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DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL ENERGY
STORAGE SYSTEM

Annual Report, June 15, 1977—June 14, 1978

By
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Charles R. Kutal

March 15, 1978

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

Department of Chemistry
University of Georgia
Athens, Georgia

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U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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Abstract

Significant progress has been made in several areas over the past year. Quantitative measurements evaluating organic sensitizers and catalysts have been carried out. An exciting new transition metal sensitizer has been discovered. A comprehensive evaluation of the characteristics of polystyrene based heterogeneous sensitizers and catalysts has been made. Recently we have successfully synthesized the first glass functionalized photosensitizers. This new class of heterogeneous supports offers several attractive features.

ORGANIC SENSITIZERS

During the past year our efforts have included (1) a detailed mechanistic study of the sensitization of the norbornadiene to quadricyclene conversion by commonly-used organic photosensitizers; (2) investigations concerning the potential use of thiocarbonyl derivatives as sensitizers; (3) a quantitative evaluation of polystyrene immobilized sensitizers; and, (4) most recently, the synthesis and preliminary evaluation of glass immobilized sensitizers as an alternative class of heterogeneous photosensitizers. The results of each of these areas will be briefly reviewed. More detailed information has been reported in the quarterly reports submitted during the year.

In an attempt to uncover evidence for existing sensitization mechanisms other than triplet-triplet energy transfer for the norbornadiene to quadricyclene conversion, we have measured the actual rate constants for quenching of the photosensitizer excited state by norbornadiene. The rate, k , at which norbornadiene quenches the excited state is given by equation 1 (where ΔE_T is the difference in triplet energies of the sensitizer and norbornadiene) if the exclusive mechanism for quenching is triplet-triplet energy transfer. Any additional mechanism for quenching by a given sensitizer would enhance the measured value of k

$$\frac{\Delta \log k}{\Delta E_T} = \frac{1}{2.3 RT} \quad \text{eqn. 1}$$

over that predicted by eqn. 1. We have measured the specific rate constants for several suitable sensitizers in an attempt to identify positive deviations and have found none, i.e., each of the values so obtained fits the relationship described by eqn. 1 where E_T for norbornadiene is $70 \pm 2 \text{ kcal mole}^{-1}$. The erratic values of the sensitization efficiencies (as a function of E_T) obtained in previous studies and in our initial screenings apparently reflect nothing more than competition with highly variable rates for alternative decay pathways of the various sensitizers.

We have thus concluded, that, while endothermic (as much as 15 kcal-mole⁻¹) energy transfer can result efficient sensitization of the norbornadiene to quadricyclene conversion, there is no need to invoke any mechanism other than physical energy transfer for the specific organic sensitizers we have studied.

Efforts have continued to find a sensitizer whose absorption spectrum better overlaps that of the solar spectrum and several thiocarbonyl derivatives have been synthesized and evaluated. Thiobenzophene ($\lambda_{\text{max}} = 599 \text{ nm}$, ethanol) and di-*t*-butylthioketone ($\lambda_{\text{max}} = 535 \text{ nm}$ in benzene) were prepared but did not appreciably sensitize the conversion of norbornadiene to quadricyclene when irradiated at 408 nm in benzene.

The bright yellow thioester (1) was tested as a sensitizer for the conversion of norbornadiene to quadricyclene at 405.8 nm. The concentration of (1) was 5.51×10^{-3} molar in each sample and the concentration of norbornadiene was varied. The samples were photolyzed for 37 hrs, after first being freeze-thaw degassed for four cycles. No loss of norbornadiene or appearance of quadricyclene was observed, but the color of (1) went from bright yellow to colorless.

In order to test the ability of 1 to act as a sensitizer the thioester was used to sensitize the conversion of t-stilbene to cis-stilbene. The following results were obtained:

<u>[t-stilbene]</u>	<u>ϕ_{cis}</u>
9.73×10^{-3}	0.47
3.41×10^{-3}	0.29
9.73×10^{-4}	0.15

If a plot of ϕ_{cis}^{-1} vs. $[\text{trans}]^{-1}$ is made by y intercept is 1.85. Therefore the limiting ϕ for cis is about .55 which shows that the sensitizer is very efficient for acceptors whose E_T is low enough to permit energy transfer to occur. For norbornadiene the E_T must be too high to allow energy transfer to occur at a sufficiently rapid rate to compete with other decay processes of the sensitizer. The synthesis and evaluation of higher energy analogs 2, 3 and 4 is currently in progress.

