bilization energy (11 kcal mol⁻¹) is obtained for an in-plane bridging configuration where the water molecule is a double proton donor at N_7 and O_6 (I). The calculations of Del Bene,²⁰ however,



have shown that the most stable complex is a wobble dimer in the N_1H and O_6 region with a stabilization energy of -10.7 kcal mol⁻¹, the configuration at N_7 and O_6 having an energy of only -6.8 kcal mol⁻¹.

The structure of Pullman is difficult to prove by infrared spectroscopy. The wavenumbers of the ν_{OH} complex bands are typical for OH---O=C and OH---N hydrogen bonds. Owing to

the cooperative effect operating in a hydrogen bond, the frequencies of the two ν_{OH} bands should be somewhat higher (lower shifts) when water acts as a double-proton donor.²¹ It can also be anticipated that the two complex bands should have about the same intensity. It appears from Figure 1 that the intensity of the high-frequency band is higher than the second one. As a consequence, a mixture of complexes having the structure II and III, with a greater participation of II, seems more likely in solution. With the phenol derivatives, however, the concentration of complexes having structure III seems to be higher, and this is suggested by the higher intensity of the second complex band (Figure 2). The complexes between TMG and the proton donors studied in this work are characterized by normal OH…O and OH…N hydrogen bonds. With stronger acid (HCl, HBr), guanine is protonated at the N₂ atom.²²

Registry No. TMG, 93739-36-7; H₂O, 7732-18-5; 4-bromophenol, 106-41-2; 3,4-dichlorophenol, 95-77-2; phenol, 108-95-2; 3-bromophenol, 591-20-8; 3,5-dichlorophenol, 519-35-5; 3,4,5-trichlorophenol, 609-19-8.

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Solid-State Electron Beam Chemistry of Mixtures of Diazoketones in Phenolic Resins: AZ Resists

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Equimolar mixtures of a 2-diazo-1-naphthaquinone and a phenolic resin are exposed to a 25-kV electron beam and UV light. The mechanism for the photochemistry is explained on the basis of the well-known Wolff rearrangement. The electron beam exposure, however, does not appear to proceed via the Wolff rearrangement but instead invokes reactions of a carbene with the phenolic resin. The carbene, formed by loss of N_2 from the diazoketone, forms chemical products with the resin which are soluble in base. In essence, this explains the functioning of a large class of electron beam resists consisting of diazoketone/resin mixtures. Electron beam exposures are also performed on mixtures of 2-diazo-1-naphthaquinone in *m*-cresol or in benzene; the results of these experiments suggest that a major product of the electron beam induced chemistry is a substituted naphthol.

Introduction

Since the pioneering work by Süs¹ formulations consisting of diazoketones in phenolic resins have been widely used by the electronics industry to produce microlithographic patterns. These materials, commonly called resists, are formulated by incorporation of a diazoketone, structurally similar to 1, in a phenolic resin like 2 (see Figure 1). The function of the diazoketone is twofold: first it acts as a solvent inhibitor by reducing the solubility of the resin toward an aqueous, inorganic base developer, like KOH; second, it serves as a photoactive compound which upon absorption of radiation converts to a base soluble material. The latter function was investigated in detail³ where it was shown that 1, when exposed to UV light, converts to a ketene intermediate 4, which, in the presence of moisture, reacts with water to form the carboxylic acid 3 (see Figure 2). Since the latter species is soluble in the basic developer this led to the reasonable conclusion that the photochemical formation of the carboxylic acid was the mechanism responsible for the positive working nature of the resist; i.e., areas exposed to light are rendered more soluble than the nonexposed areas. These observations are summarized in Figure 2.

(3) Pacansky, J.; Lyerla, J. R. IBM J. Res. Dev. 1979, 23, 42.

The fact that the particular ketene intermediate 4 did not react with the acidic -OH groups of the resin 2, when exposures were carried out in air (at least to the detectability of infrared measurements), was quite unexpected. In order to explore an explanation for this observation, experiments were conducted under conditions of high vacuum; these experiments not only showed that the ester 5 of the carboxylic acid 3 was formed but also revealed that the reaction proceeded through a ketene intermediate.⁴ In effect, after the ketene is formed it may partition itself along two reaction paths, depending on rates, i.e., with the -OH groups of water or the resin. The fact that the rate for the ketene-water reaction is much faster than the rate for the ketene-resin led to the conclusion that the solid state may have hindered the latter reaction; the ketene-resin reaction requires a significant amount of molecular movement, and the solid state may constrain this motion to decrease its rate. On the other hand, permeation of the atmosphere into the polymeric resist or water hydrogen bonded to the phenolic OH groups of the hydroscopic resin, cannot be excluded as major factors which facilitate the ketene-water reaction.

