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DEVELOPMENT OF A PRACTICAL PHOTOCHEMICAL ENERGY STORAGE SYSTEM

Quarterly Report

Richard R. Hautala
Charles R. Kutal

Date Published—June 15, 1977

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

University of Georgia
Department of Chemistry
Athens, Georgia

MASTER

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Division of Energy Storage Systems

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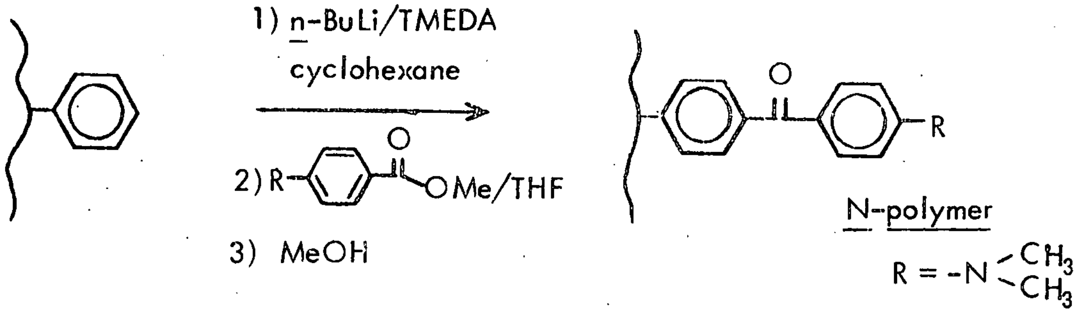
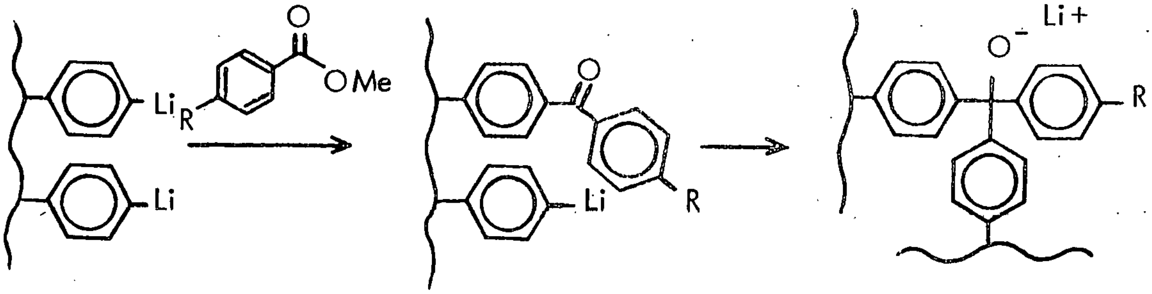
Department of Chemistry
University of Georgia
Athens, Georgia 30602

POLYMERIC ORGANIC SENSITIZERS

Recent work has involved the analysis of the functionalized polymer primarily being used in our photochemical studies. This polymer, referred to as N-polymer in earlier reports,[1,2] was prepared by the following reaction sequence using a macroreticular polystyrence resin which is cross-linked with divinylbenzene.



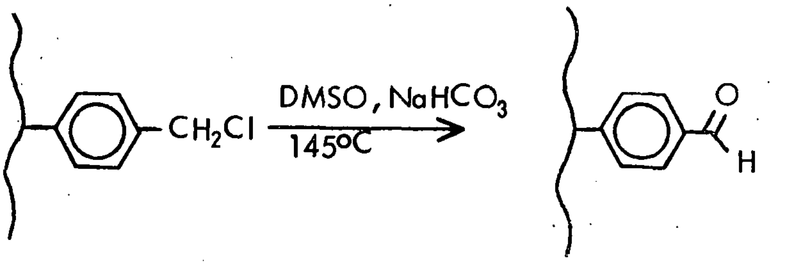
Analysis indicated 0.343 meq/gram of nitrogen which is a 3.7% ring substitution. The nitrogen content alone does not verify the structure of the polymer, for the synthetic conditions allow "site-site" interaction. The lithiated polystyrene after initially attacking the ester could conceivably attack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



The oxime will be formed to determine if alcohol formation is a significant side reaction. Ultimately if the analysis procedure is satisfactory, the procedure will also be applied to N-polymer used in the prototype to determine whether or not any change in the resin has ocurred upon extensive photolysis.

Work involving 4,4-(N,N-dimethyl)aminobenzophenone as a sensitizer for quadricyclene formation demonstrates that the maximum (extrapolated) efficiency of sensitization is a function of its concentration (all absorbances ≥ 2). This could be due to self-quenching of the triplet state at high concentrations.

