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DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL
ENERGY STORAGE SYSTEM

Annual Report, June 15, 1976—June 14, 1977

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ENERGY RESEARCH AND
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Abstract

Significant progress toward the development of a solar energy storage system based on the norbornadiene-quadracyclene interconversion has been achieved during the past year. New sensitizers and catalysts have been discovered and conditions found where single cycles of the photosensitization step and the catalytic reversion step appear to be quantitative. Both sensitizers and catalysts have been successfully incorporated onto insoluble polymeric supports. The long term stability of these components is currently being tested using a recently constructed prototype device designed for multiple recycling experiments. Investigations are also underway on design modifications which will allow incorporation of the norbornadiene-quadracyclene system into currently available state-of-the-art solar collectors.

POLYMERIC ORGANIC SENSITIZERS

During the past year, several organic sensitizer chromophores have been incorporated covalently into insoluble polystyrene structures. Each of the soluble monomeric chromophores (I - IV)

has been shown to sensitize the conversion of norbornadiene to quadricyclene with varying degrees of efficiency, stability, solar spectral overlap, etc. We have compared the performance of each of the monomers with the corresponding polymeric sensitizers below.

Our recent results extending some studies reported earlier¹ are summarized below. For details see the accompanying quarterly report.²

1. Polymer N is by far the most attractive currently available sensitizer (homogeneous or heterogeneous) for the conversion of norbornadiene to quadricyclene.
2. Polymer N can be prepared in a number of different ways synthetically. We have found no significant difference in performance for the methods tried thus far.
3. The porosity of the polymer does not appear to affect its performance.

4. For physical and optical reasons the highest quantum efficiencies measured thus far are obtained using benzene as a solvent.
5. Other than the relatively minor effect described above (4) Polymer N can be used effectively with a variety of solvents including neat norbornadiene.
6. The only discernible effect attributable to percent loading of the chromophore on the polymer is related to the reduced quantum efficiency at longer wavelengths where the extinction coefficient falls dramatically.
7. The material balance between norbornadiene and quadricyclene using Polymer N is excellent at all degrees of conversion studied. This contrasts with the behavior of some monomeric sensitizers.³
8. The quantum efficiency using Polymer N remains high even to high percent conversions.

POLYMERIC INORGANIC SENSITIZERS

During the past year we have continued our investigation⁴ of the sensitized conversion of norbornadiene to quadricyclene using transition metal compounds. Particularly significant is our recent discovery⁵ of the first example of an inorganic sensitizer in which the metal is not in a low oxidation state. The compound, $\text{Ir}(\text{bipy})_2(\text{bipy}')\text{OH}^{+2}$ (where bipy' denotes that the ligand is bound to iridium through only one nitrogen), possesses a long lifetime and high phosphorescence quantum yield in solution, and absorbs at considerably longer wavelengths than previous transition metal sensitizers. Quantum yields for quadricyclene production are ~ 0.08 at 302 nm, ~ 0.18 at 366 nm, and ~ 0.08 at 406 nm in 0.1M norbornadiene/methanol solution. The presence of the polar solvent (needed to dissolve the +2 ion) may have caused some decomposition of the sensitizer as evidenced by a decrease in quantum yield with time of irradiation. Consequently, the values reported above probably represent lower limits. Conceivably, the inability⁴ of other transition metal compounds with relatively high energy triplet states (e.g. $\text{Ir}(\text{phen})_2\text{Cl}_2^+$, $\text{Rh}(\text{phen})_3^{+3}$) to function as sensitizers may also be due to the effects of the polar solvents employed. Fortunately this problem can be circumvented by immobilizing the charged sensitizer candidate onto an appropriate polymeric ion exchange resin. We have recently prepared the sulfonated resin shown below (the carboxylate analog has also been synthesized) using macroreticular styrene-divinylbenzene copolymer beads. Immobilization of $\text{Ir}(\text{phen})_2\text{Cl}_2^+$ is easily accomplished by

equilibrating a solution of the compound with the resin. A sample of this material in contact with 0.5M norbornadiene-benzene solution was irradiated with 366 nm light. The quantum yield for quadricyclene production is at least 0.05. By comparison, no sensitization is observed if a homogeneous solution of $\text{Ir(phen)}_2\text{Cl}_2^+$ and norbornadiene in 20% ethanol-80% benzene solution is irradiated at the same wavelength.

