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Dye Sensitized Photo-oxidation of Diphenylamine

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Synopsis. Evidence is presented to show that excited O_2 $(1\Sigma_g{}^+, 1\Delta_g)$ is an intermediate in the dye (methylene blue, rose bengal, eosin) sensitized oxidation of diphenylamine which yeilds *N*-phenyl-*p*-benzoquinonimine. The relative rates in different solvents are reported and a mechanism is suggested.

Evidence has been presented for the non-participation of O_2 $({}^1\Sigma_g^+$ or ${}^1\Delta_g)$ in the ketone or dye sensitized oxidation of a number of aliphatic amines and *N*-substituted anilines.[1-3] In the benzophenone sensitization of diphenylamine (DPA) diphenyl nitroxide formed through triplet DPA in the presence of oxygen is reported[4] while in the absence of oxygen 4-(*N*-phenylamino)-phenyl-diphenylmethanol has been identified.[5] Sensitization of DPA which is apparently quite complex[2] thus has appeared to fall in line with general mechanistic features of other similar amines. We report here the isolation of a unique product in its oxidation sensitized by methylene blue, rose bengal and eosin (all known for initiating reactions through their triplet states[6]) along with other kinetic features suggesting the participation of first excited singlet state of oxygen.

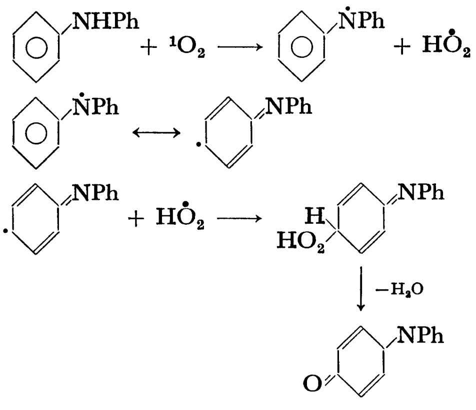
Experimental

All reagents were BDH grade and were purified by repeated crystallization and fractional distillation. The dyes had their maxima in spectrograde methanol in the visible at; methylene blue 645 nm; rose bengal 550 nm, eosin 515 nm. Photolysis assembly consisted of a white light bulb, a 320 nm cut off glass filter and a pyrex cell (50 mm dia × 10 mm) maintained at 26±2 °C in an air thermostat. Oxygen concentrations were varied by maintaining different partial pressures of it in the cell. Mixtures of dry nitrogen and oxygen at a total pressure of one atmosphere were used for the purpose. The reaction mixture after evaporation of the solvent was fractionated by column chromatography over alumina with benzene as eluent. The brown product after crystallization from petroleum ether was identified as *N*-phenyl-*p*-benzoquinonimine (PBQ) by mp 101—102 °C (reported 101.5 °C); identity of its IR in KBr with the reported spectrum and understandable NMR in CS_2.[7] PBQ on hydrolysis with 10^{-2} M HCl at 65 °C gave aniline and *p*-quinone which were identified by UV spectra after chromatographic separation. The product yields in these runs were kept between 2.4 and 3.0% in order to avoid any secondary products through secondary photolysis. In the kinetic runs the monitoring was done at 448 nm where PBQ has a maximum in alcohols with blank as reference on a Hilger and Watt spectrophotmeter.

Hydrogen peroxide was shown to have no reaction with DPA in alcohols at the concentrations examined. To solutions of hydrogen peroxide (0.3 M) in excess and DPA (0.05 M) in alcohol-water mixtures in the ratio 5: 1, varying amounts of NaOCl (0.2 M) were added dropwise from the burette. After the instantaneous reaction at 26 °C the reaction mixture was double diluted with water and extracted with ether. The ether layer was evaporated and column chromatographed. The yields were kept below 8.0% and no attempt was made to carry the reaction to completion because of the observed further oxidation of PBQ at larger concentrations. NaOCl alone gave a different mixture of products.