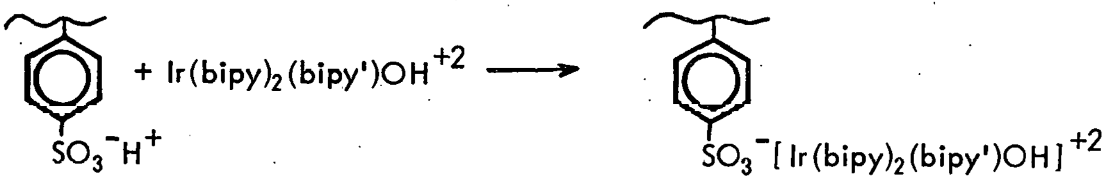
This effect has been surveyed using a functionalized polymer support. By



limiting the reaction times, the amount of ring substitution was varied from 5 to 10 percent. The substitution was determined by IR which allows comparison of the aldehyde stretching frequency at 1690 cm^{-1} versus one of the stronger bands from the polystyrene. Initial studies show that the quantum yield for production of quadricyclene is fairly constant over this concentration range.

POLYMERIC INORGANIC SENSITIZERS

During the past quarter we have continued our investigation[2] of the promising sensitizer, $Ir(bipy)_2(bipy')OH^{+2}$. The +2 charge on this compound facilitates its immobilization onto a sulfonated polystyrene-divinylbenzene (20% crosslinked) resin. A sample of the polymer bound sensitizer in contact with a 0.5M norbornadiene-benzene



solution was irradiated with 366 nm light, resulting in a quantum yield for quadricyclene production of 0.06. By comparison, the quantum yield obtained upon irradiating the sensitizer in homogeneous solution is ~0.20. The reason for the decreased efficiency is not apparent at this point, but we have noted an apparent inverse relationship between quantum yield and the extent of loading of the sensitizer on the polymer. Further work is underway to explain this behavior as well as to better characterize the polymeric sensitizer itself.

We have also conducted some sensitization studies of the related compound, $Ir(bipy)_2(bipy')OH_2^{+3}$, in methanol-benzene solution. Thus at 366 nm the quantum yield for quadricyclene production is 0.7, whereas at 406 nm the value is 0.2-0.3. These high efficiencies, as well as the ability to absorb light out to ~480 nm, make $Ir(bipy)_2(bipy')OH_2^{+3}$ an attractive candidate for further study. During the next quarter, we plan to immobilize the compound onto the sulfonated resin and determine its sensitization efficiency under a variety of conditions.

CATALYSIS OF THE CONVERSION OF NORBORNADIENE TO QUADRICYCLANE

A. Polymer-Supported Catalysts

During this quarter kinetic studies have continued on both the polystyrene-anchored cobalt(II) tetraarylporphyrin catalysts and the polymer-anchored palladium(II) chloride complexes obtained from palladium(II) chloride and diphenylphosphinated polystyrene in acetonitrile solution. Many of these results are summarized in the attached manuscript (Appendix A) entitled "Attached Metal Complex Catalysts for a Solar Energy Storage System". This manuscript was prepared for the Division of Petroleum Chemistry of the American Chemical Society in connection with presentation of this work at a symposium on the "Design and Characterization of Attached Metal Complex Catalysts" at the National Meeting of the American Chemical Society in Chicago at the end of August, 1977.

Since the preparation of this manuscript further work has been done on improving the preparation of the sulfonamide-linked polystyrene-anchored cobalt(II) tetraphenylporphyrin (structure IV in Appendix A). In the near future we plan to prepare samples of this polymer-anchored cobalt complex with different degrees of loading in order to see the effects of metal content on the catalytic activity and the susceptibility towards deactivation.

B. Triphenylcyclopropenylnickel Catalysts

The previous quarterly report[2] discussed in detail various structure-activity relationships in the series of triphenylcyclopropenylnickel complexes. During this quarter some detailed studies were carried out of the kinetics of the conversion of quadricyclane to norbornadiene catalyzed by $[(C_6H_5)_3C_3Ni(CO)Cl]_2$.

A dichloromethane solution of a measured quantity of $[(C_6H_5)_3C_3Ni(CO)C$, (2 to 15 mg.) was treated with a dichloromethane solution containing a measured quantity of quadricyclane. The reaction temperature was controlled by an external bath thermostatted at 30 ± 0.1°C or by an ice bath at 0 to 0.5°C. At various time intervals 1 ml. of the homogeneous reaction solution was withdrawn and analyzed by gas chromatography using a $\frac{1}{8}$" x 6' to 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 and norbornadiene to the methylene chloride.

The most significant results from these kinetic studies are summarized below.

(1) Quadricyclane concentration versus time at various concentrations of the nickel catalyst.

