2-Arylsulphonamido-5-alkyl-1,3,4-thiadiazoles (*4*) (*Table II*)

A solution of 0.06 mole of the arylsulphonyl chloride in 25 ml pyridine was slowly added with stirring to a solution of 0.06 mole of 2-amino-5-alkyl-1,3,4-thiadiazole in 25 ml pyridine. The resulting solution, after being allowed to stand overnight at room temperature, was slowly added to an excess of 6 *N* hydrochloric acid. The crude product separated, usually as a solid but sometimes as a yellow gum which crystallized on standing. It was dissolved in dilute sodium hydroxide, treated with charcoal, and reprecipitated with hydrochloric acid. The 2-arylsulphonamido-5-alkyl-1,3,4-thiadiazole was recrystallized from alcohol–water.

Microanalyses were performed by Dr. Carl Tiedcke, Teaneck, N.J., U.S.A.

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NOTE ON THE PHOTOOXIDATION OF TETRAMETHYLRUBRENE*

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Badger's group (1) first noticed that tetramethylrubrene (5,6,11,12-tetra-*p*-tolylnaphthacene) crystals change from their normal deep red to a colorless form on exposure to sunlight. This is not a widely observable phenomenon in as much as substances which are photochemically active when dissolved in a suitable solvent do not normally undergo the same reaction in the pure crystalline form. Rubrene (5,6,11,12-tetraphenylnaphthacene) was found to exhibit the same type of decoloration on exposure to ultraviolet irradiation (3), but in this case specially prepared thin films on a large area substrate were necessary. In each case the product is a transannular peroxide.

It is the purpose of this note to report the results of some experiments on the photooxidation of tetramethylrubrene crystals. The experiments were done at 25° C in cells with plane quartz windows. The light source was a 1-kw AH6 water-cooled mercury arc. The apparatus was as previously described by Hochstrasser and Ritchie (3), and differential pressure measurements could be made to within 0.002 mm Hg at total pressures below 25 mm Hg. The oxidation was followed by noting the changes of oxygen pressure in a constant volume system as the crystals were illuminated with near monochromatic light. The small crystals were scratched on to the surface of a quartz disk (in the absence of absorbable light) and the disk was then carefully sealed on to one end of a cylindrical cell. The cell was then evacuated, oxygen allowed in to a known pressure in the dark, and when stability was maintained the crystals were illuminated and the decrease in pressure determined as a function of time. Experiments involving intermittent illumination and irradiation with light at two wavelengths were performed.

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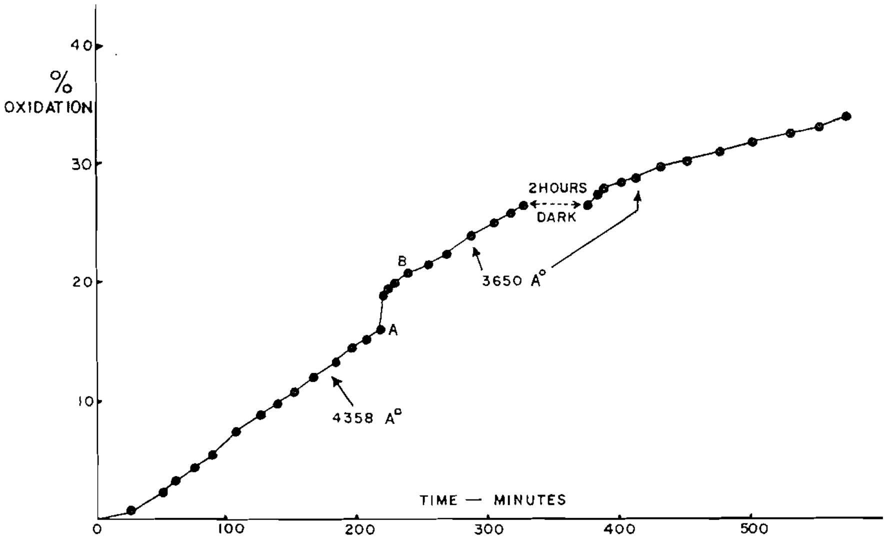

FIG. 1. Photooxidation of tetramethylrubrene crystals (10^{-6} mole of crystal; quanta at 3650 Å approximately double 4358 Å; O_2 pressure 25 mm).

A typical result is shown on Fig. 1 where the extent of the oxidation is plotted against time of irradiation. At A the illumination was discontinued and the crystals left in contact with oxygen for 30 minutes, then reirradiated. The magnitude of the increased rate from A to B was a function of the time of dark contact with oxygen. These results indicate that the photooxidation of tetramethylrubrene is diffusion-controlled. The effects observed when the intensity or the wavelength of the exciting light was changed were again indicative of a diffusional rate-determining step. The absolute rates of oxidation were not reproducible with different crystalline deposits, but the initial rate constants were all of the order of 10^{-10} mole second^{-1} and the quantum yields were approximately 10^{-4} depending on the oxygen pressure. The peroxide is in thermal equilibrium with oxygen but the dissociation is occurring at a negligible rate at this temperature.

Such a system is interesting in as much as not many similar cases are known and certainly not in relation to the combination of molecular oxygen with an aromatic hydrocarbon. As has already been pointed out, crystals of rubrene do not oxidize at a measurable rate even in an atmosphere of oxygen. During the formation of the transannular peroxide a drastic structural change must occur as shown in Fig. 2. Microscopic examination of partly oxidized crystals shows that the oxidation is occurring at the crystal surface.

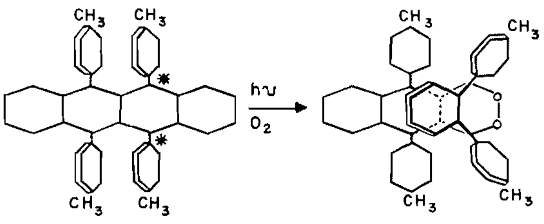

FIG. 2. Schematic representation of the photooxidation of tetramethylrubrene.

It is reasonably well established that oxidations of this type occur via the triplet state of the molecule attained after intersystem-crossing from the first excited singlet state (4). In a molecular crystal intersystem-crossing will manifest itself as localization of excitation energy within the crystal. This arises from the theory of molecular crystals (2) which shows that the singlet levels of the isolated molecule will be split in the crystal into a broad band ($\sim 3000 \text{ cm}^{-1}$), while the triplet splitting will be very small by virtue of the fact that the transition moment integral between the ground singlet and first triplet is negligibly small. In order that the reaction with oxygen can occur, this energy must be transported to the surface of the crystal, where there is an oxygen molecule available. It is the availability of oxygen which is the limiting factor in this case. To accomplish photooxidation, the oxygen must first traverse the peroxide layer. Here the rate of diffusion is measurable, and the observation of a diffusion-controlling step suggests that one reason why other aromatic hydrocarbons containing the basic anthracenic structure do not apparently react with oxygen to any great extent is the imperviousness of the peroxide layer to oxygen. With a bulky molecule such as tetramethylrubrene or even rubrene under special conditions this layer becomes permeable. The discovery of an effect such as this opens up a wide field which should yield much information regarding the transport of electronic excitation energy in molecular crystals. In the near future it is proposed to commence a detailed rotating sector and intensity study of the photooxidation of tetramethylrubrene single crystals.

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