Results and Discussion

In the photolysis of 5.0×10^{-4} to 1.0×10^{-2} M of DPA with 3.0×10^{-5} to 7.5×10^{-4} M of the dye, time study and UV/visible spectra demonstrated PBQ to be a primary product. Unlike previous studies increase in oxygen concentration increased the extent of reaction.[3c] The relative reaction rates in different solvents were $CH_3OH=1.00$, $C_2H_5OH=0.78$, *iso*-$C_3H_7OH=0.55$, *n*-$C_4H_9OH=0.69$, $CH_3CN=0.78$, $CH_3OH-H_2O(9:1)=1.68$, $CH_3OH-H_2O(8:2)=2.76$, $CH_3OH-H_2O(7:3)=3.95$. Viscosity effect decreasing the rates is apparent in alcohols. In isopropanol an additional decrease appears because of the availability of easily abstractable tertiary hydrogen. The effect of water cannot be a pure dielectric effect in view of the rate in acetonitrile. The life time of singlet oxygen is also less in water.[8] It appears, therefore, that water is stabilizing some of the intermediate radical species. A very likely course for the reaction is;



There exist the possibilities of (a) intial hydrogen abstraction from N–H by the triplet dye and (b) direct attack of singlet O_2 at the *para* position as proposed in the photo-oxidation of phenols.[9,10] However, both of these require a hydrogen abstraction by the inter-

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mediate peroxy radical mechanisms and in view of the low concentration of the substrate as compared to the solvent and bond strengths of N–H and *tert*-C–H (in isopropanol)[11] the rate in isopropanol should be higher. On the contrary the rate is higher in methanol. Also H_2O_2 is a product which militates against these possibilities.

A specific search for tetraphenyl hydrazine did not detect it. This is evidence of the greater stability of the conjugated structure of the radical. The reaction sequence is helped by the resonance stabilization of the radical as expected.

To further substantiate the participation of singlet oxygen, these species were generated chemically by the well-known reaction of $NaOCl+H_2O_2$.[12,13] In alcohols with similar concentrations of DPA, PBQ was formed with parallel kinetic features (*cf.* effect of solvents).

It is thus established that excited $O_2(^1\Sigma_g^+, ^1\Delta_g)$ is an intermediate in the dye sensitized oxidation of diphenyl amine which proceeds through hydrogen abstraction by $^1O_2$.

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References

1) M. Santhanam and V. Ramakrishnan, *Chem. Commun.*, **1970**, 344.

2) H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 7270 (1972).

3) a) R. F. Bartholomew and R. S. Davidson, *Chem. Commun.*, **1970**, 1174. b) R. F. Barholomew and R. S. Davidson, *J. Chem. Soc., C*, **1971**, 2342. c) R. F. Bartholomew and R. S. Davidson, *ibid., C*, **1971**, 2347. d) R. F. Bartholomew, R. S. Davidson, and M. J. Howell, *ibid., C*, **1971**, 2864.

4) M. Santhanam and V. Ramakrishnan, *Indian J. Chem.*, **8**, 374 (1970).

5) C. Pac, H. Sakurai, and T. Tosa, *Chem. Commun.*, **1970**, 1311.

6) K. Gollnick, "Advances in Photochemistry," ed. by W. A. Noyes, Jr., G. S. Hammond, J. N. Pitts, Jr., Interscience Publishers, Vol. 6, (1968), p. 1.

7) a) R. Lantz and J. Gascon, *Bull. Soc. Chim. Fr.*, **1959**, 1161. b) H. J. Teuber and W. Schmidtke, *Chem. Ber.*, **93**, 1257 (1960).

8) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1029 (1972).

9) K. Pfoertner and D. Boese, *Helv. Chem. Acta*, **53**, 1553 (1970).

10) I. Saito, S. Kato, and T. Matsuura, *Tetrahedron Lett.*, **1970**, 239.

11) G. Glockler, *Discuss Faraday Soc.*, **10**, 26 (1951).

12) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879, 3880 (1964).

13) T. Yamase, H. Kokado, and E. Inoue, This Bulletin, **45**, 726 (1972).