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The Dye-sensitized Photolysis of Aryl Aryldiazo Sulfone

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Synopsis. The amethyst violet (AV)-sensitized photolysis of *p*-tolyl *p*-anilinobenzenediazo sulfone (TABS) has been investigated in a ethanol-water (9.3: 0.7, v/v) solution. The experimental data on the quantum yield of the sensitized photolysis and the AV fluorescence or phosphorescence intensity were explained in terms of AV-excited singlet sensitization. Studies of both the photoproducts and the heterogeneous photopolymerization of acrylamide supported the mechanism involving the homolytic dissociation of diazosulfone.

Brief reviews of the diazosulfones-imaging system have been published by Dinaburg.$^{1)}$ When irradiated with actinic light, diazosulfones decompose in the areas illuminated, whereas the non-illuminated parts preserve the ability to undergo coupling reactions with the formation of azo dyes, like usual diazonium compounds. Our purpose was to find a dye-sensitized photolysis for this system, since the dye sensitization will ensure an increase in the overall photosensitivity. The present note will describe the results of the amethyst violet (AV)-sensitized photolysis of *p*-tolyl *p*-anilinobenzenediazo sulfone (TABS) in an ethanol-water solution. The absorption spectra were recorded on a Hitachi 624 spectrophotometer. The fluorescence and phosphorescence measurements were carried out on a Hitachi MPF-2A spectrofluorimeter. The ESR spectra were recorded on a Varian E-12 X-band spectrometer with 100 kHz magnetic field modulation. Unless specified otherwise, all the experiments were performed at room temperature. Degassing from the solution was carried out by the usual freeze-pump-thaw cycle at 10^{-4} mmHg. The 546 nm irradiation was performed by the use of a 500-W super-high-pressure mercury lamp, equipped with two filters (Toshiba VO-52+KL-54). The light intensities were measured by Reineckate actinometry. The dark reaction of *p*-anilinobenzenediazonium sulfate ($2—4\times10^{-5}$ M) with sodium *p*-toluenesulfinate (STS) ($5\times10^{-4}—3\times10^{-3}$ M) to give TABS in ethanol-water solution was spectrophotometrically studied in order to measure the equilibrium constant (K) for the TABS formation.$^{2)}$ Its value was determined from the straight line in Benesi-Hildebrand's plot;$^{3)}$ the resulting value became greater with an increase in the ratio of ethanol in the ethanol-water solvent (Table 1). In the variation in the ethanol-water ratio, the extinction coefficient of TABS at the wavelength (450 nm) of its absorption maximum was unchanged at 2.9×10^4 M^{-1} cm^{-1}. Some quantitative measurements were made with ethanol-water of 9.3: 0.7, v/v. TABS was stable in the dark during the experimental procedure. The dye-sensitized photolysis of TABS was followed by a change in the absorbance of the solutions at 450 nm. The absorbance of the solution at 546 nm was unchanged during continuous illumination, irrespective of the presence of oxygen.

TABLE 1. EQUILIBRIUM CONSTANTS FOR TABS FORMATION

Ethanol/ water, (v/v)	9.6/0.4	9.4/0.6	9.3/0.7	9.2/0.8	9.1/1.0
K, 10^3 M^{-1}	9.5	7.8	5.2	3.7	1.2

TABLE 2. EFFECTS OF OXYGEN, [AV], [TABS], AND 546 nm LIGHT INTENSITY (I_{abs}) ON QUANTYM YIELD (η)

I_{abs} 10^{-5} E/l min	[AV] 10^{-5} M	[TABS] 10^{-5} M	η	
8	3.3—3.5	5	0.038$^{a)}$	0.035$^{b)}$
			0.036$^{c)}$	0.038$^{d)}$
5.6	4	4	0.048$^{a)}$	
4	4	4	0.057$^{a)}$	
2	4	4	0.081$^{a)}$	
0.8	4	4	0.130$^{a)}$	
8	2.0	2.9	0.026$^{a)}$	
8	3	2.9	0.023$^{a)}$	
8	4	2.9	0.017$^{a)}$	
8	4	3.5	0.025$^{a)}$	

a) aerobic b) N_2 bubbled c) O_2 bubbled d) deaerated

With $\leq5\times10^{-5}$ M TABS and $\leq4\times10^{-5}$ M AV in an ethanol-water (9.3: 0.7, v/v) solution, the quantum yield (η) for TABS elimination was determined, based on the total absorbed intensity of the 546 nm irradiating light (Table 2). An oxygen effect seemed to be absent in this system at least, since the η value of about 0.04 was unchanged after a thorough degassing of the solution. The η value decreased with a decrease in the TABS concentration and with an increase in the AV concentration or the 546 nm light itensity ($\leq8\times10^{-5}$ E. absorbed/l min).

