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DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL
ENERGY STORAGE SYSTEM

Quarterly Report, July 1—September 30, 1977

By
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September 15, 1977

Work Performed Under Contract No. EY-76-S-09-0893

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U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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CATALYSIS OF THE CONVERSION OF NORBORNADIENE TO QUADRICYCLANE

During this quarter the portion of this project concerned with catalysis has concentrated on the development of increased understanding of the cobalt(II) porphyrin catalyst discussed in previous quarterly reports.^{1,2} Of potential importance is the observation that the activity of partially deactivated catalysts can be partially restored by treatment with titanium(III) solutions thereby suggesting that a major cause of the losses of activity of catalysts upon repeated recycling arises from oxidation of cobalt(II) to cobalt(III). During this quarter we have also studied in detail the previously discovered³ molybdenum catalyst $[(CF_3)_2C_2S_2]_3Mo$ and the closely related nickel catalyst $[(CF_3)_2C_2S_2]_2Ni$.

Cobalt(II) Porphyrin Catalysts

Several new batches of both carboxamide-linked (I) and sulfonamide-linked (II) polystyrene-anchored cobalt(II) porphyrin catalysts have been prepared by previously reported methods.^{1,2} Their rates of reaction for the conversion of quadricyclane to norbornadiene relative to their cobalt contents are summarized in Table 1. In this table batches 16B-3A and 16B-5A are carboxamide-linked; all other batches are sulfonamide linked. All rates listed in Table 1 were determined using 10 ml. of 0.1M. quadricyclane in benzene and are the average of at least two rate determinations.

A charge of polymer batch 16A-1A was subjected to extensive recycling (Table 2). In general some decrease in activity was noted for each successive run. After runs 6, 8, 14, 17, 18, and 19 the catalyst was reduced with titanium(III) chloride solutions prepared as specified. In all cases this titanium(III) reduction resulted in some restoration of the lost catalytic activity but never to the initial value (run 1). After run 21 the catalyst was treated with potassium benzophenone ketyl in tetrahydrofuran. This was also effective in restoring lost catalytic activity but appeared to change the nature of the catalyst. Thus after potassium benzophenone ketyl reduction the normally maroon catalyst beads became green, possibly because of reduction to cobalt(I). The green color of these highly reduced beads persisted upon exposure to air.

Table 1
Standard Rates of Reaction for Polymer Bound
Cobalt(II) Tetraphenylporphyrin Derivatives

BATCH	% Co	moles Co per gram	$\frac{kw}{\text{sec}^{-1} (\text{g/l})^{-1}}$	$\frac{km}{\text{sec}^{-1} (\text{mole/l})^{-1}}$
16A-1A	0.45	7.6×10^{-5}	1.90×10^{-4} $\pm .34 \times 10^{-4}$	2.50 $\pm .45$
16A-2A	0.34	5.8×10^{-5}	2.28×10^{-4} $\pm .19 \times 10^{-4}$	3.95 $\pm .33$
16B-1A	0.31	5.3×10^{-5}	2.20×10^{-4} $\pm .25 \times 10^{-4}$	4.18 $\pm .48$
16B-2A	0.28	4.8×10^{-5}	8.02×10^{-5} $\pm .15 \times 10^{-5}$	1.69 $\pm .32$
16B-3A	0.45	7.6×10^{-5}	1.43×10^{-4} $\pm .26 \times 10^{-4}$	1.87 $\pm .34$
16B-4A	0.48	8.2×10^{-5}	1.55×10^{-4} $\pm .14 \times 10^{-4}$	1.90 $\pm .17$
16B-5A	0.46	7.8×10^{-5}	4.26×10^{-6} $\pm .37 \times 10^{-6}$	0.055 $\pm .0047$

Table 2
Recycling Study

0.1069 g batch sulfonamide-linked polymer 16A-1A; 10. ml 0.1 M quadricyclane in benzene