This very promising result with the polymer immobilized sensitizer is currently being examined in considerable detail. Thus quantitative studies concerning the effects of various parameters (such as norbornadiene concentration, percent loading of the sensitizer on the polymer, polymer porosity, etc.) on the quantum efficiency of the polymer bound sensitizer are underway. A thorough study of sensitization by polymer bound $\text{Ir(bipy)}_2(\text{bipy}')\text{OH}^{+2}$ is also planned.

CATALYSIS OF THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE

Last year in connection with the development of effective catalysts for the conversion of quadricyclane to norbornadiene which could be used in the photochemical energy storage system we emphasized extensive screening of a wide variety of transition metal complexes for the desired catalytic activity.⁶ This year the portion of the research program devoted to catalysis focused on the intensive study of a limited number of catalytically active structural types with the objectives of defining structure-activity relationships and anchoring the most active catalyst structures of satisfactory stability onto polystyrene matrices. We have also initiated some kinetic studies on some of the more promising polymer-anchored catalysts. Details of our work in these areas are outlined below.

A. Triphenylcyclopropenylnickel Catalysts

Late last year we found that the halides⁷ $[(\text{C}_6\text{H}_5)_3\text{C}_3\text{Ni}(\text{CO})\text{X}]_2$ (1: X = Cl and Br)

were active catalysts for the conversion of quadricyclane to norbornadiene. This year we have investigated the catalytic activity of a wide variety of triphenylcyclopropenylnickel complexes. The results of this screening are summarized in Table 1. Since many of these triphenylcyclopropenylnickel complexes were previously unknown, some of their physical properties are also summarized in Table 1. However, we have not yet had an opportunity to fully characterize many of the new $(C_6H_5)_3C_3NiL_nCl$ ($n = 1$ and 2) derivatives owing to difficulties in getting analytically pure crystalline samples. Thus in several cases in Table 1, the composition of the $(C_6H_5)_3C_3NiL_nCl$ derivative is inferred mainly from the ratios of $[(C_6H_5)_3C_3Ni(CO)X]_2$ to ligand used for its preparation.

In addition to the compounds listed in Table 1, we have also prepared from $[(C_6H_5)_3C_3Ni(CO)X]_2$ and the Grignard reagents $RMgX$ ($R = CH_3, C_2H_5, (CH_3)_2CH,$ and $(CH_3)_3C$) some dark red to black solids which are very active catalysts for the conversion of quadricyclane to norbornadiene. However, we have not been able to obtain sufficiently pure samples of these materials for reliable analyses. Proton n.m.r. spectra of these materials suggest the absence of nickel-bonded alkyl groups and the possibility that these complexes contain the ether in which the Grignard reagent was prepared as a coordinated ligand. In any case the air-sensitivity of these ill-defined nickel-containing materials would appear to make them unpromising candidates for catalysts in a practical photochemical energy storage system.

The data in Table 1 suggest that blocking coordination positions on the nickel atom with relatively strong ligands such as cyclopentadienyl or pyridine reduces or eliminates the catalytic activity of the resulting complexes in accord with expectations. Furthermore, in most cases complexes of the stoichiometry $(C_6H_5)_3C_3NiLCl$ are more catalytically active than complexes of the stoichiometry $(C_6H_5)_3C_3NiL_2Cl$ apparently because the second ligand blocks coordination positions needed for the catalytic action. An exception to this principle is the high catalytic activity of $(C_6H_5)_3C_3Ni(PCI_2C_6H_5)_2Cl$, apparently a consequence of the low basicity of the $C_6H_5PCI_2$ ligand arising from the electronegativity of its two chlorine atoms.

Further work is planned on the $(C_6H_5)_3C_3NiL_nCl$ derivatives with the objectives of characterizing them in more detail by conventional chemical and spectroscopic methods, determining in greater detail the structural features affecting their catalytic activity, and developing methods for chemically anchoring the more promising species onto polystyrene.

TABLE I

SOME TRIPHENYLCYCLOPROPENYLNICKEL COMPOUNDS AND THEIR CATALYTIC ACTIVITIES FOR THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE

