PHOTOCHEMISTRY OF ALIZARIN ADSORBED ON A GLASS SURFACE

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Summary

Photochemical processes at the gas–solid interface are interesting, but difficult to study. Photoeffects involving alizarin (1,2-dihydroxy-9,10-anthraquinone) adsorbed on the inside surface of a gas chromatographic capillary column were investigated. Alizarin interacts strongly with the polar surface environment resulting in a large red shift of the absorption band. Aromatic or aliphatic N-substituted amines were passed through the column in the carrier gas stream. Irradiation of the column caused a photochemical reaction to occur on the adsorbed alizarin surface. An excited triplet state was produced followed by exciplex formation between alizarin and amine. The final product of the photoreaction was a dealkylated amine.

A new approach to the study of photoprocesses on surfaces using standard gas chromatographic equipment was demonstrated. Specific mass spectrometric and sensitive flame ionization detectors were applied. The technique was found to be sensitive to photoeffects at very low concentration.

1. Introduction

Organic molecules often change their spectroscopic, chemical and photochemical properties when adsorbed or immobilized on surfaces. Such heterogeneous systems play significant roles in the functioning of living organisms and in energy production or transportation. Quinoidal compounds very often play a key role in heterogeneous photochemical processes. However, because the study of surface photochemistry is experimentally difficult, little is known about the photochemistry of adsorbed quinoidal compounds.

Spectroscopic and photochemical properties of organic molecules adsorbed on polar surfaces have been reviewed by Nichols and Leermakers [1]. The spectra and photochemistry of molecules adsorbed on silica gel in inert solvents have been investigated by Leermakers *et al.* [2]. They reported

spectral shifts of the absorption bands and environmental influences on photochemical reactions. Similar effects of polar environments on photo-processes involving organic molecules adsorbed at gas–solid interfaces have been reported [3 - 5]. Much less work has been done with gas–solid systems than with liquid–solid systems.

In solution, quinones undergo many photochemical reactions which have been summarized in a comprehensive review [6]. Electron paramagnetic resonance [7, 8] and laser photolysis techniques combined with conductance measurements and kinetic spectroscopy [9] have been used to study photoprocesses involving quinones. For example, it was found that the excited triplet state of duroquinone abstracts electrons from diphenylamine. Daubendiek *et al.* [10] investigated energy transfer at the gas–solid interface using anthraquinone as a sensitizer in a crystalline form with reactants in the gas phase. Their results were similar to those obtained for the same sensitizer in solution.

Gas chromatography is recognized as an excellent tool for physico-chemical studies in general [11] and has been applied to the study of reactions occurring on columns [12], but it has not been employed to investigate photoprocesses. Leermakers and James [13] observed photo-chemical reactions within a liquid chromatography column. They used a glass column with a sensitizer in the stationary phase to cause photochemical reactions to occur during the chromatographic process.

Any processes affecting the chemistry of the gas–solid interaction will affect the chromatographic behavior of the column. Glass capillary columns are transparent, allowing light to reach the gas–solid interface. Small effects at extremely low concentrations of substrates are easily detected with standard gas chromatographic detectors. A variety of surfaces are readily prepared using techniques developed for the preparation of analytical columns. Therefore glass capillary gas chromatography should be an excellent technique for studying photochemical processes on surfaces. Sakodynski *et al.* [14] and Suslick [15] proposed using light to enhance separation in gas chromatography, but did not carry out any photochemical gas chromatography experiments. Recently our group [16] reported the observation of photochemical reactions at the gas–solid interface using glass capillary gas chromatography. In this procedure a non-volatile photochemically interesting substance was adsorbed on the internal surface of an etched glass capillary column. A constant concentration of volatile reactant was passed through the column. The photoreaction products were detected during column illumination by selective mass spectroscopy and sensitive flame ionization detection.

The basic requirements of a gas chromatographic stationary phase are a high boiling point, a low volatility, thermal stability and efficient adsorption on an etched soft glass surface [17, 18]. Alizarin (1,2-dihydroxy-9,10-anthraquinone), a natural dye with a distinct yellow color [19], satisfies these requirements and is a suitable choice as a photochemically active stationary phase.

Organic amines have electron-donating properties and form exciplexes with aromatic hydrocarbons [20, 21]. Most of them are volatile and thermally stable. In most experiments organic amines were used as reactants in the gas phase.

2. Experimental details

2.1. Equipment

A 400 W quartz–iodine lamp was installed inside the oven of a gas chromatograph. The photochemical reaction products were observed either by a flame ionization detector or by a mass spectrometer. The equipment used in this work has been described previously [16].

In the wavelength-dependent investigations of photochemical reactions colored solutions were employed as filters. These were prepared by dissolving appropriate substances in water and placing the solutions in a thin layer between two cylinders surrounding the light source. A Perkin–Elmer model 340 UV–visible–near-IR spectrophotometer was used to obtain the absorption spectra of the solution filters.