Run	$k_w (\text{sec}^{-1} (\text{g/l})^{-1}) \times 10^4$ [note a]
1	2.59 $\pm$.042
2	1.84 $\pm$.047
3	1.44 $\pm$.019
4	1.29 $\pm$.013
5	1.39 $\pm$.012
6	1.31 $\pm$.011
Reduction 1 [note b]	
7	1.67 $\pm$.022
8	1.56 $\pm$.013
Reduction 2 [note b]	
9	1.71 $\pm$.012
10	1.55 $\pm$.012
11	1.46 $\pm$.0090
12	1.39 $\pm$.0079
13	1.37 $\pm$.0082
14	1.34 $\pm$.0099
neat quadricyclane, 10 ml, no. 1	
15	0.695 $\pm$.0037
neat quadricyclane, 10 ml, no. 2	
16	0.502 $\pm$.0081
17	0.530 $\pm$.0075
Reduction 3 [note b]	
18	0.727 $\pm$.0090
Reduction 4 [note b]	
19	0.830 $\pm$.0086
Reduction 5 [note b]	
20	0.979 $\pm$.019
21	0.874 $\pm$.0097
Reduction 6 [note b]	
22	1.07 $\pm$.020
23	1.04 $\pm$.012

Notes

[a] kw; weight normalized rate constant.

The error represents internal consistency of the run, initial error in weighing out the catalyst, and error in measuring the volume of reaction solution. Physical loss and temperature error are not considered.

[b] Reductions:

The following reduction solutions, volumes and times were used. Appropriate washing followed. All operations were under H_2 .

Reduction 1

Solution: 4 ml $TcCl_3$, 30 ml CH_3OH , evacuated to near dryness (similiquid paste), then added 80 ml THF, excess Sn metal. Stirred 12 hours, red-brown solution.

Reduction: 5.0 ml of solution, 30 minutes

Reduction 2

Solution: 5 ml $TcCl_3$ per 50 ml CH_3OH , excess Sn metal
stirred 1 hour, then the flask was evacuated to remove excess HCl.
blue solution.

Reduction: 5 ml solution, 30 minutes

Reduction 3

Solution: from reduction 2, turquoise-green

Reduction: 5 ml, decolorized after 15 minutes

5 ml more added, stirred 45 minutes.

Reduction 4

Solution: 4 ml $TcCl_4$ in 20 ml benzene, then 10 ml CH_3OH , after 10 minutes
50 ml THF and excess Zn
stirred 4 hours. Solution maroon in color.

Reduction: 5 ml for 1 hour

Reduction 5

Solution: from reduction 4

Reduction: 10 ml for 12 hours

Reduction 6

Solution: Potassium benzophenone ketyl in THF

1.0 g benzophenone, 50 ml THF, excess K

stir 24 hours. solution purple (opaque).

Reduction: 5.0 ml, 12 hours.

Reductions 1 to 5 gave polymer in various shades of red. Reduction 6 gave a dark green polymer and probably contains Co^{I} TPP.

In order to evaluate the effects of diffusion on apparent catalytic activity some kinetic runs were performed on a finely powdered sulfonamide-linked catalyst (II) with increased accessible surface area relative to the normally used beads. This enhanced considerably the catalytic activity of the polystyrene-anchored cobalt(II) porphyrin by factors of 6 to 9 thereby indicating that the reaction rates with the originally used polystyrene bead catalysts were diffusion limited. Specific rate data with various quantities of finely grouped porphyrin II are summarized in Table 3. While this dependence of the reaction rate on the particle size is a rather substantial experimental difficulty in evaluating the effects of various parameters on the reaction rates, it could have some use in a practical photochemical energy storage system. Thus the rates of reaction (i.e. apparent activity of the catalyst) in the catalytic reactor for the conversion of quadricyclane to norbornadiene in the photochemical energy storage system can be simply controlled by varying the sizes of catalyst beads.

Table 3
 R_o versus Weight of Catalyst for
Ground Powder Catalyst of Batch 16A-1A

Run	W(mg)	V(ml)	$\frac{W}{V} (\frac{g}{e})$	$k_o (\text{sec}^{-1})$
1	6.968	10.50	0.6638	3.63×10^{-4}
2	7.557	9.799	0.7712	4.68×10^{-4}
3	10.127	10.00	1.013	7.29×10^{-4}
4	15.647	10.01	1.572	1.614×10^{-3}

All runs used the same prepared solution of 0.1 M quadricyclane in benzene.