2: $x = -H$

3: $x = -NO_2$

4: $x = (CH_3)_2N-$

Quantitative studies involving polymer N have been carried out. Polymer N was prepared by the following reaction sequence using a macroreticular polystyrene resin which is cross-linked with divinylbenzene.

Analysis indicated 0.343 meq/gram of nitrogen which is a 3.7% ring substitution. The nitrogen content alone does not verify the structure of the polymer, for the synthetic conditions allow "site-site" interaction. The lithiated polystyrene after initially attacking the ester could conceivably attack again to give the precursor to a tertiary alcohol and we have recently obtained spectral evidence for such.

The extent to which this interferes with the performance of polymer N has not yet been ascertained. Studies involving the quantum efficiency of sensitization as a function of norbornadiene concentration have been carefully done and compared with the monomeric counterpart, 5.

The limiting quantum efficiency for 5 was found to be 100% whereas that for polymer N was found to be 78%. This has been attributed to light losses due to reflection from the translucent polymer surface.

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 limiting quantum yield in benzene for the initially prepared sample of this sensitizer was 0.2 at 366 nm. This is lower by 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. 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.

INORGANIC SENSITIZERS

During the past year we have continued to search for new, improved transition metal sensitizers as well as attempt to optimize the effectiveness of existing ones. One strategy we have employed centers upon the incorporation of a strongly absorbing chromophore into a transition metal compound which can coordinate a molecule of NBD. Thus compounds such as $\text{Cu}(\text{phen})\text{BrPPh}_3$, $\text{Cu}(\text{bipy})\text{BrPPh}_3$, $\text{Mo}(\text{CO})_4(\text{bipy})$, and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{bipy})$ (phen is 1,10-phenanthroline, bipy is 2,2'-bipyridine) were tested but found to be ineffective and/or prone to decomposition. The recently reported $\text{Ru}(\text{bipy})_2(\text{NBD})$ represents an intriguing example of this type, and its sensitization behavior is currently being examined.

Second and third row transition metal compounds containing ligands with delocalized π systems (some examples are listed in Table 1) display several interesting properties. To wit --

- (i) the absorption spectrum appreciably overlaps the wavelength region of available solar radiation,
- (ii) the ground state is generally inert to ligand substitution processes,
- (iii) the lowest lying excited state, which can be quite long-lived ($\sim 1 \mu\text{sec}$) in room temperature fluid solution, undergoes a diverse assortment of intermolecular processes with added substrates) recently reported examples include oxidation-reduction and electronic energy transfer.

The features noted above make these transition metal compounds exceedingly attractive as potential sensitizers for the NBD to Q conversion. Thus we have recently undertaken an exploratory study aimed at screening a variety of candidates. Our preliminary quantum yield data are collected in Table 1 along with the orbital assignment and approximate energy, E_L , of the lowest lying excited state in each of the compounds examined.

Table I.

Quantum Yields for Q Production in the Presence of Transition Metal Compounds Containing Ligands with Delocalized π Systems

Compound ^a	Nature of Lowest Lying Excited State ^b	E_L^c (kcal)	Solvent	Quantum Yield (at 366 nm)
$\text{Ru}(\text{bipy})_3^{+2}$	$d\pi^*$	49	5% methanol - 95% benzene	$< 2 \times 10^{-3}$
$\text{Ru}(\text{phen})_3^{+2}$	$d\pi^*$	50	20% ethanol - 80% cyclohexane	$< 6 \times 10^{-3}$
$\text{cis-Ir}(\text{phen})_2\text{Cl}_2^+$	$d\pi^*$ or $d-d$	60	20% ethanol - 80% cyclohexane	$< 4 \times 10^{-3}$
$\text{Rh}(\text{phen})_3^{+3}$	$\pi\pi^*$	63	20% ethanol - 80% cyclohexane	$< 4 \times 10^{-3}$
$\text{Ir}(\text{bipy})_2(\text{OH}_2)(\text{bipy}')^{+3 d}$	$\pi\pi^*$	61	5% methanol - 95% benzene	0.7
$\text{Ir}(\text{bipy})_2(\text{OH})(\text{bipy}')^{+2 e}$	$\pi\pi^*$	64	methanol	0.09

^a[NBD] = 0.5 M unless otherwise stated

^bOrbital designations have the following meaning: $d\pi^*$, metal to ligand charge transfer state; $d-d$, ligand field state; $\pi\pi^*$, ligand localized state. In cases where configurational mixing is important, only the predominant contributing state is listed.