In the oxygen quenching experiments, various lengths of Teflon tubing (inside diameter, 1/32 in; outside diameter, 3/32 in) (Cole–Palmer, Chicago, IL) were fitted into the carrier gas stream before the column. Since Teflon is permeable to oxygen from the atmosphere, increasing the length of tubing increases the concentration of oxygen in the gas phase.

To produce a constant low concentration of reactant, a 15 mm melting point capillary tube containing a liquid sample was fitted in the carrier gas stream with a tee fitting. The reactant mass flow rate was of the order of 1 ng min^{-1}.

The procedure for preparing the glass capillary column has been described previously [16]. Alizarin (Fisher Reagent Chemicals, Fair Lawn, NJ) was adsorbed on the etched glass surface from its solution in triethylamine–ethyl ether.

The prepared columns were inspected and evaluated by microscopy using a Leitz Wetzlar microscope (model SM-LUX). No alizarin crystals were observed.

The photochemical reactions in solution were conducted in 5 mm nuclear magnetic resonance (NMR) tubes. A tube containing a saturated solution of alizarin was irradiated in a chromatographic oven at 140 °C. Solvent fumes from the tube were removed from the oven by venting through a length of Teflon tube. A 200 MHz Nicolet Nt 200 Fourier transform (FT) NMR spectrometer (Mountain View, CA) was used to study the solutions for reaction products.

2.2. Reagents

Anisole and phenetole (Mathenson, Coleman and Bell, East Rutherford, NJ) were used as the samples. Other reagents used have been described previously [16].

3. Results and discussion

As has been previously reported [16], alizarin reacts photochemically with various aromatic and aliphatic amines inside a glass capillary gas chromatographic column. The product of the reaction using N,N-dimethylaniline is N-methylaniline.

The aliphatic amine N,N-diethylcyclohexylamine reacted similarly. Figure 1 shows the intensity variation of the mass spectroscopic parent peak during illumination of a glass capillary column containing alizarin as the stationary phase and a constant low concentration of N,N-diethylcyclohexylamine in the carrier gas. Before the lamp was turned on, the mass spectrum of the reactant was obtained indicating that no reaction occurred in the dark. During illumination the reactant concentration decreased to about half its initial value. After the lamp was turned off, the reactant concentration returned to the initial level. Figure 2 shows the mass spectrum of the photoreaction products. This mass spectrum has been corrected for the presence of unreacted N,N-diethylcyclohexylamine. The product is N-ethylcyclohexylamine. The photoreaction product concentration was followed by monitoring the corrected intensity of m/e = 84 (parent peak for N-ethylcyclohexylamine). The results are presented in Fig. 3. The product concentration increased during illumination of the column and reached a maximum 6 min
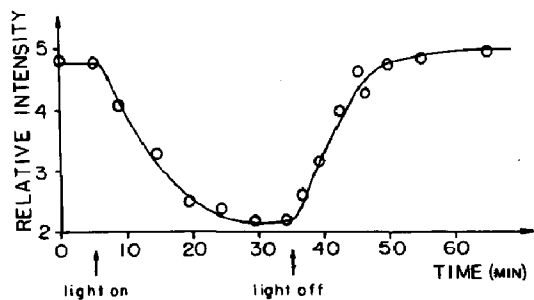

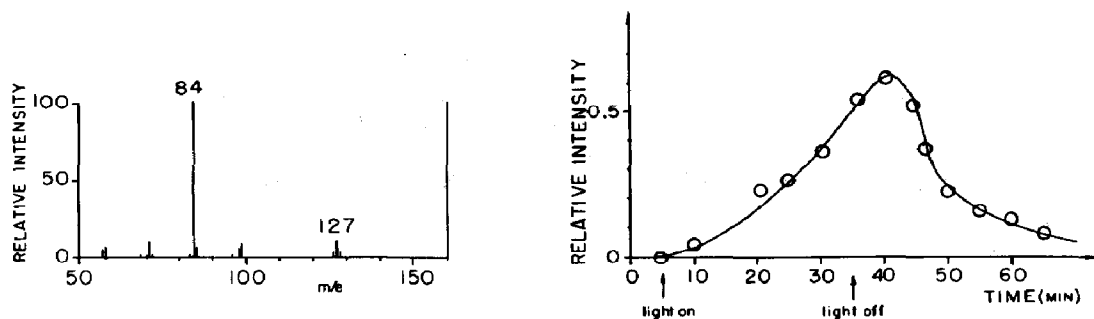Fig. 1. Intensity of peak m/e = 112 during column illumination.