$[(CF_3)_2C_2S_2]_3Mo$ and $[(CF_3)_2C_2S_2]_2Ni$ as catalysts

The two complexes $[(CF_3)_2C_2S_2]_3Mo$ and $[(CF_3)_2C_2S_2]_2Ni$ derived from bis(trifluoromethyl)dithietene and some of their reduction products were evaluated as catalysts for the conversion of norbornadiene to quadricyclane (Table 4) using a variety of solvents in the cases of the neutral compounds. In general only the neutral compounds $[(CF_3)_2C_2S_2]_3Mo$ and $[(CF_3)_2C_2S_2]_2Ni$ had catalytic activity; reductions of these compounds to the corresponding mono- and dianions immediately resulted in loss of their catalytic activity. The choice of solvent was also rather critical. Thus treatment of quadricyclane with $[(CF_3)_2C_2S_2]_3Mo$ in dichloromethane resulted in considerable amounts of polymerization, in benzene resulted in considerable amounts of norbornadiene as well as polymer formation, in pyridine resulted in no catalytic activity presumably because of reduction to the catalytically inactive anion, and in acetone resulted in a rapid and exothermic reaction to give an as yet unidentified adduct but none of the desired norbornadiene. These results, although not yet fully interpreted, suggest that $[(CF_3)_2C_2S_2]_3Mo$ is not likely to be a useful catalyst for the photochemical energy storage system. Furthermore, the loss of catalytic activity of $[(CF_3)_2C_2S_2]_3Mo$ upon reduction to anion precludes anchoring a catalytic active system with this structural unit onto an ion exchange polymer. However, before abandoning this approach completely for the development of a catalyst for our photochemical energy storage system, we plan to prepare other $(R_2C_2S_2)_3Mo$ and $(R_2C_2S_2)_2Ni$ derivatives ($R \neq CF_3$) and evaluate their catalytic activities in order to see whether such modification of substituents might lead to more useful systems.

Table 4 $[(CF_3)_2C_2S_2]_3Mo$ AND $[(CF_3)_2C_2S_2]_2Ni$ AND THEIR DERIVATIVES AS
CATALYSTS FOR THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE

Compound	Solvent	Catalyst Concentration mmole/liter	Quadricyclane Concentration mole/l			Notes
			t=0	t=30 min.	t=20 hr.	
$[(CF_3)_2C_2S_2]_3Mo$	CH_2Cl_2	0.947	0.48	0.44	?(polymer)	polymerization
	C_6H_6	0.947	0.41	0.25	0.0	some polymer
	norbornadiene	0.947	0.58	0.58	0.51	some polymer
	hexane	0.947	0.61	0.51	0.36	some polymer
	CH_3OH/THF	0.947	0.56	0.56	0.46	
	pyridine	0.947	0.12	0.12	0.12	
	$(CH_3)_2CO$	0.947	0.48	0.00		no norbornadiene
$[(C_6H_5)_4As]^+ [(CF_3)_2C_2S_2]_3Mo^{2-}$	C_6H_6	0.947	0.46	0.43	0.42	
	$(CH_3)_2CO$	0.947	0.63	0.63	0.60	
$[C_6H_5)_4As]^+ [(CF_3)_2C_2S_2]_3Mo^{2-}$	C_6H_6	0.947	0.49	0.48	0.47	
$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2] Mo[S_2C_2(CF_3)_2]_2$	C_6H_6	0.947	0.64	0.64	0.62	
$[(CF_3)_2C_2S_2]_2Ni$	CH_2Cl_2	3.78	1.02	0.88	0.65	no polymer
	$(CH_3)_2CO$	3.78	1.00	1.00	0.78	
	norbornadiene	3.78	0.95	0.93	0.79	small amount of polymer
$[(C_2H_5)_4N]^+ [(CF_3)_2C_2S_2]_2Ni^-$	CH_2Cl_2	3.54	1.1	1.1	1.1	
$[(C_2H_5)_4N]^+ [(CF_3)_2C_2S_2]_2Ni^{2-}$	CH_2Cl_2	3.99	1.2	1.2	1.2	

ORGANIC SENSITIZERS

The quantum efficiency as a function of norbornadiene concentration has been studied using N-polymer as a sensitizer and hexane as a solvent. This presents analytical problems for the measured norbornadiene concentration after equilibration with the polymer.⁴ Therefore benzene was used in the following study because it does not produce any significant concentration change (through polymer adsorption). The following results were obtained at 313 and 366 nm with benzene as the solvent:

[norbornadiene], M	ϕ (313 nm)	[norbornadiene], M	ϕ (366 nm)
.50	.50	.50	.51
.25	.38	.25	.44
.101	.24	.10	.33
.05	.15	---	---

The limiting quantum efficiency evaluated by a Stern Volmer treatment is .68 at 313 and .58 at 366 nm. The efficiency of N-polymer sensitization is being probed using stilbene isomerization, but these studies have been complicated due to preferential selectivity of the polymer for cis and trans-stilbene (relative to the solvent).

