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Dissociative Electron Capture of Diazoquinones: Matrix Isolation ESR Study

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Abstract: It is postulated that the electron beam exposure process of the AZ-type resists (those containing diazoquinones as the labile component) is initiated by dissociative electron capture producing a phenoxy radical anion and N_2. Na atoms and model diazoquinone molecules, 1-oxo-2-diazonaphthoquinone, 2-oxo-1-diazonaphthoquinone, and *o*-diazobenzoquinone, were cocondensed in argon matrices, and the Na-to-diazoquinone electron transfer was induced by mild radiation ($\lambda > 580$ nm). ESR examination of the matrices revealed that the three diazoquinones all readily captured low-energy electrons and dissociated to yield the respective phenoxy anion radicals resulting from N_2 cleavage as postulated.

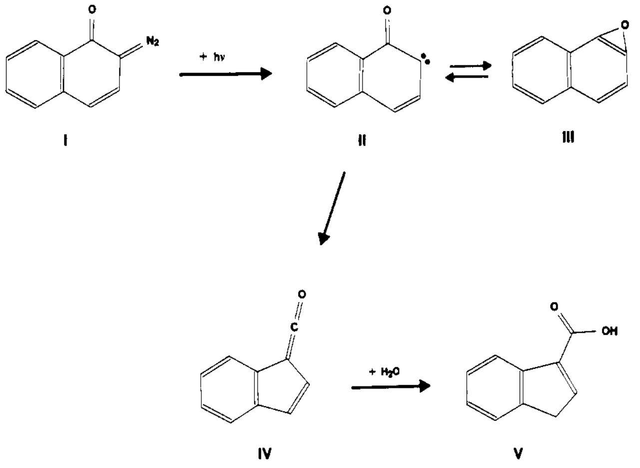
Introduction

The AZ-type photoresists are widely used as the positive imaging layer in semiconductor microlithography.[1] They are typically composed of matrix resin, phenol/formaldehyde copolymer, and photolabile components, substituted diazonaphthoquinones. The photoactivation process of diazoquinones has been studied by photoproduct analysis in solution,[2,3] by trapping reactive intermediates in the solid state at low temperatures,[3–6] and by nanosecond flash photolysis.[7,8] The reaction sequence involving Wolff rearrangement (Scheme I) has been established. Near-UV radiation (300–450 nm) is commonly used for the exposure, and in this wavelength range, the diazoquinone component is the only chromophore.

The AZ-type photoresists are also used in electron beam and X-ray lithography.[9] The mechanistic study of the process under these more energetic radiations has not been as extensive. It has been surmised that the electron beam process would be much less efficient energetically compared to the optical process as the energy of the electron beam is dissipated throughout the material. However, Broyde reported earlier that, when measured in terms of the solubility of the exposed resists, the electron beam process of AZ-type resists consumed much less energy in comparison to the optical process.[10]

Kaplan and Meyerhofer then measured spectroscopically (UV) the sensitivity of the AZ-type resists upon optical and electron beam exposure.[11] They determined the quantum yield of 0.3 ± 0.03 for the optical process, corresponding to 10.4 eV per reacted diazoquinone molecule. For electron beam exposure, it was shown that the beam energy of 13 eV was consumed per reacted molecule in pure diazoquinone, but only ~7 eV in the actual resist formulation if the correction was made for the weight fraction of the labile component. Energy transfer from the resin component was thus strongly indicated.

Scheme I



Pacansky et al. demonstrated that the ketene (IV) was indeed formed not only in photoexposure but also in electron beam exposure of the AZ-type resists.[12] They suggested, as the possible mechanism in the electron beam process, (1) direct activation of neutral diazoquinone to the relevant excited state by electron impact, or (2) ionization of diazoquinone followed by recombination (with an electron), reaching the relevant excited state of the neutral species.

The solubility rate for resist formulations increases with both increasing dose and percent consumption of sensitizer in photoexposure, as expected. In electron beam exposure at higher dose and percent sensitizer consumption, the solubility rate reaches a maximum and then starts to decrease.[10,11] This difference is most likely due to cross-linking of matrix resin that occurs in electron beam exposure.