Compound ^a	Color	Catalytic Activity ^b
$[\text{Ph}_3\text{C}_3\text{Ni}(\text{CO})\text{Cl}]_2^c$	orange	+++
$[\text{Ph}_3\text{C}_3\text{Ni}(\text{CO})\text{Br}]_2^c$	orange	+++
$\text{Ph}_3\text{C}_3\text{NiPy}_2\text{Cl} \cdot \text{Py}^d$	red	-
$\text{Ph}_3\text{C}_3\text{NiCp}^e$	orange	-
$\text{Ph}_3\text{C}_3\text{Ni}(\text{bipy})\text{Cl}^f$	dark red	+
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPh}_2\text{Me})\text{Cl}$	brown	+
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPh}_2\text{Me})_2\text{Cl}$	dark orange	+
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPh}_3)\text{Cl}^f$	dark brown	++
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPh}_3)_2\text{Cl}$	dark red	+
$\text{Ph}_3\text{C}_3\text{Ni}[\text{P}(\text{OPh})_3]\text{Cl}^f$	brown	+++
$\text{Ph}_3\text{C}_3\text{Ni}[\text{P}(\text{OPh})_3]_2\text{Cl}$	orange	-
$\text{Ph}_3\text{C}_3\text{Ni}[\text{P}(\text{OMe})_3]_2\text{Cl}$	orange	-
$\text{Ph}_3\text{C}_3\text{Ni}[\text{P}(\text{OPr}^i)_3]_2\text{Cl}$	orange	-
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPh}_2\text{Cl})_2\text{Cl}$	yellow	-
$\text{Ph}_3\text{C}_3\text{Ni}(\text{PPhCl}_2)_2\text{Cl}^f$	yellow	+++

a) bipy = 2,2'-bipyridyl; Py = pyridine; Me = methyl; Prⁱ = isopropyl, Cp = cyclopentadienyl, Ph = phenyl

b) The catalytic activities are indicated as follows:

- no detectable activity
- + minimum detectable activity (5% to 10% conversion even upon prolonged standing at room temperature
- ++ moderate activity (some conversion in short periods at room temperature; major amounts of conversion at higher temperatures or prolonged standing at room temperature)
- +++ high activity resulting in an immediate exothermic nearly complete conversion of quadricyclane to norbornadiene

c) E. W. Gowling and S. F. A. Kettle, Inorg. Chem., **4**, 604 (1965).

d) D. L. Weaver and R. M. Tuggle, J. Am. Chem. Soc., **91**, 6505 (1969).

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f) The approximate compositions of these previously unreported compounds were verified by carbon and hydrogen analyses.

B. Polymer-anchored Cobalt(II) Porphyrin Catalysts

The demonstrated^{8,9} high catalytic activity of cobalt(II) porphyrins for the conversion of quadricyclane to norbornadiene coupled with the existence of known methods¹⁰ for chemically anchoring cobalt(II) porphyrins onto polystyrene make these compounds attractive candidates for polymer-anchored catalysts in the photochemical energy storage system. Accordingly, we have now prepared in quantities sufficient for recycling experiments the three polystyrene-anchored cobalt(II) tetraarylporphyrins schematically represented as structures I, II, and III (Poly = polymer, X = terminal group). All three of these polymers have been shown to be active catalysts for the conversion of quadricyclane to norbornadiene. In qualitative experiments all three polymers convert quadricyclane to norbornadiene so rapidly that pure quadricyclane boils vigorously when poured onto the polymer. Preliminary quantitative kinetic experiments on III are described later in this report.

For the preparation of the polymers I and III tetra (p-carboxyphenyl)porphyrin was first converted to tetra (p-chlorocarbonylphenyl)porphyrin by treatment with thionyl chloride. The keto-linked polymer I was then followed by introduction of the cobalt with cobalt(II) acetate in boiling acetic acid. The carboxamide-linked polymer III was obtained from tetra (p-chlorocarbonylphenyl)porphyrin by treatment with aminopolystyrene in tetrahydrofuran solution in the presence of excess triethylamine followed by introduction of the cobalt with cobalt(II) acetate. Analysis of this polymer indicated 0.44% cobalt which is approximately twice the metal concentration achieved by Rollman. For the preparation of the sulfonamide-linked polymer II the reported¹¹ ammonium salt of tetra (p-sulfonatophenyl)porphyrin was converted to the corresponding sulfonyl chloride by conversion to the corresponding triethylammonium salt followed by treatment with thionyl chloride. The resulting tetra (p-chlorosulfonylphenyl)porphyrin was anchored onto aminopolystyrene. Cobalt was then introduced into the resulting porphyrin polymer to give the sulfonamide-linked polymer II by a procedure completely analogous to the preparation of the carboxamide-linked polymer III outlined above. The aminopolystyrene used in this work was obtained by nitration of a macroreticular polystyrene + 20% divinylbenzene resin to the extent of 13.6% using nitric acid in a mixture of acetic acid and acetic anhydride followed by reduction of this nitropolystyrene with stannous chloride in a mixture of hydrochloric acid and acetic acid. Although we do not yet have complete analytical data on our polymers, simple considerations of color intensity indicate that we have achieved considerably greater loading of porphyrin units onto the polystyrene in the cases of the sulfonamide- and carboxamide-linked polymers II and III, respectively, than in the case of the ketone-linked polymer I.