^cApproximate energy of lowest lying excited state in compound.

^dbipy' denotes a monodentate bound 2,2'-bipyridine ligand

^e[NBD] = 0.1 M

The high sensitization efficiency of $[\text{Ir}(\text{bipy})_2(\text{OH}_2)(\text{bipy}')]^{+3}$ (Structure 1)

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

is surprising, at least to the extent that the energy and orbital parentage of its lowest excited state are comparable to those of other compounds tested. It is interesting to note that electronic energy transfer from this state to the lowest triplet in NBD would be endothermic by ~ 6 kcal. While an energy barrier of this magnitude should hamper efficient sensitization because of an unfavorable Boltzmann factor, the long excited state lifetime of the sensitizer would tend to ameliorate this effect. Thus energy transfer presents a viable, but by no means exclusive, pathway for sensitization. Clearly, further work is required to resolve this question.

Another attractive feature of $[\text{Ir}(\text{Bipy})_2(\text{OH}_2)(\text{bipy}')]^{+3}$ (or any charged sensitizer) is the ease with which it can be immobilized onto a solid support. We have recently prepared a sample of carboxylated silica gel via the reactions shown in eqn. 1. Immobilization is accomplished by equilibrating a solution of $[\text{Ir}(\text{bipy})_2(\text{OH}_2)(\text{bipy})]^{+3}$ with the functionalized silica. Initial studies have shown that the resultant

heterogeneous sensitizer is quite effective (quantum efficiency ≥ 0.5) in effecting the NBD to Q conversion. Studies aimed at characterizing the immobilized transition metal compound and improving its sensitization efficiency are planned for the coming year.

CATALYSIS OF THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE

Our work last year concentrated on the development of effective catalysts for the conversion of quadricyclane to norbornadiene based on triphenylcyclopropenylnickel derivatives, polystyrene-anchored cobalt (II) tetraarylporphyrin derivatives, and polystyrene-anchored phosphine palladium (II) chloride complexes.⁸ This year we have investigated in greater detail the kinetics of the conversion of quadricyclane to norbornadiene by the polystyrene-anchored catalysts in efforts to develop systems which retain their catalytic activities upon repeated recycling. In addition, we have investigated in greater detail the structure-activity relationships of the metal dithiolenes as catalysts for the conversion of quadricyclane to norbornadiene in view of the indications from our preliminary screening results of the catalytic activity of $[(CF_3)_2C_2S_2]_3Mu$.⁹

A. Polymer-Anchored Cobalt(II) Tetraarylporphyrin Catalysts

The polymer-anchored cobalt (II) tetraarylporphyrin catalysts used for the work this past year were linked to macroreticular polystyrene through carboxamide and sulfonamide linkages. The aminopolystyrene used for the preparation of these materials was obtained from unfunctionalized polystyrene by nitration followed by reduction of the nitro groups with stannous chloride. This aminopolystyrene was then coupled with the tetra (p-chlorosulforphenyl)porphine and the tetra (p-chlorocarbonyl)phenylporphine obtained from the respective acids or acid salts to give the sulfonamide-linked and the carboxamide-linked polystyrene-anchored tetraarylporphyrins, respectively. These coupling reactions were effected in chlorinated hydrocarbon solvents using tertiary amines as proton scavengers. Cobalt was incorporated into these polystyrene-anchored tetraarylporphyrins by treatment under nitrogen with cobalt (II) acetate 4-hydrate in boiling acetic acid. The resulting materials can be schematically represented by structures Ia and Ib.