When a beam of high-energy electrons traverses through a material, a swarm of thermal energy electrons are generated through cascading ionization processes. When the energy of the primary beam is ~10 keV, for example, the total number of secondary electrons produced is estimated to be 10^3 times that of the primary electrons.[13] Resists of the epoxylated poly(meth)-acrylate type and the poly(butene sulfone) type have been especially developed as high-sensitivity electron beam resists.[14,15]

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(1) See, for example: Thomson, L. F.; Willson, C. G.; Bowden, M. J. S. *Introduction to Microlithography*; American Chemical Society: Washington, DC, 1984.

(2) Süs, O. *Justus Liebigs Ann. Chem.* **1944**, *556*, 65.

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(6) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 725.

(7) Tanigaki, K.; Ebbesen, T. W. *J. Phys. Chem.* **1989**, *93*, 4531.

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(9) See, for example: Moreau, W. M. *Semiconductor Lithography*; Plenum Press: New York, 1986.

(10) Broyde, B. *J. Electrochem. Soc.* **1970**, *117*, 1555.

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(12) Pacansky, J.; Coufal, H. *J. Am. Chem. Soc.* **1980**, *102*, 410.

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(14) Thompson, L. F.; Feit, E. D.; Heidenreich, R. D. *Polym. Eng. Sci.* **1974**, *14*, 529.

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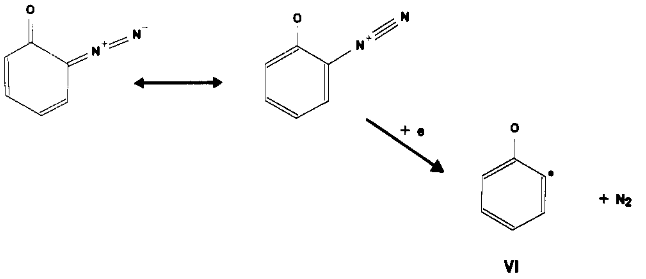
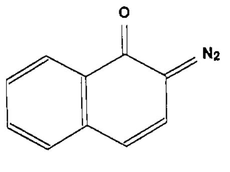
Scheme II



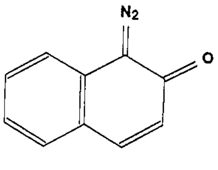
We have shown recently that the high electron beam sensitivity of these resists is due to dissociative electron capture by the electrophilic sectors, the epoxy ring, and the sulfone moiety, respectively.[16,17]

We surmised, on the basis of the valence bond structures of diazoquinone, that the electron beam exposure process of the AZ-type resists might also be that initiated by dissociative electron capture (see Scheme II). The phenoxy anion radical VI, upon recombination with a positive hole, would change to the oxo carbene (as II in Scheme I) and undergo Wolff rearrangement, or it may react with the polymer matrix without rearrangement.

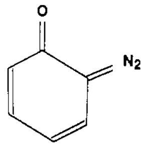
To characterize the initial chemical reaction of these sensitizers in the electron beam process, we have examined, using the matrix isolation ESR technique, the consequence of electron capture by diazoquinone molecules. We report here the results of that study. The following three diazoquinones were examined: 1-oxo-2-diazonaphthoquinone (2-DANQ), 2-oxo-1-diazonaphthoquinone (1-DANQ), and *o*-diazobenzoquinone (*o*-DABQ). The study revealed that the three diazoquinones examined all readily captured low-energy electrons and dissociated to yield the respective anion radicals resulting from N_2 cleavage.