Fig. 2. Mass spectrum of the photoreaction product (N-ethylcyclohexylamine) for the alizarin–N,N-diethylcyclohexylamine system.

Fig. 3. Intensity variation of peak m/e = 84 during column illumination.

after the light was turned off. The concentration then tailed off towards zero. The maximum concentration of the product occurs later than the reactant minimum because the product is a secondary amine which is retained in the column more strongly than the tertiary amine reactant. These results are similar to those previously observed for N,N-dimethylaniline [16]. In both cases photochemical dealkylation of the amine was observed.

Additional experiments were performed using N,N-diethylaniline, N-ethylaniline and unsubstituted aniline. In the first two cases dealkylation of the amine leads to formation of N-ethylaniline and aniline respectively.

With aniline as the reactant, no identifiable reaction products were eluted from the column. Figure 4 shows the variation in intensity of the aniline parent peak during illumination. All peaks of the mass spectrum followed the same curve. Turning the light on decreased the concentration of aniline leaving the column. After the light was turned off the aniline concentration increased to a level higher than that initially present before returning to the initial value. This effect was not observed on a plain glass column. There are a number of possible explanations for the lack of any identifiable photochemical reaction products in the column effluent. However, the fact that the aniline concentration exceeded the initial level for a time after the lamp was turned off is harder to explain. Apparently, the photochemical reaction between alizarin and aniline produced a more strongly retained intermediate which was reconverted to aniline before being eluted from the column. This more strongly retained intermediate is probably an exciplex formed between aniline and an excited triplet state of alizarin. The proposed mechanism is consistent with the experimental results for N-alkyl anilines. For these, the presence of a convenient leaving group allows the reaction to proceed past the exciplex to an identifiable product.
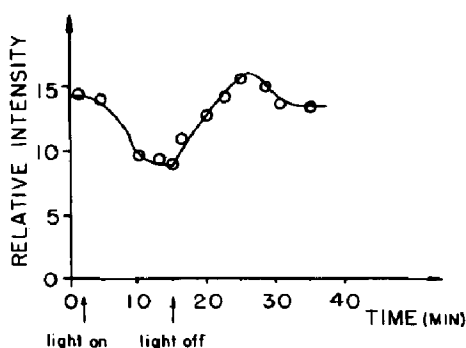

Fig. 4. Intensity variation of peak m/e = 93 during column illumination.

The chromatographic separation of photochemical products from the reactant and from each other aids in the identification of the products, especially when a mass spectrometer is not available for use as a detector. The flame ionization detector is more commonly available, is more sensitive, is less expensive and in addition allows a wider variation in experimental con-
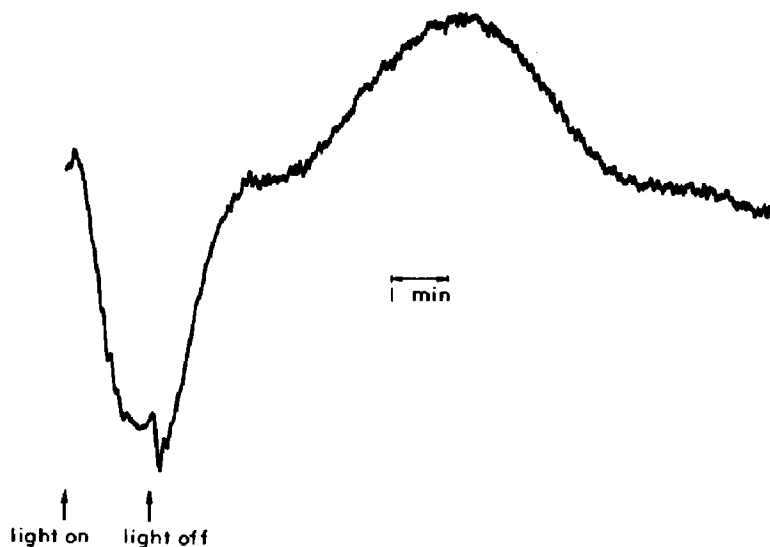
Fig. 5. Chromatogram for the alizarin–N,N-dimethylaniline chemical system using an OV-101 analytical column coupled to the alizarin reaction column.

ditions. The alizarin reaction column provides some separation, but it is not very efficient. Greater efficiency can be achieved by coupling an analytical column to the end of the reaction column. Figure 5 shows the chromatogram obtained with a flame ionization detector for the N,N-dimethylaniline–alizarin system coupled to a 10 m OV-101 analytical column. The main product peak for N-methylaniline is well separated from the negative reaction peak. The sharp drop in the chromatogram immediately after the lamp was turned off is probably due to the presence of an unretained product. A molecule small enough to be unretained would be difficult to detect by mass spectroscopy.

The extent of reaction is conveniently measured as the depth of the negative reaction peak in a chromatogram. In the following experiments the alizarin column alone provided sufficient separation of the products.

