

## A Silica-supported Inorganic Photosensitizer

Paul A. Grutsch and Charles Kotal\*

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

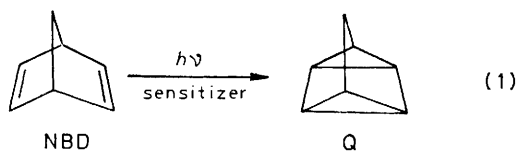
Adsorption of  $[\text{Ir}(\text{bipy})_3\text{OH}]^{2+}$  (bipy = 2,2'-bipyridine) onto silica gel does not adversely affect the efficiency with which this transition metal complex photosensitizes the valence isomerization of norbornadiene to quadricyclene.

Several benefits can be realized from immobilizing a photosensitizer onto an insoluble matrix. Prominent among these are i, a facile separation of the sensitizer from the photo-product(s), ii, a lessening of undesirable sensitizer self-quenching processes, and iii, the ability to alter sensitizer properties (*e.g.* excited-state energies, lifetimes, reactivities) by appropriate modification of the matrix environment. Other practical advantages pertinent to a solar energy storage system have been noted.<sup>1,2</sup> We report here our finding that the adsorption of  $[\text{Ir}(\text{bipy})_3\text{OH}]^{2+}$ , † (1) (bipy = 2,2'-bipyridine) onto the surface of silica gel affords a highly efficient, heterogeneous photosensitizer for the endoergic valence isomerization of norbornadiene (NBD) to quadricyclene (Q), [equation (1)].

The nitrate salt of (1) was prepared by a literature procedure.<sup>3</sup> Silica gel (Baker 60-200 mesh) was dried by heating at 150 °C for 30 h. A 2.5 g sample of this material was mixed with 10 ml of acetonitrile, and the resulting suspension stirred for 30 min with 5 ml of an acetonitrile solution containing  $2.5 \times 10^{-3}$  M (1). After removal of the liquid by filtration, the silica gel was washed successively with 10 ml of acetonitrile and three 10 ml portions of ether, and was then dried in air. Measurement of the electronic absorption spectrum of the filtrate revealed that >99% of the iridium complex originally in solution had been adsorbed onto the silica gel. Spectral and photochemical studies of silica-supported (1) were conducted on unstirred slurries of the solid in pure NBD. Samples were

de-aerated by bubbling with nitrogen prior to photolysis. Irradiations and product analyses were performed using equipment and procedures described previously.<sup>4</sup>

As shown in Figure 1, the absorption spectrum of silica-supported (1) in NBD closely resembles that of the complex dissolved in acetonitrile. The luminescence spectra of (1) in the



† Since the structure of (1) is the subject of considerable controversy (W. A. Wickramasinghe, P. H. Bird, and N. Serpone, *J. Chem. Soc., Chem. Commun.*, 1981, 1284), our formulation of the ion as  $[\text{Ir}(\text{bipy})_3\text{OH}]^{2+}$  is meant to convey only its stoichiometry.

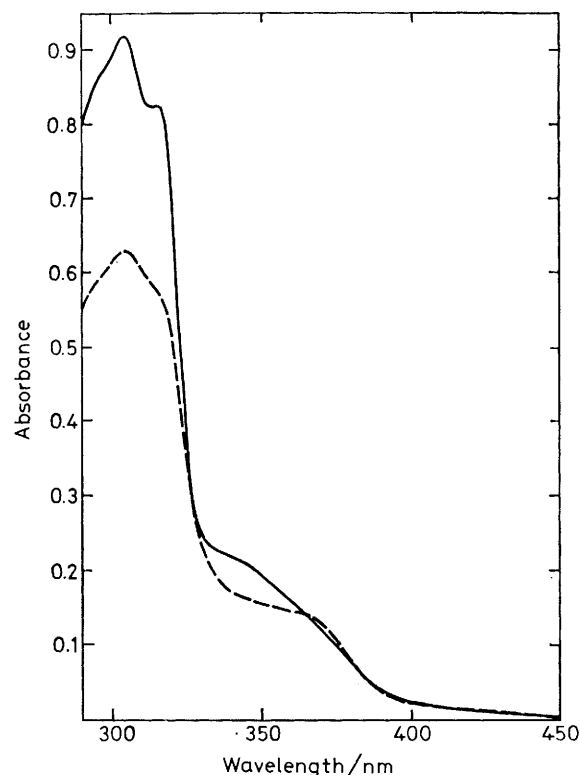


Figure 1. Electronic absorption spectra of (1) in two different environments: — in MeCN solution, and - - - adsorbed onto silica gel.

two environments are also very similar. We conclude from these results that the adsorption of (1) onto the surface of silica gel has little effect on the energies of its low-lying electronic states.

Irradiation of silica-supported (1) (absorbance  $>4$  in a 3 mm cell) at 366 nm in the presence of NBD results in the production of Q. Under the assumption that all of the incident light is absorbed by the heterogeneous sample (*i.e.* light scattering is minimal<sup>‡</sup>), the quantum yield for the sensitized isomerization is 0.7–0.8. By comparison, the limiting quantum yield (*i.e.* extrapolated to infinite NBD concentration) for sensitization by (1) in acetonitrile solution is  $0.72 \pm 0.05$ .<sup>§</sup> This close correspondence of the homogeneous and heterogeneous sensitization efficiencies of (1) requires that essentially all of the iridium sensitizer adsorbed onto the silica gel be accessible to the NBD liquid phase. Moreover, it follows that (1) suffers no detrimental effects from being in close proximity to the

---

<sup>‡</sup> Light scattering should be unimportant owing to the high absorbance by (1) and the similarity in the refractive indices of silica gel and NBD.

<sup>§</sup> This value represents the initial quantum yield measured at low percentage conversion. The quantum yield decreases with time of irradiation owing to competitive quenching of the sensitizer excited state by Q.

highly polar silica surface, in contrast to the recently reported behaviour of the organic photosensitizer, 4-(*N,N*-dimethylamino)benzophenone.<sup>5</sup>

The present study demonstrates the principle that ionic transition-metal photosensitizers, which might otherwise be incompatible with organic systems, can function effectively when immobilized onto a siliceous support. The insolubility of (1) in hydrocarbons, for example, precludes its use as a homogeneous sensitizer in pure NBD because of negligible light absorption.

We thank the U.S. Department of Energy for its financial support.

*Received, 5th May 1982; Com. 504*

### References

- 1 R. R. Hautala, R. B. King, and C. Kotal in 'Solar Energy: Chemical Conversion and Storage,' eds. R. R. Hautala, R. B. King, and C. Kotal, Humana Press, Clifton, New Jersey, U.S.A., 1979, p. 333–369.
- 2 C. Kotal, *Adv. Chem. Ser.*, 1978, **168**, 158.
- 3 R. J. Watts, J. S. Harrington, and J. Van Houten, *J. Am. Chem. Soc.*, 1977, **99**, 2179; J. L. Kahl, K. Hanck, and K. DeArmond, *J. Inorg. Nucl. Chem.*, 1979, **41**, 495.
- 4 P. A. Grutsch and C. Kotal, *J. Am. Chem. Soc.*, 1979, **101**, 4228.
- 5 R. R. Hautala and J. L. Little, *Adv. Chem. Ser.*, 1980, **184**, 1.