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MASTER

DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL
ENERGY STORAGE SYSTEM

Quarterly Report

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The emphasis of our work during this past quarter has been on improvement of the performance of immobilized photosensitizers. Prolonged use of Polymer N in the recycling prototype has resulted in gradual deterioration of the behavior

(P) : polystyrene-matrix

of this photosensitizer. Furthermore the opacity of the beads results in an inherent 20% loss in efficiency apparently through light reflection. In an attempt to improve the characteristics with respect to these points we have devoted considerable effort in the synthetic grafting of sensitizer chromophores to glass surfaces. Some success has already been achieved, and we are pleased to report the first successful silica-grafted photosensitizer. Our experience with the polystyrene grafted sensitizers, such as polymer N, has shown that details concerning the synthetic pathway (such as per cent loading, types of site-site interactions, particle size and synthetic sequence) markedly influence the performance. Clearly, enhanced characteristics can be expected with systematic refinements. Our preliminary results on both organic and inorganic systems are described below.

ORGANIC SENSITIZERS

In order to compare the photochemistry in solution to that of the chromophore on polymer N, 4-dimethylamino-4'-methylbenzophenone was synthesized. This compound should be very similar to N-polymer in its photophysical properties. The comparison was performed at 366 nm using benzene as the solvent and varying the initial concentration of norbornadiene. By plotting the inverse of the quantum yield of quadricyclene versus the inverse of the concentration of the norbornadiene, the reciprocal of the y-intercept will be the limiting quantum yield for quadricyclene formation. The homogeneous sensitizer was found to have a limiting quantum efficiency of 1.00 versus 0.78 for the heterogeneous sensitizer (N-polymer). The difference in these values is probably due to the fact that the heterogeneous sensitizer is wasting energy by reflection and scattering of the light.

A new class of heterogeneous sensitizers using silica gel as the support was evaluated. The chromophore is bound to the silica gel by a silicon to carbon bond (sensitizer SG1). The procedure is described below. Silica gel was dried at

400–500°C for six hours under H₂ flow. This leaves only isolated (non-adjacent) hydroxyl groups. The remaining OH groups were converted to Cl by treatment with CCl₄ vapor in N₂ flow at 450–550°C. Chlorine loading was generally determined by titration of the acid liberated on hydrolysis. Analysis of three batches gave Cl content ranging from 1.22 to 1.55 meq/g.

Two routes, differing only in the method of forming lithiophenyl silica, were employed for photosensitizer synthesis.

Method 1 (reaction 2) proceeds through treatment of chlorinated silica gel with 1 equivalent of p-lithiobromobenzene per chlorine. p-Bromophenyllithium

was prepared from the required quantity of n-butyllithium and a six to eight fold excess of p-dibromobenzene (the excess is required to prevent formation of dilithiobenzene or lithiated phenyl silica; reaction 3.) Treatment of p-bromophenyl silica with 1 equivalent of n-butyl lithium in ether produces what is assumed to be p-lithiophenyl silica. (The available Br is assumed to be the same as initial available Cl).

In method 2 (reaction 4), the chlorinated silica is treated with one equivalent of phenyl lithium in ether followed by deprotonation with n-butyl lithium-tetramethylethylenediamine in cyclohexane to give lithio phenyl silica. The site of lithiation (p, o, m) is uncertain in this procedure. The procedure is quite analogous to that employed for polystyrene.

Treatment of the lithiophenylsilica with a large excess (6-8x) of methyl-4-(N,N-dimethylamino)benzoate forms the supported analogue of 4-(N,N-dimethylamino) benzophenone (reaction 5).

Reasonable UV-visible transmission spectra can be obtained on these sensitizers. The sensitizer is mixed with 5 to 10 parts unfunctionalized silica gel and spectra are run in solvent mixture versus unfunctionalized silica in 1 mm path length cells. The $\lambda_{\max}$ is solvent dependent and somewhat variable from preparation to preparation, however the values of 335-350 nm in non polar solvent (benzene or cyclohexane) is consistent with the proper ketone functionality. Treatment of the silica sensitizers with acid and then observation of the spectrum generally reveals an absorption band >400 nm assigned as arising from the triphenylcarbinol with N,N-dimethylamino substituent.

An authentic sample of supported carbinol, prepared by treatment of lithio phenyl silica with 4 (N,N-dimethylamino)benzophenone, also shows this behavior in acid.

Notably, two batches of silica prepared with 50-75% lithiation of available phenyl's did not give this behavior with acid treatment.

Reactions

1) G = silica gel matrix; silicon is a surface atom

The limiting quantum in benzene for the initially prepared sample of this sensitizer was 0.2 at 366 nm which was smaller by approximately a factor of four compared to N-polymer under similar conditions. Work is currently in progress to determine the source of the inefficiency and to improve the characteristics.

INORGANIC SENSITIZERS

During the past quarter we have continued our investigation of the attractive sensitizer, $\text{Ir}(\text{bipy})_2(\text{bipy}')\text{OH}_2^{+3}$. While this compound exhibits a high sensitization efficiency in homogeneous solution, we have found that it loses much of its effectiveness when immobilized onto a polystyrene matrix. The reason for this effect is not

N-N = bipy (2,2'-bipyridine)

clear, and attempts to characterize the immobilized sensitizer by electronic spectroscopy have been unsuccessful due to the opaqueness of the polymer matrix. In an attempt to circumvent this difficulty, we have recently prepared a carboxylated silica gel via the sequence shown in eqn. 1. Significantly, we find that $\text{Ir}(\text{bipy})_2(\text{bipy}')\text{OH}_2^{+3}$ immobilized onto this nearly transparent support functions as a very

efficient (quantum efficiency ≥ 0.5) sensitizer. This extremely encouraging initial result is currently being repeated, and studies under a variety of experimental conditions will be undertaken during the next quarter.