Plotting ln[quadricyclane] versus time gave a straight line at the beginning of the reaction corresponding to a pseudo first order reaction. However, after several minutes these straight lines began to bend upward indicating retardation of the reaction by products from the reaction or from decomposition of the catalyst. This retardation began at about 2 minutes in reactions performed at 30°C and at about 10 minutes in reactions performed at 0°C. In both cases the onset of the rate retardation corresponded to similar points of conversion of quadricyclane to norbornadiene.

(2) Quadricyclane concentration versus time at various concentrations of quadricyclane.

Again the initial straight line plot of ln[quadricyclane] versus time curved upward after several minutes indicating a retardation of the reaction rate. The smaller the quadricyclane concentration the later the onset of this retardation.

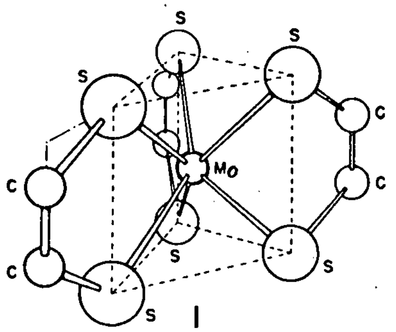
(3) Quadricyclane concentration versus time in the presence of excess norbornadiene.

Increasing amounts of added excess norbornadiene result in increasing retardation of the reaction rate. In 7M norbornadiene the reaction was inhibited completely.

These observations suggest that norbornadiene deactivates the triphenylcyclopropenylnickel catalyst apparently by blocking required coordination positions. A similar deactivating effect was also observed by coordinating solvents such as methanol and tetrahydrofuran. In any case the actual nickel catalyst in these reactions does not appear to be the triphenylcyclopropenylnickel derivative since unchanged $[(C_6H_5)_3C_3Ni(CO)Cl]_2$ could not be recovered from the reaction solution after completion of the catalytic reaction.

C. Trigonal Prismatic Molybdenum Catalysts

Some initial kinetic studies on the conversion of quadricyclane to norbornadiene catalyzed by the molybdenum complex $[(CF_3)_2C_2S_2]_3Mo$ (I) were performed. Straight line plots of ln[quadricyclane] versus time were obtained in several cases. This catalyst system appeared to be less sensitive towards deactivation by either oxidation or norbornadiene complexation than the other catalysts investigated. However, there was some evidence for side reactions leading to apparently polymeric materials. Further studies on this rather intriguing system are required before definite conclusions can be drawn.



I

CF$_3$ groups not shown

D. Miscellaneous

The following paper was presented by R. B. King at the Fifth North American Meeting of the Catalysis Society, April, 1977, in Pittsburgh, Pennsylvania:

R. B. King, E. M. Sweet, R. M. Hanes, and S. Ikai, "Catalysis in a Solar Energy Storage System."

PROTOTYPE SYSTEMS

The prototype system described in the 1976-1977 annual report has been tested with the following results:

Energy Storage step: A solution of 50 ml. of benzene and 150 ml. of norbornadiene was irradiated for 440 hr. in the presence of a polymer-supported p-dimethylaminobenzophenone sensitizer. The final mixture contained 143 ml. of quadricyclane (by v.p.c.).

Energy release step: The solution was pumped (2.5 ml/min.) through a ¼" x 1 ft. catalyst bed packed with carboxamide-linked polystyrene-supported cobalt(II) porphyrin. The catalytic reactor was immersed in 750 ml. of water at 23°C. During a period of 1 hr. this water was heated to 44°C

Energy released: (21°C temperature rise) x (0.75 kcal./deg. C) = 15.75 kcal.

Energy available: (140 g. quadricyclane) x (0.25 kcal./g.) = 35 kcal.

Percent available energy released: $\frac{15.75}{35} \times 100 = 45\%$

The 440 hr. (2 ½ week) reaction time for the conversion of norbornadiene to quadricyclane made the use of this system impractical for the evaluation of its stability towards repeated recycling. Therefore this solar energy storage prototype was modified so that the photoreactor portion consisted of a flat face 10 cm. cell with a 4 mm. path length irradiated by two 100 watt medium pressure mercury flood lamps. The results from the evaluation of this modified solar energy system prototype are as follows:

Energy storage step: Norbornadiene (60 ml) was pumped through this modified photochemical reactor at 1 ml./min. for 262 hr. using the same polymer-supported sensitizer. The final mixture contained 39 ml. of quadricyclane and 21 ml. of norbornadiene (by v.p.c.).

Energy release step: The solution was pumped (1 ml./min.) through the ¼" x 1 ft. catalyst bed packed with the same cobalt catalyst. The catalytic reactor was immersed in 750 ml. of water at 21.5°C. During a period of 75 min. this water was heated to 27°C.