2-DANQ



1-DANQ



o-DABQ

Experimental Section

The technique of cocondensing Na atoms and molecules of some electron affinity in an argon matrix at ~4 K, and effecting an electron transfer by mild radiation (580 nm), was described some years ago.[18] The resulting anions are isolated from the Na cations and are usually unaffected by the ensuing radiation. In the present series of experiments, diazoquinone molecules were sublimed from a glass vessel heated to 80–100 °C and were trapped in argon matrices together with Na atoms vaporized from a resistively heated stainless steel tube (250 °C). Extra care was required for sublimation of diazoquinones as they all began to decompose at a temperature where their vapor pressure was sufficient for deposition (>1 mm).

The ESR spectrometer used was an X-band system (IBM Instruments, Model 200D). All the spectra were observed while the matrices were maintained at ~4 K, and the frequency of the system locked to the loaded sample cavity was 9.420 GHz. For photoirradiation of the argon matrices, a light beam from a high-pressure xenon–mercury lamp (Oriel, 1 kW) was passed through a water filter and a broad-band interference filter (600 ± 50 nm) and was focused on the cold finger 40 cm away.

2-DANQ was synthesized as follows: A suspension of 4-toluenesulfonylhydrazine (1.86 g) in dichloromethane (30 mL) was added to a stirred solution of 1,2-naphthoquinone (1.58 g) in dichloromethane (30 mL), cooled in an ice bath, and protected from light. After 5 h the solution was purified on an alumina column (Brockman activity III) while protected from light. The yellow fraction was collected and evaporated to leave a red oil, 1.6 g, which solidified. Recrystallization from hexanes gave orange crystals, mp 75-77 °C (lit.[19] mp 77 °C), which were stored in a refrigerator.

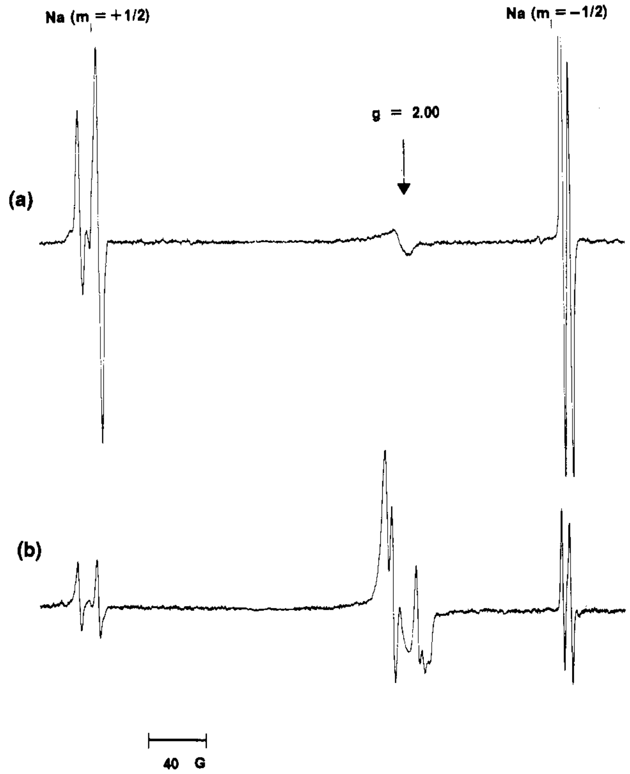


Figure 1. (a) ESR spectrum of an argon matrix containing Na atoms and 2-DANQ molecules observed as prepared. The section encompassing the inner two components of the Na quartet is shown. (b) The spectrum of the same matrix observed after irradiation with yellow light (λ = 600 ± 50 nm) for 8 min. The Na atom signals ($m_I = \pm^1/_2$) are split by the multiple trapping site effect.

1-DANQ and *o*-DABQ were prepared according to the literature procedures.[19,20]

Results and Discussion

The ESR spectrum of an argon matrix in which 2-DANQ and Na atoms were cocondensed, observed prior to photoirradiation, was dominated by the signals due to isolated Na atoms ($3s^1$). The Na atom signals comprised a sharp, widely spaced quartet due to the isotropic hfc (hyperfine coupling) interaction with the ^{23}Na nucleus ($I = ^3/_2, A = 330$ G).[21] The individual components are often split further by a multiple trapping site effect.