Formulations based on mixtures of diazoketones and phenolic resins are not only used as positive photoresists but are also used as positive electron beam resists where now the *electron beam*

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⁽²⁾ Elliot, D. J. Integrated Circuit Fabrication; McGray-Hill: New York, 1982.

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Figure 1. Structures of diazoketone 1 and phenolic resin 2.



Figure 2. Summary of UV-induced photochemical pathways for 1 in 2.

exposure is performed within a vacuum system. In this case, if the solid-state electron beam chemistry parallels the solid-state photochemistry, it is difficult to rationalize the positive working nature of the resist. That is, if UV excitation and electron beam excitation of the diazoketone lead to formation of a ketene via the Wolff rearrangement within a vacuum system (Figure 2), one would anticipate that, in each case, a relatively insoluble (to KOH developer) carboxylic acid ester is produced. In view of this, when used for electron beam exposures the resist would probably be at best a poor negative one.

In a preliminary communication,⁵ the results for electron beam exposure of a diazoketone at T = 10 K were presented. The electron beam irradiation produced the ketene which was relatively insensitive to further exposure. Hence, as a result of these studies it is logical to conclude that the next step is the reaction of the electron beam generated ketene with the phenolic resin to produce a carboxylic acid ester. However, as shown in this report, when



Figure 3. The UV exposure of a thin film consisting of an equimolar mixture of diazoketone 1 in phenolic resin 2. The exposure was conducted in the presence of air at room temperature, before exposure (--) after UV exposure (--) to a 150-W high-pressure Xe lamp fitted with a 10-cm water filter and a Corning 0-53 glass filter. The time of exposure was 11 min.



Figure 4. The infrared spectra of a thin film consisting of an equimolar mixture of diazoketone 1 and resin 2 (a) before exposure and (b) after exposure to UV light emitted from a 150-W high-pressure Xe lamp fitted with a 10-cm water filter and a Corning 0-53 glass filter. The time of exposure was 18 min. The sample temperature was maintained at 10 K during the exposure and while spectra were being recorded.

the irradiation is performed at room temperature, the carboxylic acid ester is not produced and the mechanism for the electron beam exposure is quite different from the UV photochemical path.

Results and Discussion

The photochemistry encountered in diazoketone/resin formulations has been reported.³ However, in order to unravel the chemical events which commence as a result of electron beam irradiation a number of experiments using electrons and photons will be presented in parallel. That is, under identical conditions, a sample of the same material is exposed to UV light or electron beams. Infrared spectroscopy is used to follow the course of each radiation induced reaction because the characteristic vibrations of functional groups are easily identifiable.

UV Exposure in Air. An equimolar mixture of diazoketone 1 and resin 2 was exposed to UV light in the presence of air at room temperature. In figure 3, infrared spectra are shown for the mixture before (dashed line) and after exposure (solid line). The salient features in both spectra are the disappearance of the absorption at $\sim 2150 \text{ cm}^{-1}$ due to the stretching motions of the diazo group and the appearance of an absorption centered at $\sim 1710 \text{ cm}^{-1}$. This latter band is due to the stretching frequency of the carboxyl groups in the 1-indenecarboxylic acid.³ Hence, upon absorption of UV light in the presence of water vapor in air, a major reaction path for the diazoketone is to convert to the 1-indenecarboxylic acid.³ This has been studied previously³ and is included in this study to provide a basis for comparison with spectra taken after electron beam irradiation.

UV and Electron Beam Exposure of Diazoketone/Resin Mixtures at T = 10 K. The infrared spectrum of an equilmolar mixture of diazoketone 1 and resin 2, recorded at T = 10 K, is shown in Figure 4a. UV exposure of the sample, at T = 10 K, transforms the diazoketone to a ketene as witnessed by the infrared absorption of the C=C=O stretching motion centered at ~2130 cm⁻¹. The infrared spectrum of the sample (recorded at T = 10 K) after UV exposure is contained in Figure 4b.