Energy released: (5.5°C temperature rise) x (0.75 kcal./deg. C) = 4.125 kcal.

Energy available: (39 g. quadricyclane) x (0.25 kcal./g.) = 9.75 kcal.

Percent available energy released: $\frac{4.125}{9.75} \times 100 = 42\%$

REFERENCES

1. Quarterly report for ERDA Contract E(38-1)-893, September 15, 1976.
2. Quarterly report for ERDA Contract E(38-1)-893, March 15, 1977.

APPENDIX A

ATTACHED METAL COMPLEX CATALYSTS FOR A SOLAR ENERGY STORAGE SYSTEM

R. B. King, E. M. Sweet, and R.M. Hanes
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The following two types of polystyrene-anchored transition metal derivatives were found to be effective catalysts for the exothermic conversion of quadricyclane to norbornadiene in the energy-release step of a photochemical energy storage cycle: (1) cobalt(II) tertraarylporphyrin derivatives linked to polystyrene through sulfonamido or carboxamido bridges; (2) polymer-anchored palladium(II) chloride complexes obtained from palladium(II) chloride and diphenylphosphinated polystyrene in acetonitrile solution. Kinetic data for the conversion of quadricyclane to norbornadiene by each of these two types of catalysts indicate that the cobalt catalysts are more active than the palladium catalysts. Furthermore, the polystyrene-anchored phosphine palladium(II) chloride catalyst is about 1000 times less active than the soluble monomeric catalyst $[(C_6H_5)_3P]_2PdCl_2$. The cobalt catalyst appears to be subject to deactivation through oxidation whereas the palladium catalyst appears to be subject to deactivation through complex formation with norbornadiene.

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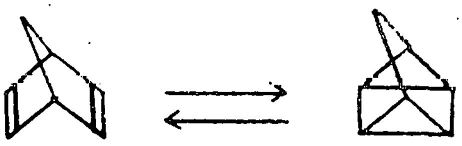
Introduction

The use of photochemical reactions to generate kinetically stable products of high energy content provides an exceedingly attractive fuel source since a virtually inexhaustible source of energy (sunlight) is converted into a usable form with no net consumption of resources. A promising method of this type for storing energy from sunlight is based on the photosensitized conversion of norbornadiene (I) to quadricyclane (II).[1]



I II

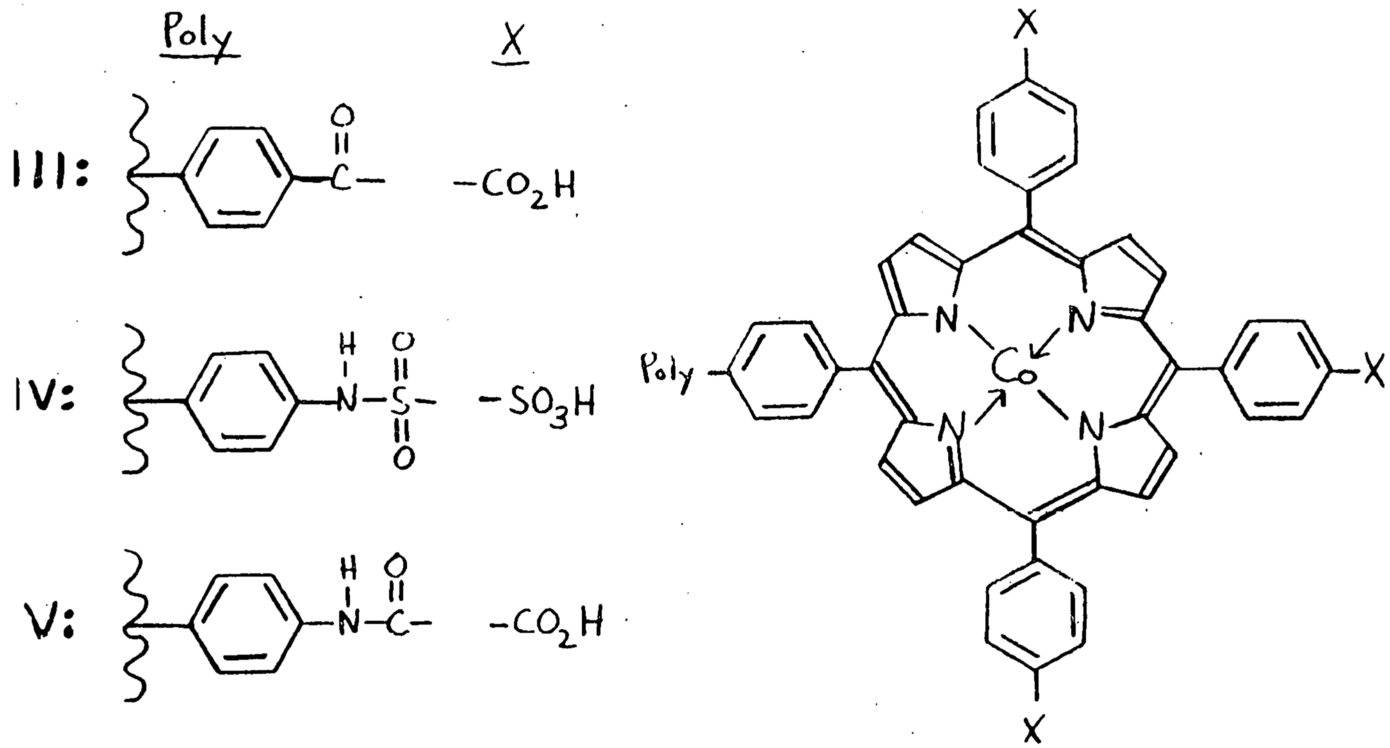
A device based on this reaction requires two steps: (1) Energy storage through the sensitized photolysis of norbornadiene (I) to quadricyclane (II) in an endothermic reaction; (2) Energy release through the catalyzed reconversion of quadricyclane (II) to norbornadiene (I) in an exothermic reaction. Sensitizers for the first step must absorb strongly in the region of available solar energy, be thermally and photochemically stable, and, of course, effect efficiently the desired sensitization. Ideal catalysts for the reverse reaction must also meet stringent criteria including long term stability as well as effecting rapid and clean conversions. Introduction of the sensitizer and catalyst onto separate polymeric supports facilitates the construction of an actual device by keeping the sensitizer and catalyst apart. An energy storage device based on these principles could result in the practical use of solar energy for heating buildings and related applications.