Figure 1a shows the central section of that spectrum encompassing the inner two components of the Na quartet. A weak, broad signal noted at the region corresponding to $g = 2.00$ is attributed to some inadvertently formed thermal decomposition product of 2-DANQ. Figure 1b shows the spectrum of the same matrix (the same section) observed after it had been irradiated with "yellow" light (λ = 600 ± 50 nm) for 8 min. A conspicuous decrease of the Na signals and the appearance of a new, complex pattern at $g = 2.00$ are ascribed to the photoinduced electron transfer from Na atoms to diazoquinone molecules. The ESR spectrum thus seen at $g = 2.00$ after photoexposure is shown expanded in Figure 2a.

Similar results were obtained from argon matrices containing Na and 1-DANQ and those containing Na and *o*-DABQ. The representative spectra (of the $g = 2.00$ section) of these matrices

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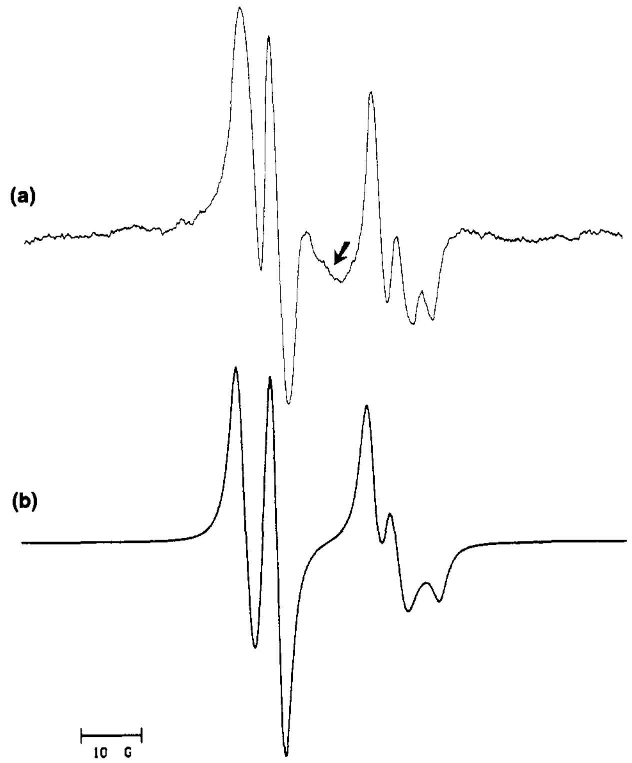

Figure 2. (a) ESR spectrum photoinduced in an argon matrix containing Na atoms and 2-DANQ molecules. The broad signal indicated by the arrow is due to thermal decomposition product(s). (b) ESR spectrum of radical VII simulated on the basis of the **g** tensor and the ortho- and meta-proton hfc tensors of the phenyl radical.