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		Z	R
1a	CARBOXAMIDE LINKED	-CO-	-CO ₂ CH ₃
1b	SULFONAMIDE LINKED	-SO ₂ -	-SO ₃ CH ₃

Five batches of sulfonamide-linked (1a) and two batches of carboxamide-linked (1b) polystyrene-anchored cobalt (II) tetraarylporphyrin catalysts were prepared with cobalt contents ranging from 0.28% to 0.48%. The standard activities with 0.1 M quadricyclane in benzene were measured for each batch (Table 1). The pseudo first order rate constants for disappearance of quadricyclane were obtained with 0.1 g of catalyst in 10 ml of solvent. These rates were normalized to standard activity conditions of 1.0 g/liter (k_w in Table 1) and to an activity based on metal content (k_M in Table 1).

No immediate correlation of activity with the metal content was apparent for these polystyrene-anchored cobalt (II) tetraarylporphyrin catalysts. There was some evidence that non-porphyrin cobalt was present, perhaps bound to unreacted pendant amino groups, since the sulfur/cobalt ratios of two batches were 3.9/1 (batch 2A-1) and 2.7/1 (batch 2B-4) as compared with a theoretical minimum of 4/1 when cobalt is bound only to tetra(p-sulfophenyl)porphine units. However, this observation must be interpreted with caution since elemental analyses are notoriously unreliable for polymer systems.¹⁰

Use of these polystyrene-anchored cobalt (II) tetraarylporphyrin catalysts in a practical photochemical energy storage system requires repeated recycling of the same charge of catalyst. For this reason, the effects of repeated use on the activities of these cobalt catalysts were examined. Thus a single 0.1 g charge of catalyst batch 1A-1 was treated repeatedly with 1.0 M quadricyclane in xylene. The activity (k_w) exhibited a steady decrease correlating well with the total volume of the solution to which the catalyst had been exposed. The extrapolated intercept for zero catalytic activity was 127 ml. corresponding to an average turnover per metal in excess of 15,000 moles of quadricyclane per gram-atom of cobalt. In a similar study on batch 2A-1 using 0.1 M quadricyclane in benzene, the decrease in activity with volume was not as regular (Table 2). Some of the lost catalytic activity could be restored by treatment of the catalyst with strong reducing agents, either titanium (III) in organic solvents or potassium benzophenone ketyl in tetrahydrofuran. This restoration of activity by treatment with strong reducing agents suggests that the loss of catalytic activity upon repeated use arises from oxidation of cobalt (II) to cobalt (III).

TABLE 1
STANDARD ACTIVITIES OF THE POLYSTYRENE-ANCHORED COBALT(II)
TETRAARYLPORPHYRIN CATALYSTS FOR THE CONVERSION OF
QUADRICYCLANE TO NORBORNADIENE

Batch	Linkage ^a	% Co	moles Co x 10 ⁵ /gram	$k_w \times 10^4$ in $\text{sec}^{-1} (\text{g/liter})^{-1}$	k_M in $\text{sec}^{-1} (\text{g-atom Co/liter})^{-1}$
1A-1	C	0.44	7.5	2.42(0.23) ^b	3.2(0.31) ^b
2A-1	S	0.45	7.6	1.95(0.19)	2.6(0.25)
2A-2	S	0.34	5.8	2.15(0.11)	3.7(0.20)
2B-1	S	0.31	5.3	2.07(0.13)	3.9(0.25)
2B-2	S	0.28	4.8	0.88(0.052)	1.8(0.11)
2B-3	C	0.45	7.6	1.37(0.11)	1.8(0.15)
2B-4	S	0.48	8.2	1.73(0.13)	2.1(0.16)

(a) C = carboxamide linked, S = sulfonamide linked.

(b) The figures in parentheses in these columns refer to standard deviations obtained from four or more runs.