⁽⁵⁾ Pacansky, J.; Coufal, H. J. Am. Chem. Soc. 1980, 102, 410.



Figure 5. The infrared spectra of a thin film (thickness = 5.2 μ m) consisting of an equimolar mixture of diazoketone 1 and resin 2: (a) before exposure; after exposure to a 25-kV electron beam, incident current density $\simeq 1 \text{ nA/cm}^2$; (b) incident charge density $Q = 40 \ \mu$ C/cm², and (c) incident charge density $Q = 100 \ \mu$ C/cm². The sample temperature was maintained at 10 K while the spectra were being recorded and during the irradiation.

The results obtained by using a 25-kV electron beam as the radiation source are shown in Figure 5. Part a is the low-temperature infrared spectrum of the equimolar diazoketone/resin mixture before exposure while parts b and c are the spectra recorded after receiving incident charge densities of 40 and 100 μ C/cm², respectively. The characteristic infrared absorption of the ketene C=C=O stretching frequency at ~2130 cm⁻¹ is clearly evident in the spectrum shown in Figure 5c. Consequently, at this low temperature, T = 10 K, electron beam exposure of the diazoketone produces a ketene,⁵ but as discussed below, the reaction path for the electron beam chemistry is not the same one taken for the photochemistry. It is pertinent to add that the intensity of the 2130-cm⁻¹ band synchronously decreases with the growth of the band due to the carbonyl stretching frequency of the ester 3 when both the UV and electron beam irradiated samples are warmed to room temperature, respectively.

UV and Electron Beam Exposure of Neat Diazoketones 1 at T = 10 K. An estimate for the yield of the ketene produced by electron beam exposure at T = 10 K, relative to the yield for the ketene produced photochemically, was obtained spectroscopically. In Figure 6a, b low-temperature infrared spectra are recorded for 1 before and after UV exposure. The ratio of the optical densities for the characteristic diazo (Figure 6a) and ketene absorptions (Figure 6b) is 1:2. In figure 7, four spectra are shown for the electron beam exposure; part a is the diazo absorption before exposure, and part c is the spectrum recorded after the sample was exposed to an incident charge density of $150 \,\mu\text{C/cm}^2$. The ratio of the optical densities for the diazo and ketene absorptions in this case is 1:0.7. Consequently, the ketene yield via electron beam excitation drops by a factor of three. We were able to rule out the possibility that the electron beam was decomposing the



Figure 6. The infrared spectra of a sample of diazoketone 1 used to measure the ratio of ketene to diazoketone: (a) before exposure, (b) after UV exposure to a 150-W high-pressure Xe lamp fitted with a 10 cm water filter and Corning glass filters 0-53 and 0-73. The time of exposure was ≈ 10 min. The irradiation and recording of spectra were performed with the sample at T = 10 K.



Figure 7. The infrared spectra of a thin film (thickness = 0.45 μ m) of diazoketone 1: (a) before exposure, (b) after exposure, $Q = 40 \ \mu$ C/cm², (c) $Q = 150 \ \mu$ C/cm², (d) $Q = 250 \ \mu$ C/cm². The accelerating voltage was 25 kV and the incident current density was $\simeq 1 \ n$ A/cm². The irradiation and recording of spectra were performed with the sample at $T = 10 \ \text{K}$.

ketene after it was formed from the diazoketone. For example, as shown in Figure 7, c and d, a slight decrease in the ketene absorption results when the sample is exposed to an additional incident charge density of $100 \ \mu C/cm^2$. Because the diazoketone 1 is totally destroyed by the electron beam after administering $\sim 80 \ \mu C/cm^2$, it is apparent that the very small amount of electron beam induced decomposition of the ketene cannot explain the lower yield.

UV and Electron Beam Exposures in a Vacuum at Room Temperature. An equimolar mixture of diazoketone 1 and resin 2 was exposed to UV light at room temperature with the system contained in a high-vacuum system. The infrared spectra recorded before (solid line) and after (dashed line) irradation with UV light are shown in Figure 8. The spectral changes in the figure follow what has been previously observed; UV excitation of the diazoketone produces a ketene via a Wolff rearrangement,⁶ which



Figure 8. The infrared spectra of a thin film consisting of an equimolar mixture of diazoketone 1 and resin 2; all spectra recorded and exposures performed at room temperature with the sample under vacuum (10^{-7} mmHg) : (--) before UV exposure; (---) after exposure to a 150-W high-pressure Xe lamp fitted with a 10-cm water filter and a Corning 0-53 glass filter. The time of exposure was 10 min.