This paper discusses research at the University of Georgia directed towards the development of suitable polystyrene-anchored metal complex catalysts for the conversion of quadricyclane to norbornadiene in the energy-release step of the solar energy storage system outlined above.

When this research program was initiated in 1975 the only catalysts known to effect the conversion of quadricyclane to norbornadiene were discrete molecular square planar complexes including particularly those of rhodium(I),[2] nickel(II),[3] cobalt(II),[3] iron(II),[3] and palladium(II).[2,4] Catalysts for related metal-catalyzed openings of other strained ring systems such as bicyclobutanes,[5-10] bicyclopentanes,[11,12] methylenecyclopropanes,[13,14,15,16] cubanes,[17] bishomocubyl derivatives,[18] cuneanes,[17] and other combinations of fused cyclobutane rings[19,20] were then limited to similar nickel(0), rhodium(I), palladium(II), and silver(I) derivatives. Methods for anchoring these catalytically active systems onto a polymeric matrix to give systems retaining the desired catalytic activity and stable towards leaching of the catalytically active metal were not obvious from the published work available at that time. Since 1975 the research work at the University of Georgia has resulted in the development of polymer-anchored catalysts for the conversion of quadricyclane to norbornadiene containing the following structural features: (1) Cobalt(II) tetraarylporphyrin derivatives linked to polystyrene through appropriate substituents on the phenyl rings; (2) Palladium(II) chloride complexes of diphenylphosphinated polystyrene. The preparation and catalytic properties of these two different types of attached metal complex catalysts are described in this paper.

Polymer-anchored Cobalt(II) Porphyrin Catalysts

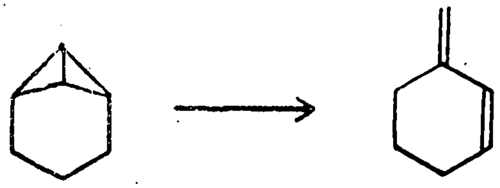
The demonstrated[3,21] high catalytic activity of cobalt(II) porphyrins for the conversion of quadricyclane to norbornadiene coupled with the existence of known methods[22] for chemically anchoring cobalt(II) porphyrins onto polystyrene made such materials attractive candidates for polymer-anchored catalysts in the photochemical energy storage system. We therefore prepared the three polystyrene-anchored cobalt(II) tetraarylporphyrins schematically represented below as structures III, IV, and V (Poly = polymer, X = terminal group). All three of these polymers were shown to be active catalysts for the conversion of quadricyclane to norbornadiene. In qualitative experiments all three polymers converted quadricyclane to norbornadiene so rapidly that pure quadricyclane boiled vigorously when poured onto the polymer. Preliminary quantitative kinetic experiments on the carboxamido-linked polymer V are described later in this paper.