TABLE 2
STUDIES ON THE REGENERATION OF RECYCLED
CATALYST USING REDUCING AGENTS^a

Run/Operation	$k_w \times 10^{-4}$ in sec. ⁻¹ (g/liter) ⁻¹
1	2.59(0.042) ^b
2	1.84(0.047)
3	1.44(0.019)
4	1.29(0.013)
5	1.39(0.012)
6	1.31(0.011)
Reduction with titanium (III) in methanol (5 ml. for 30 min.)	
7	1.67(0.022)
8	1.56(0.013)
Reduction with titanium (III) in methanol (5 ml. for 30 min.)	
9	1.71 (0.012)
10	1.55(0.012)
11	1.46(0.0090)
12	1.39(0.0079)
13	1.37(0.0082)
14	1.34(0.0099)
15 ^c	0.69(0.0037)
16 ^c	0.50(0.0081)
17	0.53(0.0075)
Reduction with titanium (III) in methanol (10 ml. for 45 min.)	
18	0.73(0.0090)
Reduction with titanium (III) in tetrahydrofuran (5 ml. for 1 hr.)	
19	0.83(0.0086)
Reduction with titanium (III) in tetrahydrofuran	
20	0.98(0.019)
21	0.87(0.0097)
Reduction with potassium benzophenone ketyl in tetrahydrofuran	
22	1.07(0.020)
23	1.04(0.012)

- (a) These runs were performed in the indicated sequence using 0.107 g of sulfonamide-linked polystyrene-supported cobalt(II) porphyrin from batch 2A-1 (Table 1). Except where indicated 10 ml. of 0.1 M quadricyclane in benzene was used.
- (b) The figures in parentheses in this column represent the error in the first order kinetics plots, volumes of reaction solutions, and initial weight of the catalyst. Variations in temperature ($\pm 0.2^\circ\text{C}$) and physical loss of catalyst on workup are not included.

TABLE 2 (continued)

- (c) These runs were made using neat quadricyclane rather than 10 ml. of 0.1 M quadricyclane in benzene.

Diffusion was shown to reduce the activity of the polystyrene-anchored cobalt (II) tetraarylporphyrin catalysts. Thus when beads of catalyst batch 2A-1 were ground to a fine powder, the activities in four runs (k_w) were greater by factors of 2 to 5 than in any runs using the whole bead catalyst. In the studies with the pulverized catalysts, the standard activities were found to increase with an increase in the ratio of weight of catalyst to the volume of the solution again suggesting that some component of the solution is responsible for the deactivation of the catalyst.

B. Polymer-Anchored Phosphine Palladium (II) Chloride Catalysts

Two batches of a polystyrene-anchored phosphine palladium (II) chloride catalyst were prepared by a procedure similar to that given in the previous annual report.⁸ Thus macroreticular polystyrene beads were diphenylphosphinated by lithiation with *n*-butyllithium¹¹ in the presence of tetramethylethylenediamine followed by addition of diphenylchlorophosphine. Palladium (II) chloride was then complexed with this polymer by stirring in acetonitrile solution to give lemon yellow beads which were active catalysts for the conversion of quadricyclane to norbornadiene. The resulting two batches of beads gave the following elemental analyses: (A) 0.70% Pd, 0.28% P, 0.39% Cl, and (B) 1.36% Pd, 0.97% P, 1.08% Cl, and 0.026% N corresponding to the elemental ratios Pd/P/Cl/N of 1/1.4/1.7/ and 1/2.4/2.4/0.14, respectively. While $(R_3P)_2PdCl_2$ coordination is not required for bonding of the palladium to the polymer, these elemental ratios, particularly the low nitrogen/palladium ratio, indicate that a substantial portion of the palladium may be in such a coordination environment.

The catalytic activities of the polystyrene-anchored phosphine palladium (II) chloride catalysts were measured for both batches A and B (Table 3). Except for the first run with a given charge of catalyst, the disappearance of quadricyclane was found to obey first order kinetics. However, the first run of a given charge was found to give a first order rate decreasing in time. Thus with batch A, the activity of the catalyst appeared to decrease between the first and second use, however, independent analysis of the final portion of the first run gave an activity quite similar to that of the second run. Unused catalyst which had been pretreated

TABLE 3

STANDARD ACTIVITIES OF THE POLYSTYRENE-ANCHORED
PALLADIUM (II) CHLORIDE CATALYSTS FOR THE CONVERSION
OF QUADRICYCLANE TO NORBORNADIENE