Figure 9. The infrared spectra of a thin film consisting of an equimolar mixture of diazoketone 1 and resin 2: all spectra recorded and exposures performed at room temperature with the sample under vacuum (10^{-7} mmHg) . The accelerating voltage was 25 kV, and the incident current density was $I \simeq 0.5 \text{ nA/cm}^2$: (a) before exposure, (b) after exposure $Q = 22 \ \mu\text{C/cm}^2$, (c) 33 $\mu\text{C/cm}^2$, (d) 70 $\mu\text{C/cm}^2$.

subsequently reacts with the phenolic OH groups of the resin to ultimately produce a carboxylic acid ester. The latter moiety, in phenolic resins, has a broad infrared absorption³ in the region $\sim 1730-1780$ cm⁻¹. One should also note that concomitant with the appearance of the ester absorption a decrease is observed in the region of the spectrum where -OH stretches are characteristically observed.

The infrared spectra recorded before and after electron beam exposure of the equimolar diazoketone 1-resin 2 sample are shown in Figure 9. The striking feature in Figure 9 is that the carbonyl absorption of the ester group appears to be completely absent in the spectrum of the electron beam irradiated material. Furthermore, the absorptions in the -OH stretching region shift to a higher frequency instead of exhibiting a decrease in optical density like in the spectrum for the UV exposure.

A plausible explanation for the dramatic differences in the ester carbonyl absorption is that the electron beam decomposes the ester after it is formed. The following experiment, designed to inves-



Figure 10. An N/N_0 versus incident charge density plot for the carboxylic acid ester 5. The ester 5 was produced by UV irradiation of a film consisting of an equimolar mixture of 1 and 2 under vacuum (10⁻⁶ mmHg) and at room temperature; this sample was subsequently exposed to a 25-kV electron beam. The incident current density was $I \simeq 1$ nA/cm².

tigate this, was performed. An equimolar mixture of diazoketone 1 and resin 2 was exposed to UV light under vacuum at room temperature; this produced the carboxylic acid ester as shown above in Figure 8. Subsequently, this sample was exposed to an electron beam under vacuum and the infrared spectrum of the sample was followed as a function of incident charge density. The results of this exposure, which are plotted in Figure 10, reveal that the ester is relatively insensitive to the electron beam within the range of incident charge densities used to decompose the diazoketone. For example, the slope of the N/N_0 versus Q plot in Figure 10 for the ester decomposition is $0.00028 \text{ cm}^2/\mu\text{C}$ while, as shown in Figure 11, the slopes for the neat diazoketone 1 and equimolar diazoketone 1 and resin 2 are 0.026 and $0.036 \text{ cm}^2/\mu\text{C}$, respectively.

A further note should be added at this point. There is a small absorption in the 1700-1750-cm⁻¹ region of the spectrum recorded after electron beam exposure. This absorption, however, is due to a secondary product and not to the carboxylic acid ester. Evidence to support this is given by comparison of parts c and d of Figure 9.

Summary of the under-Vacuum Electron Beam Exposure of the Diazoketone/Resin System. The photochemical Wolff rearrangement is the mechanism by which a diazoketone after excitation loses N_2 and converts to a ketene. All of this occurs on a reaction path that presumably does not have a minimum between the diazoketone and ketene. As shown in Figure 2, reasonable evidence for the ketene is in fact the two trapping experiments, i.e., in air, the thermal reaction of the ketene with water to form the indene carboxylic acid and, under vacuum, the thermal reaction with phenolic -OH groups to form the carboxylic acid ester.

For the case of the vacuum electron beam exposures we have two observations that apparently lead to a paradox. The first is electron beam exposure produces a ketene but with a much lower yield at low temperatures. The second is that the carboxylic acid ester does not appear to be formed when the vacuum electron beam exposures are performed at room temperature.

⁽⁶⁾ Wölff, W. Justus Liebigs Ann. Chem. 1912, 394, 25.