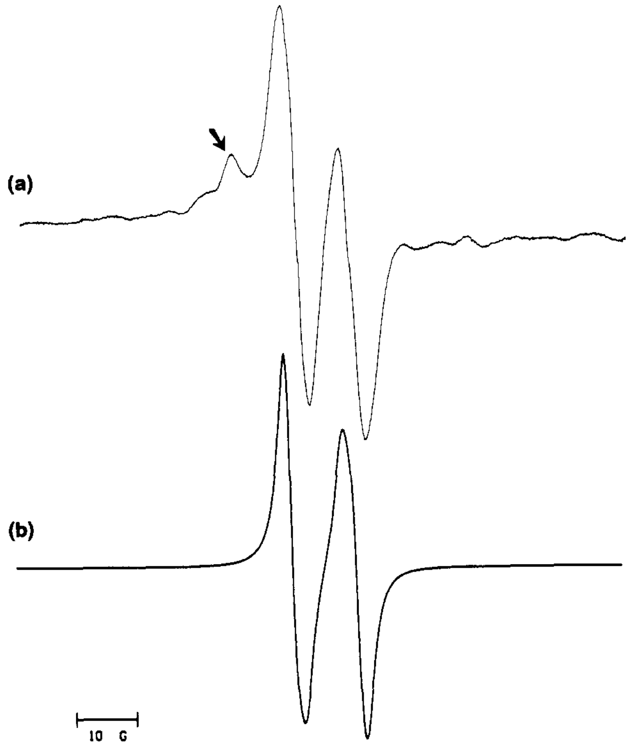

Figure 3. (a) ESR spectrum photoinduced in an argon matrix containing Na atoms and 1-DANQ molecules. The broad signal indicated by the arrow is due to thermal decomposition product(s). (b) ESR spectrum of radical VIII simulated on the basis of the **g** tensor and the meta-proton hfc tensor of the phenyl radical.

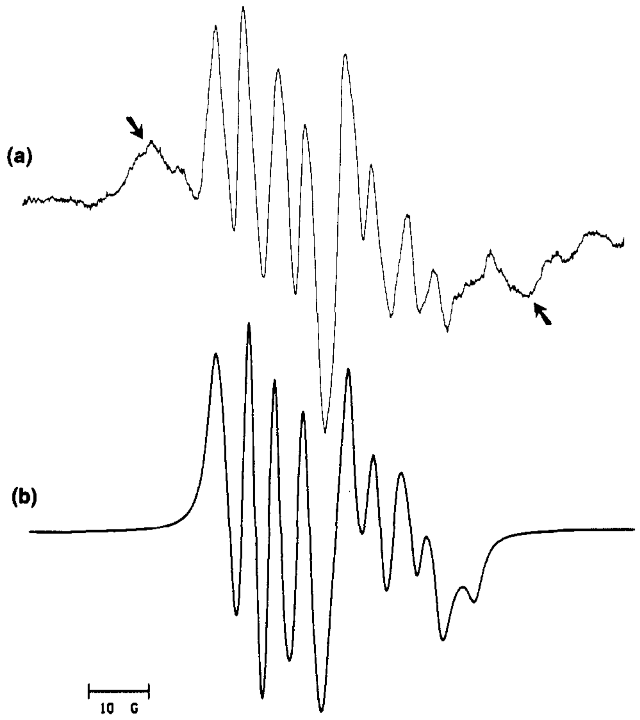

Figure 4. (a) ESR spectrum photoinduced in an argon matrix containing Na atoms and *o*-DABQ molecules. The broad signals indicated by arrows are due to thermal decomposition product(s). (b) ESR spectrum of radical VI simulated on the basis of the **g** tensor and the ortho- and meta-proton hfc tensors of the phenyl radical.

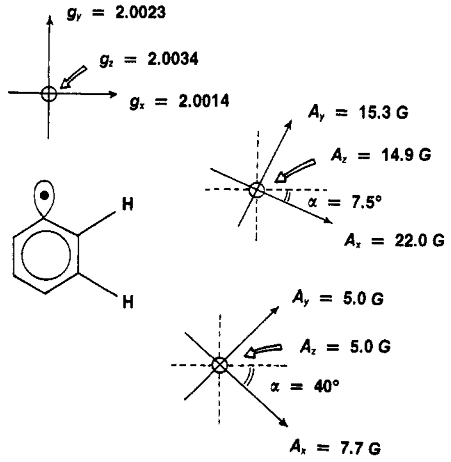

Figure 5. The **g** tensor and the ortho- and meta-proton hfc tensors of the phenyl radical (from ref 22).

observed after photoirradiation are shown in Figures 3a and 4a, respectively. In these traces the broad signals indicated by arrows are related to thermal decomposition product(s) of diazoquinones; their intensity relative to the sharp pattern (originating from electron capture by parent molecules) increased with increasing temperature of sublimation.