For the preparation of the polymers III and V the tetra(p- carboxyphenyl)porphyrin obtained from p- carboxybenzaldehydeand pyrrole by a published procedure[23] was first converted to tetra(p-chlorocarbonylphenyl)porphyrin by treatment with thionyl chloride. The ketone-linked polymer III was then obtained by a Friedel-Crafts reaction of the tetra(p-chlorocarbonylphenyl)porphyrin with polystyrene followed by introduction of the cobalt with cobalt(II) acetate in boiling acetic acid. The carboxamide-linked polymer V 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.[22] For the preparation of the sulfonamide-linked polymer IV the reported[24] ammonium salt of tetra(p-sulfonatophenyl)porphyrin was converted to the corresponding sulfonyl chloride by treatment with thionyl chloride after conversion to the corresponding triethylammonium salt. 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 IV by a procedure completely analogous to the preparation of the carboxamide-linked polymer V 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 considerably greater loading of porphyrin units onto the polystyrene has been achieved in the cases of the sulfonamide- and carboxamide-linked polymers IV and V, respectively, than in the case of the ketone-linked polymer III.

A Polymer-anchored Phosphine Palladium(II) Chloride Catalyst

Hogeveen and Volger[2] observed that 1,5-cyclooctadienedichloropalladium(II), $C_8H_{12}PdCl_2$, and trihaptoallylchloropalladium dimer, $[C_3H_5PdCl]_2$, were effective catalysts for the conversion of quadricyclane to norbornadiene. Most recently Dauben and Kielbania[25] observed that $[(C_6H_5)_2P]_2PdCl_2$ was an effective catalyst for the conversion of the tricycloheptane VI to the methylenecyclohexene VII. 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.



VI VII

Macroreticular polystyrene beads were diphenylphosphinated by treatment with n-butyllithium followed by treatment with diphenylchlorophosphine.[26] 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. Two independent samples of beads prepared by this general method gave the following elemental analyses: Sample I: Pd, 0.70%; P, 0.28%; Cl, 0.39%, Sample II: Pd, 1.1%; P, 0.97%; Cl, 1.08%; N, 0.026%. These analytical data are insufficient to define an exact structure for this polymer. However, the absence of significant amounts of coordinated acetonitrile is indicated by the low nitrogen analysis. Sample II has a considerably higher phosphine loading on the polystyrene but a smaller percentage of palladium-complexed phosphorus atoms.

Quantitative Kinetic Studies

Experimental Method

About 0.1 g. of the polymer-anchored catalyst was treated with 10.0 or 20.0 ml. of 1.00 M quadricyclane in benzene or xylene containing 0.25 M or 0.50 M of benzene, ethylbenzene, or xylene as an internal gas chromatography standard. The reaction temperature was controlled by an external bath thermostated at 30 ± 0.1°. 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 1/8" x 6' or 10' x 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 the internal standard compared to the ratio at zero time and 1.00 M 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° before further recycling.

The kinetics of these reactions can be analyzed as pseudo first order reactions since although the quadricyclane concentration is constantly decreasing, the catalyst concentration remains constant throughout the conversion of quadricyclane to norbornadiene. Thus, the observed pseudo 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 $k = k_0V/(60W)$ where V is the volume of the solution in liters, W is the weight of the catalyst in grams, and the 60 converts the time scale from minutes to seconds. Except as otherwise noted all plots of -ln(concentration) versus reaction time were approximately linear over 5 to 7 half lives. A rate constant k_M was also calculated on the basis of the metal concentration determined by metal analyses on the polymers.

Representative kinetic data obtained in this matter are summarized in Tables 1 and 2 for the cobalt(II) porphyrin and palladium(II) chloride catalysts, respectively. These data include runs obtained by successively recycling the same batch of catalyst in different reactions. Such data are important for the evaluation of the suitability of these attached metal complex catalysts for use in the norbornadiene-quadricyclane photochemical energy storage system where repeated recycling with the same batch of catalyst will occur.

Results

A. The polystyrene-anchored carboxamide-linked cobalt(II) porphyrin catalysts (Table 1)

The rate constants k for the quadricyclane to norbornadiene conversion catalyzed by the polystyrene-anchored carboxamide-linked cobalt(II) porphyrin V were found to decrease with repeated recycling of the same batch (Table Ia and Ib). This decrease in activity upon recycling was less severe but still significant in the series of runs performed under nitrogen (Table Ib). 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.