Figure 11. An N/N_0 versus incident charge density plot for a film (Δ) of neat diazoketone 1 and a film (\odot) consisting of an equimolar mixture of 1 and 2. The irradiation was performed under vacuum (10⁻⁶ mmHg) and at room temperature. The accelerating voltage of the electron beam was 25 kV, and the incident current density $I \simeq 1 \text{ nA/cm}^2$.

If the ketene was produced via Wolff rearrangement at low temperature then the carboxylic acid ester should certainly form as a result of the room temperature exposure. In view of this we conclude that the mechanism for the vacuum electron beam exposure does not involve a Wolff rearrangement. Instead we propose that a carbene formed by loss of N2 from the diazoketone plays a central role in the chemistry that ensues after electron beam exposure. The proposed mechanism for the electron beam induced chemistry discussed thus far is summarized in Figure 12. Electron beam exposure at low temperatures produces a carbene 6, which upon further electron beam excitation rearranges to a ketene. The carbene 6 may exist for relatively long periods of time at T = 10 K because of the frozen, immobile environment at this temperature. In effect, this dramatically retards carbene reactions with the resin and opens a channel for further excitation of the carbene to ketene. At room temperature, however, the electron beam generated carbene rapidly reacts with the resin and hence has too short a lifetime for further excitation to ketene to be an issue.

As also shown in Figure 12, the net result of the reaction of the carbene with the resin is labeled "Products". In essence this part of the problem is perhaps the most important because it reveals why electron beam resists based on diazoketone/resin formulations are positive working and also elucidates the mechanism in Figure 12. Thus far, the most significant clue for the identity of the chemical products are the new infrared absorptions that appear in the -OH stretching region shown in Figure 9. A clear assignment of other new absorptions is difficult because they are obscured by the spectral features due to the resin. As a consequence, we have performed electron beam irradiations using mixtures of a simpler diazoketone with *m*-cressol or benzene. Of course, the ultimate goal is to identify all of the products; however, due to the technological importance of the reaction some spectroscopic analysis at this point in time is pertinent.

Electron Beam Exposures at Atmospheric Pressures of Nitrogen on the Diazoketone 7-m-Cresol (8) System. In order to simplify the system under consideration the parent diazoketone, 2-diazo-1-naphthaquinone, 7, was irradiated in the presence of



Figure 12. Summary of the chemistry and a proposed mechanism for the electron beam excitation of diazoketone 1 and resin 2.



Figure 13. The structures for diazoketone 7, *m*-cresol, 8, and, benzene, 9, used for the electron beam exposures at 175 kV and under 1 atm of dry nitrogen gas.

m-cresol 8 (see Figure 13 for structures). In addition, these samples and the diazoketone/benzene experiments reported below were irradiated by a 175-kV electron beam under a blanket of N2. Hence, quantities of material sufficient for chemical and spectroscopic analysis are produced (see the Experimental Section for more details). Equimolar mixtures of diazoketone 7 and m-cresol were exposed to the 175-kV electron beam and infrared spectra were recorded as a function of absorbed dose. Figure 14 contains spectra for D = 0, 90, 180, and 360 Mrad. The electron beam chemistry responsible for the spectral changes is a result of the transformation of the diazoketone to another chemical entity which subsequently reacts with the m-cresol. This conclusion results from the following observations: (1) exposure of *m*-cresol under identical conditions creates no detectable changes in its IR spectrum; and (2) changing the molar ratios of the diazoketone to m-cresol in the direction of higher dilution has no apparent effect on the IR recorded after irradiation.

The first important result gleaned from Figure 14 is that the 1-indenecarboxylic acid ester³ is not produced and as a consequence no evidence can be obtained here for a Wolff rearrangement to a ketene. We should add that, under identical conditions, the particular diazoketone 7 and *m*-cresol (8) were exposed to UV light and as expected the indene acid ester was rapidly and efficiently produced.