AV showed a strong fluorescence maximum at 565 nm in ethanol-water (9.3: 0.7, v/v). The steady-state fluorescence intensity decreased with an increase in the AV concentration ($\geq2\times10^{-5}$ M). To check whether or not AV singlets were involved in the sensitization, we examined the effect of added TABS upon the fluorescence intensity of AV (2×10^{-5} M) in degassed solutions. Figure 1 shows the Stern-Volmer plot for the quenching of the fluorescence of AV by TABS. No new emission was detected in the presence of TABS. The fluorescence quenching was scarcely affected by oxygen. STS and water also caused a decrease in the fluorescence intensity, but their quenching constants of 13 and 6.8×10^{-2} M^{-1} were very small in comparison with the value of TABS (3.9×10^3 M^{-1}). The facts that the oxygen effect seemed to be absent in both the AV fluorescence intensity and the quantum yield of the sensitized TABS photolysis, that the AV fluorescence intensity decreased with an increase in the AV and TABS concentrations, and

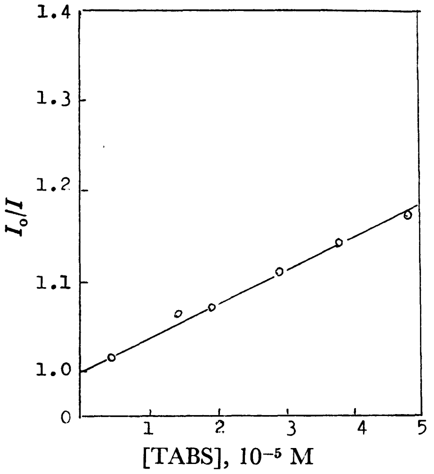

Fig. 1. Quenching of AV fluorescence by TABS, [AV]= 2×10^{-5} μ

that the quantum yield increased with a decrease in the AV concentration and an increase in the TABS concentration support the AV excited singlet sensitization.[4] In addition, AV (10^{-6}—10^{-5} M) emitted a phosphorescence exhibiting its maximum intensity at 730 nm in a deaerated EPA matrix (77 K), and its intensity was significantly reduced by oxygen. Those results may exclude the involvement of excited triplet AV in the sensitization, since the quantum yield of AV-sensitized photolysis should be significantly reduced by oxygen, if the above hypothesis occurs.[5]

The AV-sensitized photolysis of TABS induced the heterogeneous polymerization of acrylamide in a deaerated system without any permanent photobleaching of AV. The molecular weights of the polymers were of the order of thousands. The absence of TABS or the presence of oxygen caused no significant photopolymerization of acrylamide. The ESR spectrum of the polymer obtained showed a broadened single line at g=2.009, but the identity of the occluded radicals in the polyacrylamide particles seemed to be uncertain because of the lack of any observable hyperfine structure. The photopolymerization results suggest that the AV-sensitized photolysis of TABS leads to the production of free radical intermediates, which then initiate the polymerization of acrylamide.

Longer periods of the AV-sensitized photolysis of the TABS (~0.4 mmol) formed by a reaction between—0.4 mmol 4DS and ~15 mmol STS in 9.3: 0.7 ethanol-water (100 ml) containing ~0.06 mmol AV under nitrogen gave up to a 90% decomposition of TABS. Sodium *p*-toluenesulfonate readily precipitated out of the solution. The reaction mixture was then poured into 100 ml of a 5% sodium carbonate aqueous solution and filtered off. The filtrate was evaporated under reduced pressure, and the diphenylamine in the residue was separated by thin-layer chromatography on Kieselgel 60 F. Direct photolysis was carried out with the TABS (~0.2 mmol) formed by a reaction between 0.2 mmol 4DS and 5 mmol STS in 50 ml of 9.3: 0.7 ethanol–water. The final products isolated were essentially the same as in the case of AV-sensitized photolysis, sodium *p*-toluenesulfonate and diphenylamine. Photoproduct studies may indicate a similarity in the behabior of TABS decomposition in direct and sensitized photolyses. The direct photolysis of aryl aryldiazosulfone has been considered to undergo homolytic decomposition in neutral media.[6] This situation and the observation of the free radical photopolymerization of acrylamide make it likely that the homolytic dissociation has occurred in the AV-sensitized photolysis of TABS, thus yielding $CH_3C_6H_4SO_2\cdot$ and $C_6H_5NHC_6H_4N_2\cdot$ radicals. The loss of nitrogen from the latter may result in the formation of diphenylamine *via* a hydrogen abstraction from ethanol. The formation of sodium *p*-toluene-sulfonate may be ascribed to the disproportionation of the tosyl radical, as has been noted by da Silva Correa and Waters.[7]

References

1) M. S. Dianaburg, "Photosensitive Diazo Compounds and Their Uses," The Focal Press (1964), p. 82.

2) C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **20**, 4601 (1961).

3) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

4) The tendency for the quantum yield to decrease with the increase in the incident light intensity may result from the quenching of the excited singlet AV by photoproducts or their precursors (free-radical intermediates) formed *via* the sensitized homolytic dissociation of TABS, although this is not clear from these observations alone.

5) Attempts to detect the TABS phosphorescence and to confirm the absence of any quenching of the AV phosphorescence by TABS failed, probably because of the lower solubility of TABS for EPA.

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