C. A Polymer-anchored Palladium Phosphine Catalyst

Hogeveen and Volger¹² observed that 1,5-cyclooctadienedichloropalladium(II), $C_8H_{12}PdCl_2$, and trihaptoallylchloropalladium dimer, $[C_3H_5PdCl]_2$, were effective catalysts in the conversion of quadricyclane to norbornadiene. Dauben and Kielbanis¹³ later observed that $[(C_6H_5)_3P]_2PdCl_2$ was an effective catalyst for the conversion of the tricycloheptane IV to the methylenecyclohexene V. These observations suggested that a polymer-anchored palladium(II) chloride complex of diphenylphosphinated polystyrene might be an effective catalyst for the conversion of quadricyclane to norbornadiene. We therefore investigated the preparation of such a polymer-anchored phosphine palladium(II) chloride catalyst.

Macroreticular polystyrene beads were diphenylphosphinated by treatment with *n*-butyl-lithium followed by treatment with diphenylchlorophosphine.¹⁴ Palladium(II) chloride was complexed with this polymer by stirring in acetonitrile solution. The resulting lemon yellow beads were an active catalyst for the conversion of quadricyclane to norbornadiene. These beads gave the following elemental analysis: Pd, 0.70%; P, 0.28%; Cl, 0.39%. This corresponds to a Pd/P/Cl ratio of 1.0/1.4/1.7. These analytical data are insufficient to define an exact structure for this polymer. However, the structure schematically represented as VI, is not inconsistent with our data when considered in light of expected experimental errors in the analysis of such systems.

VI

D. Other Approaches to Polymer-anchored Catalysts

Some other approaches to polymer-anchored catalysts for the conversion of quadricyclane to norbornadiene were investigated during the past year. Two of these approaches are outlined below.

The high activity of rhodium(I) complexes as catalysts for the conversion of quadricyclane to norbornadiene^{6,12} made of interest the anchoring of a rhodium(I) system onto a polystyrene polymer. Accordingly, the 1,5-cyclooctadiene complex

$[\text{C}_8\text{H}_{12}\text{RhCl}]_2$ ¹⁵ was equilibrated with diphenylphosphinated polystyrene¹⁴ to give a species presumed to be of the type $\text{C}_8\text{H}_{12}\text{RhLCl}$ where L represents trivalent phosphorus atoms from the polymer. However, this polymer proved to have low catalytic activity. Additionally, the rhodium polymer linkage was not particularly stable towards the reaction conditions. Each reaction with quadricyclane produced a yellow solution indicating the presence of rhodium species in the solvent. For this reason it is questionable if any of the polymer-attached rhodium(I) species are catalytically active since it is possible that the entire observed catalysis of quadricyclane to norbornadiene originated from dissolved free $[\text{C}_8\text{H}_{12}\text{RhCl}]_2$ which is a species of known high catalytic activity.

We also investigated the possibility of bonding to an ion-exchange resin an active catalyst for the conversion of quadricyclane to norbornadiene. Treatment of Dowex 1, 1x 8-50 ion-exchange resin in the chloride form with a solution of pentacyanocobaltate(II) gave a resin containing $\text{Co}(\text{CN})_5^{3-}$. This polymer showed limited activity over a period of hours for the conversion of quadricyclane to norbornadiene in tetrahydrofuran solution. One factor limiting the activity of the system actually used was the fact that the ion-exchange resin was not swollen by the tetrahydrofuran solvent suggesting that the reactive sites were limited to the surface of the polymer.

Since neither of the above two systems presently appear particularly promising, work on them has been suspended in order to allow us to concentrate on the apparently more promising cobalt(II) porphyrin and phosphine palladium(II) chloride polymer-anchored catalysts I, II, III and VI.

E. Quantitative Kinetic Studies

During the past year some quantitative kinetic studies were initiated on the conversion of quadricyclane to norbornadiene using both the polymer-anchored cobalt(II) porphyrin and the phosphine palladium(II) chloride catalysts. Some preliminary data are now available on both the carboxamido-linked polymer-anchored cobalt(II) porphyrin III and the polymer-anchored phosphine palladium(II) chloride VI.

