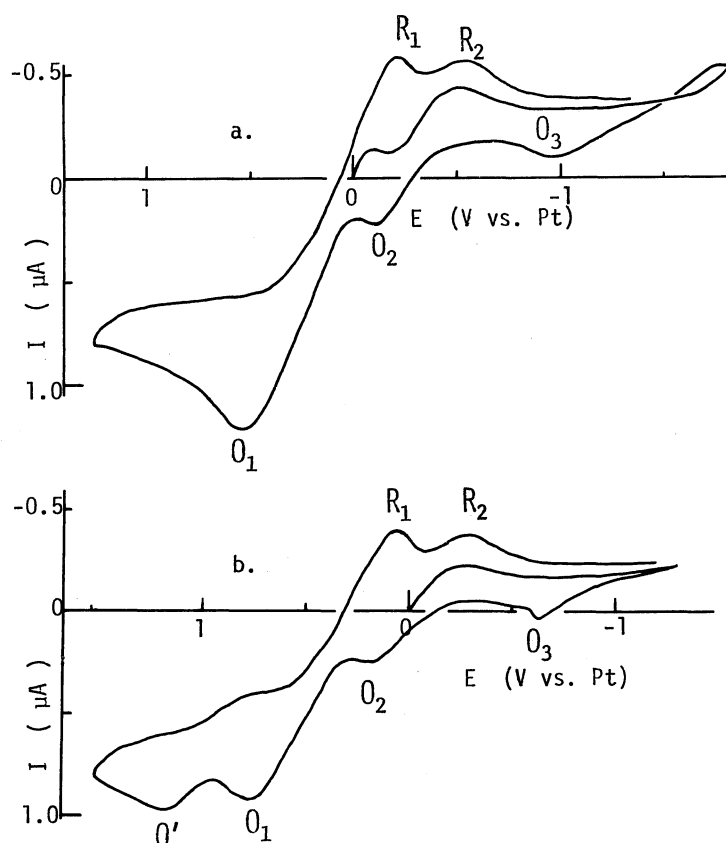
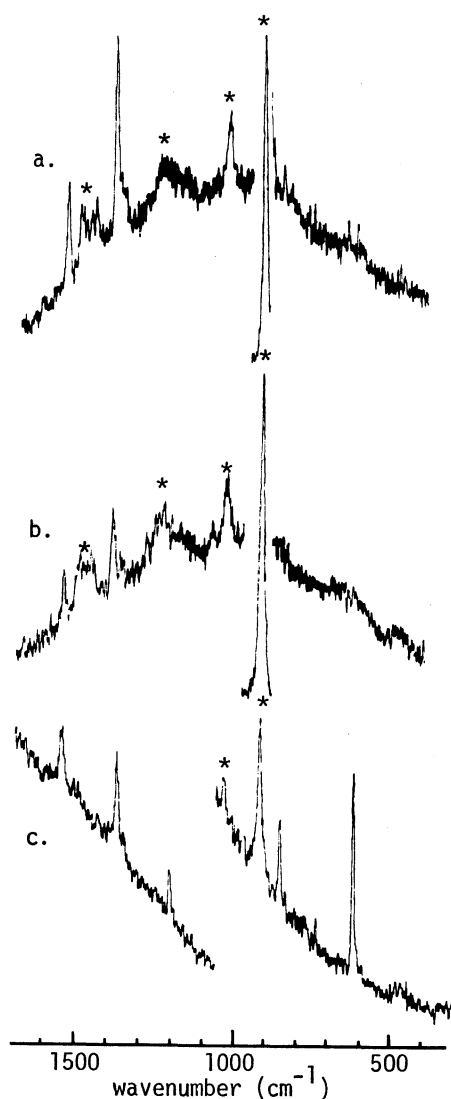


Fig. 1 Sweep voltammograms at a scan rate of 20 mV/sec
 a. before electrolysis.
 b. after electrolysis. Parent molecule was not present

Fig. 2 Resonance Raman spectra of electrolysis solution.
 a. before electrolysis.
 b. in the anode compartment after electrolysis.
 c. in the cathode compartment after electrolysis.
 * solvent peaks



With the similar reason the peak height of R_2 corresponding to reduction of the anion radical was lower than the peak height of R_1 because the anion radical generated at peak R_1 migrates far from the working electrode.

The resonance Raman scattering peaks of the anion radical are observed in figs. 2a and 2b at 1387 and 1535 cm^{-1} . The scattering peaks from the dianion are observed in fig. 2c at 618, 848, 1200, 1369 and 1543 cm^{-1} . As the resonance Raman scattering from the naphthacene anion radical was weaker than the scattering from the dianion, the scattering peaks of the anion radical were hindered by the peaks of the dianion and a background emission as shown in fig. 2c. The naphthacene carbanion would show no resonance effect because it has no absorption at 632.8 nm. When the laser beam was arranged to pass through the cell within 1 mm from the cathode and the laser beam intensity was decreased by 1/100 with a neutral density filter, the dianion concentration was observed to be higher than the bulk concentration. The dianion concentration was calculated from the ratio of the Raman scattering peak height at

848 cm^{-1} of the dianion against the solvent peak height at 914 cm^{-1} . Thus a self absorption effect was prevented, as the both peaks appear closely. With no neutral density filter the dianion concentration near the cathode was the same as the bulk concentration, where the convection of the dianion occurred by thermal effect because of absorption of the laser light.

When the solution containing only anion radical was electrolyzed, quantitative amounts of the parent molecule and the dianion vs. electricity passed should be generated at the anode and the cathode, however the concentration of the dianion observed was rather small because of its protonation. During the electrolysis the rate of decrease of the reactant, the anion radical, was more in the cathode compartment against the value estimated from the current passed, and that was less in the anode compartment. The above phenomena were explained by assuming the transfer of the anion radical and the lithium cation because of passage of current. The transport number of the anion radical was estimated at about 0.3.

Conclusion

The naphthacene dianion generated by electroreduction was detected by the resonance Raman and visible absorption spectroscopies. From the results obtained by the former method the dianion concentration near the cathode was higher than the bulk concentration. Interesting sweep voltammograms were shown in the solution without any supporting electrolyte. A transport number of the anion radical was estimated at about 0.3 in THF when the counter ion was lithium cation.

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