<u>System</u>	<u>Solvent</u>	<u>Quadricyclane conc. (M)</u>	<u>$k_w \times 10^4$ in $\text{sec.}^{-1} (\text{g./liter})^{-1}$</u>	<u>k_M in $\text{sec.}^{-1} (\text{g.-atom Pd/liter})^{-1}$</u>
<u>Polymer Batch A, Charge 1</u>				
Run 1	Average	1.0	0.20	0.31
	Initial		0.31	0.47
	Final		0.13	0.02
Run 2	xylene	1.0	0.15	0.23
Run 3	xylene	1.0	0.16	0.24
Run 4	xylene	1.0	0.041	0.062
Run 5	xylene	1.0	0.018	0.028
<u>Polymer Batch A, Charge 2 (pretreated with excess norbornadiene)</u>				
Run 1	xylene	1.0	0.14	0.21
<u>Polymer Batch A, Charge 3</u>				
Run 1	benzene	1.0	0.29	0.44
<u>Polymer Batch B, Charge 1</u>				
Run 1	benzene	1.0	0.94	0.63
Run 2	benzene	1.0	0.36	0.24
Run 3	benzene	1.0	0.19	0.13
Run 4	benzene	1.0	0.10	0.07
<u>$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$</u>				
Run 1	benzene	0.5		80

with norbornadiene was found to give an activity for its initial run similar to that of the second run with untreated catalyst. These observations suggest the formation of a polymer-bound palladium-norbornadiene complex.

The catalytic activities of both batches A and B of the polystyrene-supported phosphine palladium (II) chloride catalyst (Table 3) were found to be substantially less than that of the homogeneous analogue $[(C_6H_5)_3P]_2PdCl_2$ and to decrease with extended use. The precise cause of this loss of catalytic activity is unclear. Possible causes include oxidation of the pendant phosphine groups leading to metal leaching or polymerization of norbornadiene within the polystyrene matrix initiated by intermediates in such phosphine oxidation.

The catalytic activities of the polystyrene-supported phosphine palladium (II) chloride catalysts (Table 3) for the conversion of quadricyclane to norbornadiene were considerably less than those of the polystyrene-supported cobalt (II) tetraphenylporphyrin catalysts (Table 1) under comparable conditions.

C. Metal Dithiolene Complexes

Some of our early screening studies⁹ revealed that the neutral molybdenum dithiolene $[(CF_3)_2C_2S_2]_3Mo$ had appreciable catalytic activity for the conversion of quadricyclane to norbornadiene. During the past year we have carried out more detailed studies on the catalytic activity of this and related metal dithiolene¹² complexes. Some of the most significant results are summarized in Table 4.

These results indicate that among the diverse metal dithiolenes investigated, only the neutral metal dithiolenes containing trifluoromethyl substituents, i.e. $[(CF_3)_2C_2S_2]_3Mo$ and $[(CF_3)_2C_2S_2]_2Ni$, are active catalysts for the conversion of quadricyclane to norbornadiene. The molybdenum complex was found to be significantly more active than the nickel complex. The catalytic activities of these neutral metal dithiolenes were destroyed upon reduction to the corresponding mono- or dianions, by substitution of the CF_3 groups with less electronegative groups such as phenyl, and by substitution of even one of the dithiolate ligands by a trivalent phosphorus ligand. Thus the presence of the highest possible metal oxidation state, the presence of strongly electron-withdrawing substituents such as CF_3 , and the exclusive presence of dithiolate ligands all appear to be necessary for metal dithiolenes to have appreciable catalytic activity for the conversion of quadricyclane to norbornadiene.

The ability for $[(CF_3)_2C_2S_2]_3Mo$ to isomerize quadricyclane to norbornadiene and the ultimate course of the reaction appeared to be rather solvent sensitive (Table 4). Thus the catalytic activity of $[(CF_3)_2C_2S_2]_3Mo$ was found to decrease when coordinating solvents were used or when water was added. Unfortunately, in no case was a clean conversion of quadricyclane to norbornadiene observed.

The treatment of quadricyclane with catalytic amounts of $[(CF_3)_2C_2S_2]_3Mo$ in benzene or dichloromethane solution at room temperature was found to produce not only the expected norbornadiene but also a polymer. Control experiments indicated that the $[(CF_3)_2C_2S_2]_3Mo$ polymerizes norbornadiene in benzene at the boiling point but not at room temperature. Addition of water to a benzene solution of quadricyclane containing $[(CF_3)_2C_2S_2]_3Mo$ was found to give small quantities of nortricyclanol in addition to slowing the rate or conversion of quadricyclane to norbornadiene.