A possible explanation for the deactivation of the cobalt(II) porphyrin catalysts upon repeated recycling is the oxidation of some of the cobalt(II) to cobalt(III) by traces of oxygen or peroxides. In an attempt to regenerate this deactivated catalyst, it was treated with ferrocene in benzene at 25° for 2 hr. hoping to reduce any cobalt(III) back to cobalt(II) with concurrent oxidation of ferrocene to ferricinium ion. The ferrocene treatment between the fourth and fifth recycles (Table Ib) prevented any loss of catalyst activity between these recycles but the catalyst continued to suffer further losses in activity upon further recycling (the sixth and seventh recycles in Table Ib) when ferrocene treatment was not included. Further limitations of the efficacy of ferrocene as a preventative against catalyst deactivation were indicated by the observation that the catalyst deactivation still occurred when the conversion of quadricyclane to norbornadiene by the polymer-anchored cobalt(II) porphyrin(V) was run in the presence of sufficient dissolved ferrocene to keep all of the cobalt sites on the polymer in the +2 oxidation state (Table Ic).

The conversion rate of quadricyclane to norbornadiene by the polymer-anchored cobalt(II) porphyrin catalyst V appeared to be very solvent sensitive. Even the minor solvent change from benzene to o-xylene (Table Id) resulted in a reproducible retardation of the reaction rate by about 40%.

B. The polystyrene-anchored phosphine palladium(II) chloride catalysts (Table 2)

Recycling studies on the conversion of quadricyclane to norbornadiene using the polystyrene-anchored palladium catalyst containing 0.70% palladium (Table 2b) indicate that the initial activity of the fresh catalyst decreases slightly upon the first recycle but that this slightly lowered activity is maintained in the second recycle. However, extensive losses of catalytic activity occurred during the third and fourth recycles.

When a portion of the fresh polystyrene-anchored 0.70% palladium(II) chloride catalyst was pre-equilibrated with a solution of norbornadiene and then used for the catalysis of the conversion of quadricyclane to norbornadiene, the observed rate constant (Table 2b) matched most closely that of the untreated palladium catalyst after the first recycle. Thus exposure to norbornadiene has an inhibiting effect on the palladium catalyst. This could arise either from formation of a norbornadiene-palladium complex bound to the polymer and with reduced catalytic activity or to metal leaching by displacement of the polymeric phosphine ligands by norbornadiene with formation of a soluble palladium complex.

If the first and last portions of the kinetic study on the fresh palladium catalyst (Table 2b) are analyzed separately, a change is observed in the rate constant during the course of the run. The initial rate constant is high but falls to a value matching that observed for the first recycle by the end of the run. This eliminates the possibility that metal leaching from the support causes the catalyst deactivation, since a rate increase during the course of a run would be expected if this were the case.

The cause of the drastic rate decreases during the third and fourth recycles of the polystyrene-anchored phosphine palladium(II) chloride catalyst (Table 2b) is unclear. Possibly upon repeated recycling adventitious oxygen or peroxides oxidizes some of the polymer-anchored phosphorus atoms to phosphine oxide units, which can lead to metal leaching from the polymer.

Comparison of the specific activity per metal atom, k_M, of the polystyrene-anchored palladium catalysts and the soluble catalyst $[(C_6H_5)_3P]_2PdCl_2$ indicates that the polystyrene-anchored catalyst containing 1.1% palladium is approximately twice as active as the polystyrene-anchored catalyst containing 0.70% palladium whereas the soluble catalyst $[(C_6H_5)_3P]_2PdCl_2$ is about 1000 times as active as the polystyrene-supported catalysts. A major cause of this rate difference is likely to be the slower diffusion of the quadricyclane to the catalyst sites inside the polymer matrix. A very large rate decrease was also observed with polystyrene-anchored $(R_3P)_3Rh(CO)H$ relative to analogous soluble monomeric rhodium(I) catalysts where rate differences of 10 to 100 were observed which were temperature dependent in the range 140° to 60°.[27]

Comparison of the specific activities per metal atom, k_M, of the polystyrene-anchored carboxamide-linked cobalt(II) porphyrin catalysts (Table 1) and the palladium(II) chloride catalysts (Table 2) indicate clearly that the cobalt catalysts are about five times more active for the conversion of quadricyclane to norbornadiene under comparable conditions. However, the relative suitabilities of these two types of catalysts for a practical solar energy storage system based on the norbornadiene-quadricyclane interconversion will depend on a variety of other factors besides their catalytic activities. Thus retention of catalytic activity on repeated recycling and freedom from side reactions in the conversion of quadricyclane to norbornadiene are likely to be as important as the initial catalytic activity in the ultimate selection of an attached metal catalyst for a solar energy storage system. Work on both the cobalt and palladium attached metal complex catalysts discussed in this paper is continuing in an effort to develop a catalyst with the properties most suitable for use in a practical solar energy storage system. Meanwhile, the polystyrene-anchored carboxamide-linked cobalt(II) porphyrin V has been successfully incorporated in a laboratory prototype of a solar energy storage system, which is currently undergoing cycling studies.