A new set of IR absorptions are formed as a result of the electron beam exposure. These have band centers at 3550, 3140, 1460, 1380, 1080, 1040, 810, and 780 cm⁻¹ and appear to be primary products of the irradiation; the most notable is the band



Figure 14. Infrared spectra of diazoketone 7 and *m*-cresol, 8, recorded as a function of absorbed dose in Mrad. The electron beam had a accelerating voltage of 175 kV and the exposure was performed under 1 atm of dry nitrogen gas.

in the -OH stretching region around 3500 cm⁻¹. Hence, in this case, and for all of the other systems studied in this report, we detect a primary product that contains an -OH group. This is more convincing for irradiations of diazoketone 7 and benzene (9).

Electron Beam Exposures at Atmospheric Pressures of Dry Nitrogen on Mixtures of the Diazoketone 7-Benzene (9) System. Mixtures of diazoketone 7 and benzene (9) were exposed to the 175-kV electron beam and infrared spectra recorded as a function of absorbed dose. Figure 15 contains spectra taken after D = 90, 180, and 300 Mrad were administered to the sample. In this case the spectral region where -OH groups characteristically absorb is not initially obscured and the increase in absorption in this region as a result of the electron beam induced chemistry is clearly evident. Furthermore, a number of the absorptions observed as a result of the electron beam exposure of the diazoketone 1 and resin 2 and diazoketone 7 and m-cresol (8) are in common with



Figure 15. Infrared spectra of diazoketone 7 and benzene, 9, recorded as a function of absorbed dose in Mrad. The electron beam had a accelerating voltage of 175 kV and the exposure was performed under 1 atm of dry nitrogen gas.

those observed for the benzene irradiations; in particular, these are the bands in the high-frequency region of the IR where OH and CH groups appear. The respective band centers for those common to all of the exposures studied herein are 3550, 3140, 1460, 1380, 1080, 1040, 810, and 780 cm⁻¹. Another broad absorption appears at $\simeq 1700$ cm⁻¹ but it is clearly due to a secondary product of the irradiation because the intensity of this band continues to increase with exposure after the diazoketones have been consumed by the radiation.

Summary of the Electron Beam Exposures of the Diazoketones 1 and 7. The experimental results reported herein reveal that electron beam excitation at room temperature does not proceed through a Wolff rearrangement. The major reaction path appears to mitigate an intermediate which reacts with aromatic CH bonds and perhaps aromatic CC bonds. The intermediate appears to also react with OH bonds; irradiations of mixtures of the diazoketones in *tert*-butyl alcohol⁷ are very similar to the resin, *m*-cresol, and benzene results presented above.

Our contention therefore, is that electron beam excitation of the diazoketones at room temperature produces a carbene which in the presence of benzene reacts with CH and CC bonds to ultimately produce substituted naphthols for example as outlined in Figure 16. At low temperatures, the carbene is confined by the rigid environment and when excited by another electron forms a ketene.

In summary, these results not only uncover a divergence between the excitation by photons and charged particulate radiation but also provide a rationale for the positive working nature of electron beam resists under diazoketones. The substituted naphthols produced by the electron beam induced chemistry are soluble in aqueous KOH developers and hence the exposed regions of the resists may be imaged by the high-energy electron beam.

Experimental Section

Materials: 2-Diazo-1-naphthoquinone (7). The starting material 2-nitro-1-naphthol (purchased from Aldrich Chemical) was converted to 2-amino-1-naphthol hydrochloride according to a

⁽⁷⁾ Pacansky, J.; Waltman, R. J., results to be published.



Figure 16. Tentative summary for a path responsible for formation of a major product when diazoketone 1 and *m*-cresol or benzene is exposed to a high-energy electron beam.

published procedure.⁸ Subsequently, the 2-amino-1-naphthol hydrochloride was converted to the diazoketone by using $NaNO_2$ and $CuSO_4$ in water. The 2-diazo-1-naphthoquinone obtained was purified by recrystallization from methanol.

Diazoketone 1. The starting material, sodium 2-diazo-1naphthaquinone-5-sulfonate (purchased from Fairmount Chemical Co., Newark, NJ) was converted to the sulfonyl chloride by using chlorosulfonic acid. The diazoketone was prepared by dissolving 2-diazo-1-naphthaquinone-5-sulfonyl chloride and 2,3,4-trihydroxybenzophenone in p-dioxane, adding a saturated solution of NaHCO₃, and stirring at room temperature for several hours. The resulting solid was washed with water and ethyl alcohol, filtered hot from acetone, and washed with diethyl ether and dried.