Our general conclusion from studying metal dithiolenes as catalysts for the conversion of quadricyclane to norbornadiene is that these systems are unpromising for use in an actual solar energy storage system. Major difficulties include side reactions leading to polymer and/or nortricyclanol formation as well as sensitivity of the catalysts towards even moderate reducing agents which can destroy the catalytic activity of the neutral dithiolenes by reducing them to the corresponding monoanions which are catalytically inactive. We therefore plan no further work with the metal dithiolenes.

TABLE 4

EVALUATION OF METAL DITHIOLENES AS CATALYSTS FOR THE CONVERSION OF
QUADRICYCLANE TO NORBORNADIENE

Catalyst (moles/liter $\times 10^3$)	Initial Quadricyclane Conc. (moles/liter)	Solvent	Other Additive (moles/liter)	Norbornadiene Production after 20 hr. (as % of total C_7H_8 hydrocarbons)
<u>A. Molybdenum Complexes</u>				
$[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.42	benzene	none	98 + polymer
$[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.47	benzene	$H_2O(0.37)$	13 + nortricyclanol
$[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.79	MeOH	none	4.3
$[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.77	MeOH	$H_2O(0.37)$	0
$[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.12	CH_2Cl_2	none	100 + polymer
61 $[(CF_3)_2C_2S_2]_3Mo(0.95)$	0.12	CH_2Cl_2	pyridine (0.083)	0.2
$[(CF_3)_2C_2S_2]_2Mo(Pf-Pf)^a(0.95)$	0.64	benzene	none	1.5
$[Ph_4As] [(CF_3)_2C_2S_2]_3Mo(0.95)$	0.46	benzene	none	4.3
$[Ph_4As]_2 [(CF_3)_2C_2S_2]_3Mo(0.95)$	0.49	benzene	none	0.8
$(Ph_2C_2S_2)_3Mo(0.95)$	0.58	benzene	none	0.1
$(Ph_2C_2S_2)_2Mo(CO)_2(0.95)$	0.78	benzene	none	0
<u>B. Nickel Complexes</u>				
$[(CF_3)_2C_2S_2]_2Ni(3.78)$	2.35	CH_2Cl_2	none	21
$[Et_4N] [(CF_3)_2C_2S_2]_2Ni(3.78)$	1.10	CH_2Cl_2	none	2.2
$[Et_4N]_2 [(CF_3)_2C_2S_2]_2Ni(3.78)$	1.19	CH_2Cl_2	none	0
$(Ph_2C_2S_2)_2Ni(3.78)$	1.08	CH_2Cl_2	none	1.7

(a) $Pf-Pf = Ph_2PCH_2CH_2PPh_2$

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- 2) R. B. King, E. M. Sweet, and R. M. Hanes, "Attached Metal Complex Catalysts for a Solar Energy Storage System," presented by R. B. King at the Symposium on Design and Characterization of Supported Metal Complex Catalysts, Division of Petroleum Chemistry, 174th National Meeting of the American Chemical Society, Chicago, Illinois, August/September, 1977: paper PETR 41 in abstracts.
- 3) E. M. Sweet, R. B. King, R. M. Hanes, and S. Ikai, "Catalysts for the Isomerization of Quadricyclane to Norbornadiene in a Photochemical Energy Storage System," presented by E. M. Sweet at the Symposium on "Inorganic Compounds with Unusual Properties. II. Molecular Catalysis and the Conversion, Production and Storage of Energy," Athens, Georgia, February, 1978.
- 4) R. R. Hautala, "The Influence of Micellar and Macromolecular Catalysis on Some Photochemical Reactions", Gordon Research Conference on Micellar and Macromolecular Catalysis, Wolfeboro, New Hampshire, August 15, 1977.
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- 7) C. Kotal, "Use of Transition Metal Compounds to Sensitize an Energy Storage Reaction", 174th American Chemical Society National Meeting, Chicago, August, 1977. Invited paper in Symposium on Inorganic and Organometallic Photochemistry.
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