In these kinetic studies about 0.1 g. of the polymer-anchored catalyst was treated with 10.0 ml. of 1.00M quadricyclane in xylene containing 0.25M or 0.50M benzene as an internal gas chromatography standard. The reaction temperature was controlled by an external bath thermostated at $30 \pm 0.1^\circ$. Aliquots (10 to 40 microliters) of the reaction mixture were withdrawn at 5 minute intervals (measured to ± 0.1 min.), diluted to 1.0 ml. with pentane, and analyzed by gas chromatography using a $\frac{1}{8}$ " x 6' or

10' 7.8% GE SF-96 on Chromosorb W column with a 60 ml./min. nitrogen flow and a flame ionization detector. Concentrations were determined by the peak area ratios of quadricyclane to benzene compared to the ratio at zero time and 1.00M quadricyclane concentration. After each run the polymer was washed for at least 10 minutes each of three times with fresh xylene and dried under vacuum at 60°.

The observed first order rate constants k_0 were obtained from a linear least squares plot of $-\ln$ (concentration) versus the reaction time in minutes. The k_0 were then converted to a normalized rate constant through the formula $k = k_0 V / (60W)$ where V is the volume of solution in liters, W is the weight of catalyst in grams, and the 60 converts the time scale from minutes to seconds. All plots were approximately linear over 5 to 7 half lives. A rate constant k_M was also calculated on the basis of the metal concentration since metal analyses on the polymers were available. The resulting kinetic data for both the cobalt and palladium polymer-anchored catalysts are summarized in Table 2. These data include runs obtained by successively recycling the same batch of catalyst in different reactions, since such data are important in evaluating the suitability of the photochemical storage system where repeated recycling with the same batch of catalyst will occur.

In the case of the carboxamido-linked cobalt(II) porphyrin polymer-anchored catalyst the rate constant k was found to decrease with repeated recycling of the same batch. This decrease in activity upon recycling was less severe but still significant in the series of runs performed under nitrogen. A plot of the rate constant k versus the quantity of solution to which the catalyst had been exposed was fairly linear suggesting that some component of the reaction solution caused deactivation of the catalyst.

In the case of the polymer-anchored phosphine palladium(II) chloride VI the rate constant k was found to decrease slightly upon the first recycling but retained this lowered activity upon further recycling. This contrasted with the polymer-anchored cobalt(II) porphyrin III which suffered continual losses of activity upon repeated recycling. The loss of activity of the polymer-anchored phosphine palladium(II) chloride VI on the first but not on subsequent recycling could arise either from metal leaching from the polymer or from formation of a palladium-norbornadiene complex on the polymer which would lower the accessibility of the coordination sites on the palladium.

Further work is planned in order to define more precisely the losses of catalytic activity upon recycling observed for both the cobalt polymer III and the palladium polymer VI. The different behaviors of the cobalt and palladium polymers noted above suggest that these losses of catalytic activity upon repeated recycling have different causes in the case of each polymer.

TABLE 2

KINETIC DATA FOR THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE
BY POLYSTYRENE-ANCHORED TRANSITION METAL CATALYSTS

	$k \text{ (sec.}^{-1} \text{ (g./l.)}^{-1}\text{)}$	$k_M \text{ (sec.}^{-1} \text{ (g.-atom metal/l.)}^{-1}\text{)}$
<u>A. Carboxamide-linked Cobalt (II) Porphyrin Polymer</u>		
a) <u>Runs in air</u>		
Fresh catalyst	1.3×10^{-4}	1.7
Recycle	0.9×10^{-4}	1.2
b) <u>Runs under nitrogen</u>		
Fresh catalyst	1.7×10^{-4}	2.2
First recycle	1.5×10^{-4}	1.9
Second recycle	1.3×10^{-4}	1.8
Third recycle	1.2×10^{-4}	1.6
Fourth recycle	0.9×10^{-4}	1.2
<u>B. Phosphine Palladium (II) Chloride Polymer</u>		
Fresh catalyst	2.8×10^{-5}	0.42
First recycle	1.6×10^{-5}	0.24
Second recycle	1.7×10^{-5}	0.26

PROTOTYPE SYSTEMS

During the past year, we have constructed two types of prototype systems. The first of these systems is designed for multiple recycling experiments designed to test the long stability of the system. These experiments have just recently begun. A photograph of the system is shown in Figure 1. This device utilizes standard photochemical arc sources to provide irradiation.

A second type of prototype is designed to test the compatibility of the norbornadiene photochemical energy storage system with standard solar energy collectors. The "State of the Art" Winston collector¹⁶ has been incorporated into the design of this prototype. Again studies using this system with actual solar illumination are just commencing in our laboratory. A photograph of this device is shown in Figure 2.

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Figure 1. Prototype model for recycling studies.

Figure 2. Duplex solar energy collector capable of both photochemical and thermal energy storage.

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