The phenolic resin 2 was purchased from Reinhold Chemical Co., New York, and was used without further purification. The *m*-cresol and benzene were obtained from Aldrich Chemical and purified according to standard chemical methods.

Film Preparation. Thin films of the neat diazoketones and equimolar mixtures of diazoketones with phenolic resin were prepared by first dissolving the respective components in diglyme and then casting a film onto a substrate by spin coating from the solution. Each film sample was placed in a vacuum oven at 50 °C for 2 h to remove solvent and anneal the films. Film thicknesses were measured with a Tencor Instruments Alpha-Step profilometer.

Sample substrates were prepared by vacuum depositing a layer of chromium, followed by >2 μ m of gold onto a 1-in.-diameter copper disk that was 3 mm thick. The chromium served as an adhesion layer for the gold. The substrates were mounted by bolting the disk to an OFHC copper block located at the end of the cold finger of a closed cycle refrigerator. Indium wire was placed between the disk and the copper block to ensure thermal and electrical contact with the sample substrate. A conducting substrate, for example, gold-plated copper, was always used to ensure that the sample was grounded and hence alleviate charging problems as a result of the electron beam exposure.

Photochemical Apparatus. The light source for the photolysis was an Eimac 150W high-pressure xenon lamp. The lamp was fitted with 10-cm water filter and Corning glass UV filters No. 0-53 (0% T at 260 nm) or No. 3-73 (0% T at 380 nm). The infrared spectra recorded after UV exposure appeared to be similar regardless of the Corning UV filter used in the lamp; only the time required to decompose the diazoketone changed.

Electron Beam Exposure Apparatus: Vacuum Studies. The course of the electron beam exposure was followed by constructing a chamber that would allow analysis of the electron beam induced reaction by specular infrared reflection spectroscopy.⁷⁻¹¹ The latter spectroscopic method was used because all of the samples



Figure 17. A description for the electron beam apparatus used for the vacuum electron beam exposures.

were exposed on conducting substrates to reduce charging problems. A schematic of the chamber and associated optics is shown in Figure 17. The chamber is constructed so that it may be attached to the sample chamber of a Perkin Elmer 621 infrared spectrometer, an electron beam gun, and an Air Products lowtemperature closed-cycle refrigerator. In this manner films may be irradiated at low temperatures and their infrared spectra recorded as a function of electron beam dose. The sample is coated on a gold-plated (vacuum deposited ~10 μ m thick) optically flat quartz or gold-plated copper disk. The infrared light from the source of the spectrometer was focused on the sample and subsequently refocused on the slits of the spectrometer by two mirrors such that the *f* number of the spectrometer was maintained and light losses were minimal.

The system was pumped down by using a Teflon-vane pump, liquid nitrogen sorption pumps, and a cryopump. The sample was cooled to 10 K by using an Air Products closed-cycle refrigerator.

The electron beam gun^{12} is pumped with two 20 L/s ion pumps and is capable of operating from 0 to 30 kV. The electron beam is focused with a magnetic lens, and positioned and raster scanned using a Celco dual ramp generator with a blanking amplifier. The path of the electron beam could be interrupted with an air-operated shutter downstream from the filament, or with a set of blanking plates.

The current in the electron beam was measured with a Faraday cup connected to a Keithly 480 picoammeter. The current measurement was made either by moving the Faraday cup into the path of the beam or by positioning the beam onto the Faraday cup. The electron beam gun was operated at a current density $\simeq 1 \text{ nA/cm}^2$ during the exposure. Current densities were measured by moving a Faraday cup into the electron beam. A Keithly picometer was used to read the charge collected in the Faraday cup.

Electron beam exposures within a vacuum system facilitate the measurement of the current density $I(A/cm^2)$ of the incident beam. The product of I and time t gives q, the incident charge density (C/cm^2) administered to a sample. Due to the relative ease with which q is measured many authors report the response of a system as a function of this value. In this report we also use incident charge density and in addition list the current density. The latter value is given so that our results may be compared with others using a different I to avoid confusion that may arise from a dose rate effect.

The incident charge density is used to determine Q, the charge density that the thin film experiences from the incident beam and

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⁽¹²⁾ Pacansky, J.; Waltman, R. J.; Maier, M. J. Phys. Chem. 1987, 91, 1225.



