Tetrahedron Letters,Vol.27,No.51,pp 6157-6160,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

SURFACE PHOTOCHEMISTRY: SEMICONDUCTOR PHOTOINDUCED VALENCE ISOMERIZATION OF QUADRICYCLANE TO NORBORNADIENE

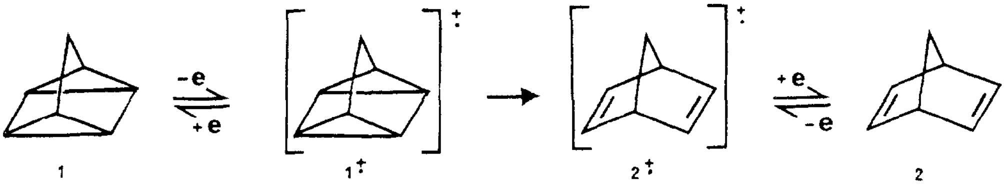
Anthony M. Draper and Paul de Mayo*
Department of Chemistry, The University of Western Ontario,
London, Ontario, Canada. N6A 5B7

Summary: Contrary to a recent report, the valence isomerization via a radical cation,of quadricyclane to norbornadiene on the surface of illuminated CdS and ZnO is described.

The quadricyclane (1) norbornadiene (2) system has been the subject of extensive investigation.[1,2,6,7] Some of the interest has been fueled by the desire to develop a system for chemical storage of solar energy.[2] Recently[3] the use of semiconductors has been suggested as catalysts for the isomerization of 2 to 1, in the form of neat liquids, in the development of such a storage system. This report impels us to describe our own conclusions concerning the same system which are at variance with those reported. That is, irradiation of CdS or ZnO in contact with a CH_2Cl_2 (ca. 0.1M) solution of 1 gives 2 as the sole product; and that of 2 under the same conditions gives no reaction.

In recent years there have been studies on the use of semiconductors as catalysts for electron transfer reactions,[4] other than oxidation.[5] Illumination of a semiconductor with light of greater energy than its band gap, creates a photoinduced hole by excitation of an electron to the conduction band. A substrate with an oxidation potential lower than that of the photoinduced hole may donate an electron to the semiconductor forming a radical cation. The photosensitized isomerization of 1 to 2, via a radical cation mechanism, is well-known in homogeneous solution.[6] Roth and Schilling,[7] in an elegant study, have established that $2^{\dot{+}}$ is of lower energy than $1^{\dot{+}}$, the radical cation rearrangement proceeding as in scheme 1. The oxidation potentials of 1 and 2 (0.91V vs SCE and 1.48V vs SCE respectively[6a]) are suitable for electron donation to the photoinduced holes of CdS and ZnO (1.6V vs SCE and 2.4V vs SCE respectively[8]).

SCHEME 1



Our results are summarized in Table 1. On ZnO both light and semiconductor are required for reaction. The faster reaction in the presence of oxygen is attributed[9] to an extension of the lifetime of the photoinduced hole, by trapping of the conduction band electron as $O_2^{-\cdot}$. On CdS the reaction

Table 1: The Conversion of Quadricyclane to Norbornadiene on CdS and ZnO.

Semiconductor[a]	[1] mol/l	Time (hrs)	Thermal (% reaction)[e] Aerated	Thermal (% reaction)[e] Degassed	Photochemical (% reaction)[e] Aerated	Photochemical (% reaction)[e] Degassed
ZnO[b]	.06	1	<1		20	8.5
CdS[c]	.1	2	1	2.2	2.6	13
CdS[d]	.25	1	21		68	

---

[a] Reaction vessels were centered in front of a 1KW high pressure Xenon lamp and irradiated with $h\nu > 340$nm; vessels were stirred with a magnetic stir bar; no reaction was observed in the absence of a seminconductor. [b] 50mg of Fisher $\geq$99% ZnO, $5m^2g^{-1}$. [c] 10mg of Aldrich gold label CdS 99.999%, $1.2m^2/g$, 100% α-type. [d] 45mg of Aldrich gold label CdS 99.99%, $20m^2/g$, polytype. [e] Sample analysis was performed by gas chromatography on a 2m x 2mm column packed with 10% OV-101 on chromosorb W, internal standard: cyclooctane.

proceeds in the dark also, and may account for as much as 30% of the illuminated reaction, depending on the CdS sample used.[10] Under degassed conditions an acceleration of the reaction is observed on CdS. This non-conventional role of oxygen has been observed before.[11] Possible explanations for the acceleration have been offered, the simplest of which is competition for active sites on the surface of the semiconductor. This is supported by the observation of an acceleration of the CdS reaction in less polar solvents (cyclohexane, pentane) whereas, with ZnO, CH_2Cl_2 is the most effective solvent.