If an excited triplet state is an important part of the reaction mechanism, then the reaction should be quenched by oxygen [22]. A controlled concentration of oxygen was added to the carrier gas stream by inserting a length of Teflon tubing into the carrier gas line before the reaction column. Since Teflon is permeable to oxygen, increasing the length of the Teflon tubing produced higher oxygen concentrations in the gas stream which decreased the extent of the photoreaction. Oxygen strongly inhibits the photochemical reaction, confirming the assumption that a triplet state is involved in the photoprocesses.

Adsorption of some organic molecules on polar surfaces shifts their electronic spectra and influences photochemical reactions. Highly polar molecules such as alizarin would be expected to interact strongly with a glass surface to produce significant changes in the molecular properties. Some information about these changes can be gained by studying the wavelength
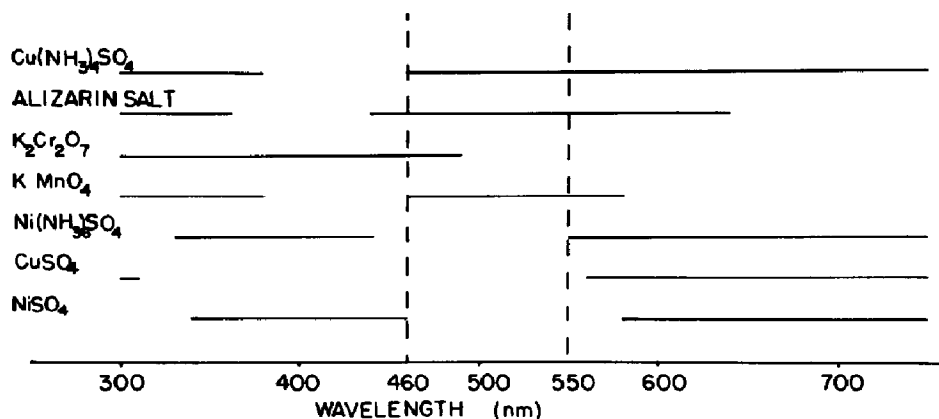
Fig. 6. Solution filters and their absorption bands.

dependence of the photoreaction. For this purpose a number of water solutions of various salts were prepared as filters. Figure 6 shows the absorption band regions of these solutions. Solutions were placed between the lamp and the column to filter out the corresponding wavelengths. It was found that solutions which did not absorb in the spectral region 460 - 550 nm did not affect the photochemical reaction in the N,N-dimethylaniline–alizarin system. Those which did absorb in this region decreased the extent of the reaction. For example, varying the concentration of $CuSO_4$–$NiSO_4$ or $Ni(NH_3)_6SO_4$ filter solutions did not produce any changes in the depth of the negative reaction peak. However, when the $KMnO_4$ filter was applied significant changes in the extent of the photoreaction were noted. The absorption band of photochemically reactive alizarin is shifted 80 nm towards the red. These results indicate that alizarin is strongly affected by the polar environment at the etched glass surface.

The photoreaction between alizarin adsorbed on the glass surface and N,N-dimethylaniline is very efficient and gives as a product N-methylaniline. It would be interesting to know how alizarin dissolved in N,N-dimethylaniline behaves when it is irradiated. Since no conclusive information was found in the literature, such an experiment was performed. An NMR tube filled with this solution was irradiated inside a chromatographic oven at 140 °C for 3 h. No indication of any chemical changes in alizarin or N,N-dimethylaniline was observed using the 200 MHz FT NMR spectrometer. This indicates that the glass surface environment is required for the reaction or at least increases the rate of reaction.

Similar but weaker photoeffects were observed for unsubstituted anthraquinone adsorbed on the column. This result indicates that the alizarin hydroxyl groups do not play a direct role in the photoprocesses.

Photoeffects were observed on an alizarin column when the aromatic ethers phenetole and anisole were used as the gas phase reactants. The shapes of the chromatograms obtained were similar to that for N,N-dimethylaniline indicating that similar dealkylation processes occurred.

4. Conclusions

Alizarin when adsorbed on a glass surface reacts photochemically with a variety of amines. With secondary and tertiary amines dealkylation of the amine occurs. With aniline there is evidence of exciplex formation but no overall reaction occurs. Anthraquinone can be used in place of alizarin and ethers in place of amines to give similar reactions.

These reactions apparently occur only on a surface. The method developed to study surface photochemistry with glass capillary gas chromatography columns was essential in this work. The sensitivity of gas chromatographic detectors made it possible to observe extremely low concentrations of reaction products in the gas stream. Combining chromatographic separation with photochemical reaction in the same column or in sequentially coupled columns provided additional information about the reaction and the products.

Acknowledgments

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