The phenoxy anion radical VI postulated in Scheme II may simply be considered an ortho-substituted phenyl radical. The ESR spectrum of phenyl radical generated in argon matrices has been thoroughly analyzed.[22] The phenyl radical is a σ radical, and its spin density is localized mostly in the nonbonding C_1 σ orbital. Its **g** tensor and the hfc tensors of the ortho- and meta-protons have been determined as shown in Figure 5. The salient features of the ESR powder pattern of the phenyl radical are thus determined by the anisotropy of the **g** tensor, the axially anisotropic hfc tensors of the ortho- and meta-protons, and their orientations relative to the **g** tensor. We hence simulated the ESR pattern of the postulated phenoxy anion radical VI, and also those of VII

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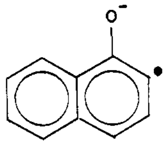
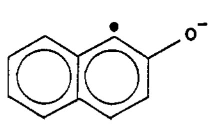
Table I. **g** Tensors and the Proton Hyperfine Coupling Tensors Used for Simulation of Radicals VII, VIII, and VI Generated from Diazoquinones

		2-DANQ, VII	1-DANQ, VIII	*o*-DABQ, VI
g tensor	g_x	2.0014	2.0014	2.0014
	g_y	2.0023	2.0023	2.0023
	g_z	2.0034	2.0034	2.0034
ortho-proton	A_x	26.6		26.6
	A_y	19.7		19.7
	A_z	19.7		19.7
	α	7.5°		7.5°
meta-proton	A_x		12.0	11.0
	A_y		9.0	8.0
(adjacent to O^-)	A_z		9.0	8.0
	α		60°	50°
meta-proton	A_x	7.0		6.0
	A_y	4.0		4.0
	A_z	4.0		4.0
	α	30°		30°

and VIII based on the **g** tensor and the ortho- and meta-proton hfc tensors of the phenyl radical. Figures 2b, 3b, and 4b are the spectra thus produced. In the simulation process, the isotropic components of the hfc tensors and the orientations of the meta-proton hfc tensors were adjusted (slightly) for the best fit. The spin Hamiltonian parameters thus chosen for the simulation are given in Table I. There is good agreement between the observed and simulated spectra for the three anion radicals.



VII

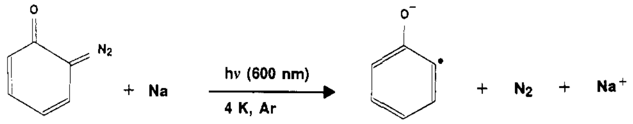


VIII

The SOMO (semioccupied molecular orbital) of the phenoxide radical VI should be very similar to that of the 2-hydroxyphenyl radical. The ESR spectrum of 2-hydroxyphenyl radical generated in argon matrices was also examined earlier.[23] The broad signals allowed determination of only the isotropic coupling constants of the ortho and meta protons; the assessed values were A(6-H) = 20 G, A(3-H) = 10 G, and A(5-H) = 5 G. Thus, the ortho-proton coupling constant of 2-hydroxyphenyl radical is slightly larger than that of the unsubstituted phenyl radical, and while the coupling constant of the meta-proton adjacent to the hydroxy group is larger than that of the phenyl radical, the coupling constant of the other meta-proton is smaller. These trends are replicated exactly in the hfc tensors of radical VI (given in Table I) and also in the hfc tensors of the corresponding protons of radicals VII and VIII.

The spectral results and the analyses presented above clearly demonstrate that diazoquinone molecules readily capture low-energy electrons and spontaneously yield the phenoxy anion radical (Scheme III) resulting from N_2 cleavage.

Scheme III



To gain further insight into the process, we examined the molecular orbitals of *o*-DABQ by EHT (the extended Hückel theory).[24] The EHT calculations of benzene and naphthalene yield the LUMO (the lowest unoccupied molecular orbital) of these molecules at −8.3 and −9.3 eV, respectively. For *o*-DABQ, the theory placed the LUMO at −10.5 eV and showed that it was very much localized at the N–N sector (60%) and correlated to the antibonding π orbital of the N_2 molecule. The electronegativity of oxygen must make the nitrogen sector of diazoquinone a strong electrophile, as inferred qualitatively by the valence bond structures shown in Scheme II.

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