If the surface isomerization of **1** to **2** be proceeding via a radical cation, then the reaction should be readily quenched by a suitable electron donor. 1,2,4,5-Tetramethoxybenzene (TMB) has a $E^{ox}_{½} = 0.81V$,[12] and is thus able to quench both the photoinduced hole of the semiconductor and the radical cation of **1**. It is, indeed, an efficient quencher for the reaction of **1** on CdS and ZnO, a plot of ϕ/ϕ_0 against [TMB] gives a straight line up to 80% quenching; slope = $81M^{-1}$ (r = .999) for CdS and slope = $111M^{-1}$ (r = .971) for ZnO. The possibility of quenching by competitive adsorption between TMB and **1** for active sites on the semiconductor surface may be ruled out: Additives with higher oxidation potentials do not show any quenching below concentrations greater than 10 times that at which TMB is effective.[13]

The following results were obtained with *neat* **2**: i) **2** Freshly distilled (argon) absorbs all the light below 330 nm (1 cm path; $\epsilon_{330} = 0.2$); ii) Irradiation of neat **2** through Pyrex yields **1**, as stated,[3] but does so faster in the *absence* of a semiconductor; iii) The reaction was, indeed,[3] slower under degassed conditions. A possible interpretation is the occurrence of direct irradiation of **2** to **1** in combination with sensitization of **2** to **1** by oxidation products formed during the irradiation under oxygen.

References

1. a) G.S. Hammond, P. Wyatt, C.D. Deboer and N.J. Turro, *J. Am. Chem. Soc.*, 1964, **86**, 2532. b) S. Murov and G.S. Hammond, *J. Phys. Chem.*, 1968, **72**, 3797. c) N.J. Turro, W.R. Cherry, M.F. Mirbach and M.J. Mirbach, *J. Am. Chem. Soc.*, 1977, **99**, 7388 and references cited therein.

2. Cf, *inter alia*, a) R.B. King, and E.M. Sweet, *J. Org. Chem.*, 1979, **44**, 385. b) G.Jones, II, S.H. Chiang and P.T. Xuan, *J. Photochem.*, 1970, **10**, 1. c) G. Jones, II, W. Schwarz and V. Malba, *J. Phys. Chem.*, 1982, **86**, 2286.

3. S. Lahiry and C. Haldar, *Solar Energy*, 1986, **37**, 71.

4. a) R.A. Barber, P. de Mayo and K. Okada, *J. Chem. Soc., Chem. Comm.*, 1982, 1073. b) A.M. Draper, M. Ilyas, P. de Mayo and V. Ramamurthy, *J. Am. Chem. Soc.*, 1984, **106**, 6222. c) H. Al-Ekabi and P. de Mayo, *J. Chem. Soc., Chem. Comm.*, 1984, 1231. d) H. Al-Ekabi and P. de Mayo, *J. Phys. Chem.*, 1985, 26, 5815. e) T. Hasegawa and P. de Mayo, *Langmuir*, 1986, **2**, 363. f) K. Okada, K. Hisamitsu and T. Mukai, *J. Chem. Soc., Chem. Comm.*, 1980, 941. f) K. Okada, K. Hisamitsu, Y. Takahashi, T. Hanaoka, T. Miyashi and T. Mukai, *Tetrahedron Lett.*, 1984, **25**, 5311.

5. M.A. Fox, *Acc. Chem. Res.*, 1983, **16**, 314.

6. a) P.G. Gassman, R. Yamaguchi and G.F. Koser, *J. Org. Chem.*, 1978, **43**, 4392. b) P.G. Gassman and K.D. Olso, *Tetrahedron Lett.*, 1983, **24**, 19. c) E. Haselbach, T. Bally, Z. Lanyjova and P. Baertshi, *Helv. Chim. Acta*. 1974, **62**, 583. d) H-D. Martin, C. Heller, E. Haselbach and Z. Lanyjova, *Helv. Chim. Acta.*, 1974, **57**, 465.

7. H.D. Roth, M.L.M. Schilling and G. Jones, II, *J. Am. Chem. Soc.*, 1981, **103**, 1246. b) H.D. Roth and M.L.M. Schilling, *J. Am. Chem. Soc.*, 1981, **103**, 7210. c) K. Rajhavachari, R.C. Hadden and H.D. Roth, *J. Am. Chem. Soc.*, 1983, **105**, 3110.

8. P.A. Kohl and A.J. Bard, *J. Am. Chem. Soc.*, 1977, **99**, 7531.

9. J.R. Habour and M.L. Hair, *J. Phys. Chem.*, 1977, **81**, 1791.

10. All samples of CdS showed some dark reaction. Dark reactions are not unknown on CdS; M. Ilyas and P. de Mayo, *J. Am. Chem. Soc.*, 1985, **107**, 5093.

11. See references 4c and d.

12. A. Zweig, W.G. Hodgson and W.H. Jura, *J. Am. Chem. Soc.*, 1964, **86**, 4124.

13. The use of 1,2,4-trimethoxybenzene and 1,3,5-trimethoxybenzene as photoinduced hole quenchers and MeOH as a competitive chemical reaction quencher have been studied. They also are effective quenchers and will be reported in detail elsewhere.

(Received in USA 2 September 1986)