DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL
ENERGY STORAGE SYSTEM

Quarterly Report

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RESEARCH SUMMARY

During the past 3-month period we completed a study of a series of copper(I) compounds which contain a strongly absorbing chromophore (e.g. $\text{CuBr}(\text{PPh}_3)-(2,2'\text{-bipyridine})$). The generally low sensitization efficiencies of these compounds preclude their use as sensitizers in a practical photochemical energy storage system. Nevertheless, some interesting mechanistic information has emerged from this study, the full details of which are being written for publication.

We have also examined the related compound, $\text{Ru}(\text{bipy})_2(\text{NBD})^{+2}$, which features a norbornadiene molecule coordinated directly to a strongly absorbing metal containing fragment.¹ Our original rationale for studying this compound was the expectation that the absorption of visible light would result in the population of an electronically excited state in which the electron density of the NBD is considerably perturbed. Relaxation of this state could then occur by a pathway which leads to the rearranged product, quadricyclene. We find, however, that the sensitization efficiency of this compound is quite low. A possible explanation for this behavior is that any Q formed in the photochemical step is thermally reconverted to NBD by the d^6 Ru center. Some precedent for Ru compounds acting as catalysts for this back reaction has in fact been reported.²

A comprehensive study of the factors which affect the sensitization efficiencies of $\text{Ir}(\text{bipy})_2(\text{bipy}')\text{OH}_2^{+3}$ is underway. We have encountered some difficulty in reproducing the literature synthesis³ of this compound and thus have had to make some modifications in the preparative method. At present we are studying the effects of the environment of the sensitizer upon its absorption and emission spectra, excited state lifetime, and sensitization efficiency. This work, which is being continued during the present 3-month period, should enhance our understanding of the mechanism of sensitization as well as allow us to optimize the overall performance of the sensitizer.

In order to elucidate the mechanism(s) by which organic sensitizers effect the conversion of norbornadiene to quadricyclene, we have undertaken a study to measure the actual rate constant for the sensitization process. If the mechanism were exclusively physical energy transfer, the rate constant should be a predictable function of the

energy difference between the triplet state of norbornadiene ($E_t \sim 70 \text{ Kcal-mole}^{-1}$) and that of the sensitizer. Positive deviations from this relationship imply the existence of an additional mechanism. We have been seeking such evidence in order to design new and more effective sensitizers. Unfortunately, the measurement of such rate constants is not only a difficult and time consuming process, but for many sensitizers no direct method is available for doing so. Consequently only those sensitizers which are amenable to flash photolytic kinetic spectroscopy or which exhibit weak fluid solution phosphorescence lend themselves to direct analysis. For key sensitizers not included in this category we have attempted to measure the rate constants by a combination of Stern-Vollmer kinetic analysis and indirect excited state lifetime measurements involving diffusion-controlled exothermic energy transfer. Our results along with those available from the literature are presented in Table I. Except for one value obtained for Michler's Ketone, the data are in accord with energy transfer as the exclusive mechanism.

As a part of the study to quantitatively evaluate the performance of silica-bound photosensitizers, we measured the variation in quantum efficiency (for quadricyclene formation) as a function of norbornadiene concentration using sensitizer 1. By Stern-Vollmer analysis, a good linear relationship (corr. coeff. 0.995) was obtained with values of 4.13 and 1.86 for the intercept and slope respectively. These data translate into a maximum limiting efficiency of 24%. In view of the many desirable properties of the silica support, we have attempted to identify the source of this

inefficiency. As indicated above, the rate constant for sensitization is related to triplet energy. Accordingly we have measured the triplet energy of 1 by phosphorescence techniques and found it to be $57 \text{ Kcal-mole}^{-1}$. This extraordinarily low value

requires that energy transfer be endothermic by some $13 \text{ Kcal-mole}^{-1}$. Consequently the performance of I_2 , which we initially regarded as being inefficient, must be considered as remarkably efficient in view of the high endothermicity. Further experiments on this interesting system are in progress.

Table 1. Rate Constants for the Sensitization of Quadricyclene Formation

Sensitizer (technique)	$E_t \text{ (Kcal-mole}^{-1}\text{)}$	Solvent	$k \text{ (M}^{-1}\text{-sec}^{-1}\text{)}$
acetophenone (2)	74.1	acetonitrile	7.0×10^9
acetophenone (1)	73.7	benzene	3.9×10^9
benzophenone (2)	69.2	acetonitrile	1.1×10^9
benzophenone (1)	68.6	benzene	9.7×10^8
benzophenone (3)	68.5	cyclohexane	8.6×10^8
dimethylaminobenzophenone(3) 66		cyclohexane	2.8×10^8
dimethylaminobenzophenone(3) 65		acetonitrile	3.5×10^8
Micheler's Ketone (2)	~ 63	cyclohexane	4.4×10^8
Micheler's Ketone (1)	~ 63	benzene	6.8×10^7
2-naphthaldehyde	59.5	benzene	8.6×10^5
2-acetonaphthone (1)	59.3	benzene	1.6×10^6
biacetyl (1)	54.9	benzene	2.8×10^5
benzil (2)	54.3	acetonitrile	4.4×10^5
benzil (1)	53.7	benzene	9.2×10^5
benzil (2)	53.4	cyclohexane	3.3×10^5
fluorenone (1)	53.3	benzene	4.6×10^5

technique: (1) flash kinetic spectroscopy ref. 4 ; (2) phosphorescence lifetime - single photon counting technique ; (3) indirect Stern-Vollmer analysis

References

1. B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehmann, and A. Ludi, J. Am. Chem. Soc., 99, 7368 (1977).
2. Quarterly report of work performed during period June 15-September 14, 1975 under DOE Contract EY-76-S-09-0893.
3. R. J. Watts, J. S. Harrington, and J. Van Houten, J. Am. Chem. Soc., 99, 2179 (1977).
4. A.J.G. Barwise et al., J. Am. Chem. Soc., 100, 1814 (1978).