Figure 18. A description for the electron beam apparatus used for the electron beam exposures at atmospheric pressures of dry nitrogen.

that fraction of the beam backscattered from the substrate. The charge density is defined as

$$Q = (1 + \eta)q$$

where η is the backscattering coefficient of the substrate. All of our experimental results are reported in terms of Q because it is a more precise measure of the number of electrons traversing a thin film. Q is readily converted to adsorbed dose using the methodology outlined previously.¹²

Electron Beam Exposure Apparatus for Exposures at Atmospheric Pressures of Nitrogen. Electron beam exposure of the samples was achieved with a CB 150 Electron Processor (Energy Sciences, Inc., Woburn, MA) which allows exposures of the samples in an atmosphere of nitrogen. A diagram of the apparatus is shown in Figure 18. Basically, the instrument consists of a shielded conveyor that transports the sample under an electron beam. Electrons emanating from a rodlike filament are accelerated and subsequently exit through a Ti/Al alloy window to form a "planar" shaped electron beam perpendicular to the direction in which the samples moves. The electron beam gun The course of the electron beam induced decomposition was followed by using infrared spectroscopy. Infrared spectra of the solid thin film samples were coated on 1-in.-diameter silicon substrates and recorded with a Perkin Elmer 580 IR spectrometer. The silicon substrates, obtained from Diode Corp., Framington, MA, are polished on both sides and are tapered (8–12 mil) to eliminate interference fringes. A bare silicon substrate was exposed to a 175-kV beam for doses up to 1000 Mrad with no new absorptions appearing.

Dosimetry was performed using the aminophenolmethane dye doped films produced by Far West Technology, Goleta, CA. The thickness of the dosimetric films was 2 mil and the absorbed dose was measured by recording the optical density at 510 nm before and after exposure as reported earlier.¹³ A silicon wafer was placed beneath the dosimetric film to obtain the fraction of the absorbed dose from backscattering of the electron beam. The absorbed dose in the sample was obtained by using the equations for stopping power of the sample and dosimeter.¹⁴

Samples of irradiated material in sufficient quantities for product analysis were prepared by using a tray made from a metal block into which a well, 3 mil deep and of area equal to 160 cm^2 , was machined. A viscous solution of material was placed in the tray to flood the well and, subsequently, the sample thickness was brought to 3 mil by pulling a straightedge across the sides of the well and the remaining solvent allowed to dry. After the sample was exposed to the 175-kV electron beam it was collected and stored in capped bottles for analysis.

Registry No. 1, 5610-94-6; **2**, 114885-79-9; **7**, 879-15-2; **8**, 108-39-4; **9**, 71-43-2; 2-nitro-1-naphthol, 607-24-9; 2-amino-1-naphthol hydrochloride, 41772-23-0; sodium 2-diazo-1-naphthoquinone-5-sulfonate, 2657-00-3; 2-diazo-1-naphthaquinone-5-sulfonyl chloride, 110928-59-1.

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Emission Characteristics and Photostability of *N*,*N*[']-Bis(2,5-di-*tert*-butylphenyl)-3,4:9,10-perylenebis(dicarboximide)

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The titled dye (1) shows very high fluorescence quantum yield values as well as photostability. The dye undergoes molecular aggregation both in the ground state (at a critical concentration of ca. 2×10^{-4} mol dm⁻³) and in the excited state (giving excimerlike emission at ca. 600 nm). It displays solvatochromism in both emission and UV-visible absorption spectra. The dye does not give laser emission upon pumping ethanolic solutions with a nitrogen laser ($\lambda_{exc} = 337.1$ nm, peak power of 100 kW) but acts as an efficient quencher of 1,4-bis(β -pyridyl-2-vinyl)benzene (P2VB) laser dye. The quenching process obeys a static type mechanism. Equimolar mixtures of dye 1 and P2VB or 2,5-distyrylpyrazine (DSP) laser dyes also give no laser emission. With even higher peak power (200 kW, pulse duration of 800 ps) a laser emission can be obtained from chloroform solutions of dye 1.

Introduction

The synthesis and spectral identification of several highly fluorescent and very highly stable perylene derivatives have been recently reported.¹ Dyes of such unique characteristics are very attractive in many areas, e.g., dye lasers, and solar energy conversion, and can serve as photosensitizers, photon counters, and

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