Efforts have continued to find a sensitizer whose absorption spectrum better overlaps that of the solar spectrum. Thiobenzophenone (λ_{max} = 599 nm, ethanol) and di-t-butylthio ketone (λ_{max} = 535 nm in benzene) were prepared but did not appreciably sensitize the conversion of norb. to quadricyclene when irradiated at 408 nm in benzene. The respective polymer sensitizers were not prepared due to synthetic obstacles. Efforts are in progress, however, to synthesize O-ethyl-1-thionaphthoate(1) which is known to an efficient sensitizer.⁵ It can also easily be incorporated onto a polymer(2):

INORGANIC SENSITIZERS

During the past quarter we have examined the effectiveness of some new classes of potential transition metal sensitizers. Compounds of the general formula $M(CO)_4(bipy)$ (bipy is 2,2' - bipyridine) are strongly colored and, furthermore, undergo ready substitution of one CO group.⁶ It was hoped that this ligand lability could be exploited to form a highly absorbing $M(CO)_3(bipy)(NBD)$ species in the presence of excess norbornadiene (NBD). It became apparent quite early in the study, however, that these compounds were unsuitable as sensitizers. Thus solutions of each compound in benzene - NBD were significantly lighter in color upon standing overnight in the dark. Exposure to light hastened this process and also caused formation of a white precipitate. Similar behavior was noted for the analogous $Mo(CO)_3(bipy)(PPh_3)$ and $Mo(CO)_2(bipy)(PPh_3)_2$ compounds. Irradiation of the above solutions with 366 nm light yielded no detectable quadricyclene. Consequently, further studies of these compounds were abandoned.

Compounds of general formula $\text{CuBr}(\text{PR}_3)(\text{N-N})$ (where R is an alkyl group and N-N is bipy or 1,10-phenanthroline (phen)) possess low lying $\text{Cu} \rightarrow \text{N-N}$ charge transfer transitions which extend into the visible wavelength region. It is possible that sensitization may occur via energy transfer from the photoexcited Cu(I) compound, similar to the behavior we have observed for $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{BH}_4$.⁷ Alternatively, by employing a bulky R group such as n-butyl, it should be possible to labilize the phosphine ligand toward substitution by NBD and thereby generate a strongly absorbing $(\text{N-N})\text{BrCu-NBD}$ species. Some pertinent photochemical data (ϕ is quantum yield for quadricyclene formation) obtained upon irradiation at 313 or 366 nm is listed in the table below.

Sensitizer	ϕ 313 nm	ϕ 366 nm
$\text{CuBr}(\text{PPh}_3)\text{bipy}$	0.2	<0.01
$\text{CuBr}(\text{PPh}_3)\text{phen}$	.03	<0.01

Clearly, the low quantum yields discourage the use of these compounds as sensitizers. Further work is underway to test the effectiveness of $\text{CuBr}[\text{P}(\text{n-butyl})_3](\text{N-N})$ type compounds which contain a bulky, and thus more readily displaceable, phosphine ligand.

Miscellaneous

The following papers concerning this project have been presented recently:

- (1) R. B. King, E. M. Sweet, and R. M. Hanes, "Attached Metal Complex Catalysts for a Solar Energy Storage System," presented at a Symposium on the Design and Characterization of Supported Metal Complex Catalysts held on August 31, 1977, at the National Meeting of the American Chemical Society in Chicago, Illinois: see Petroleum Division Abstracts, p. 1201.
- (2) C. Kotal, "Use of Transition Metal Compounds to Sensitize an Energy Storage Reaction," presented at a Symposium on Organometallic and Inorganic Photochemistry held on August 31, 1977, at the National Meeting of the American Chemical Society in Chicago, Illinois: see Inorganic Division Abstracts, paper 120.

REFERENCES

- (1) Quarterly report of ERDA Contract E(38-1)-893 dated December 15, 1976.
- (2) Quarterly report of ERDA Contract E(38-1)-893 dated March 15, 1977.
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- (6) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).
- (7) P. A. Grutsch and C. Kotal, *J. Am. Chem. Soc.*, 99, 6460 (1977).