Acknowledgment: We are indebted to the U.S. Energy Research and Development Administration for partial support of this work under Contract E(38-1)-893. We also acknowledge helpful discussions with Professor R.R. Hautala and Professor C. R. Kutal during the course of this project.

LITERATURE REFERENCES

1. R. R. Hautala, J. Little, and E. M. Sweet, Solar Energy, in press.
2. H. Hogeveen and H. C. Volger, J. Am. Chem. Soc., 89, 2486 (1967).
3. J. Manassen, J. Catal., 18, 38 (1970).
4. P. G. Gassman and D. S. Patton, J. Am. Chem. Soc., 90, 7276 (1968).
5. P. G. Gassman and T. J. Atkins, J. Am. Chem. Soc., 93, 1042 (1971).
6. P. G. Gassman and T. Nakai, J. Am. Chem. Soc., 93, 5897 (1971).
7. P. G. Gassman and F. J. Williams, J. Am. Chem. Soc., 94, 7733 (1972).
8. P. G. Gassman, G. R. Meyer, and F. J. Williams, J. Am. Chem. Soc., 94, 7741 (1972).
9. P. G. Gassman and T. J. Atkins, J. Am. Chem. Soc., 94, 7748 (1972).
10. R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, J. Am. Chem. Soc., 93, 5894 (1971).
11. R. Noyori, T. Suzuki, and H. Takaya, J. Am. Chem. Soc., 93, 5896 (1971).
12. P. G. Gassman, T. J. Atkins, and J. T. Lamb, J. Am. Chem. Soc., 94, 7757 (1972).
13. R. Noyori, T. Odegi, and H. Takaya, J. Am. Chem. Soc., 92, 5780 (1970).
14. R. Noyori, Y. Kumagai, I. Umeda, and H. Takaya, J. Am. Chem. Soc., 94, 4018 (1972).
15. P. Binger, Angew. Chem. Int. Ed., 11, 309 (1972).
16. P. Binger and J. McMeeking, Angew. Chem. Int. Ed., 12, 995 (1973).
17. L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 6366 (1970).
18. L. A. Paquette, Accts. Chem. Research, 4, 280 (1971).
19. W. Merk and R. Pettit, J. Am. Chem. Soc., 89, 4788 (1967).
20. J. Wristers, L. Brener, and R. Pettit, J. Am. Chem. Soc., 92, 7499 (1970).
21. H. D. Wilson and R. G. Rinker, J. Catal., 42, 268 (1976).
22. L. D. Rollmann, J. Am. Chem. Soc., 97, 2132 (1975).
23. A. D. Adler, F. R. Longon, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, J. Org. Chem., 32, 476 (1967).
24. E. B. Fleischer, J. M. Palmer, F. S. Srivastava, and A. Chatterjee, J. Am. Chem. Soc. 93, 3162 (1971).
25. W. G. Dauben and A. Kielbania, Jr., J. Am. Chem. Soc., 94, 3669 (1972).
26. D. C. Evans, M. H. George, and J. A. Barrie, J. Polym. Chem., 12, 247 (1974).
27. R. M. Hanes, Ph.D. Thesis, University of Alabama, 1976.

TABLE 1

KINETIC DATA FOR THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE BY THE POLYSTYRENE-ANCHORED CARBOXAMIDE-LINKED COBALT(II) PORPHYRIN CATALYST (V)

	Solvent	$k(\text{sec.}^{-1}(\text{g./l.})^{-1})$	$k_M(\text{sec.}^{-1}(\text{g.-atom metal/l.})^{-1})$
a) Runs in air			
Fresh catalyst	benzene	1.3×10^{-4}	1.7
Recycle	benzene	0.9×10^{-4}	1.2
b) Runs under nitrogen			
Fresh catalyst	xylenes	1.6×10^{-4}	2.1
First recycle	xylenes	1.5×10^{-4}	2.0
Second recycle	xylenes	1.3×10^{-4}	1.7
Third recycle	xylenes	1.2×10^{-4}	1.6
Fourth recycle	xylenes	0.90×10^{-4}	1.2
Treatment with 0.1 M ferrocene in benzene at 25° for 2 hr.			
Fifth recycle	xylenes	0.93×10^{-4}	1.2
Sixth recycle	xylenes	0.73×10^{-4}	1.0
Seventh recycle	xylenes	0.65×10^{-4}	0.9
c) Runs under nitrogen in the presence of 0.05 M ferrocene			
Fresh catalyst	benzene	1.8×10^{-4}	2.4
First recycle	benzene	1.5×10^{-4}	2.0
Second recycle	benzene	1.4×10^{-4}	1.8
Third recycle	benzene	1.3×10^{-4}	1.7
d) Study of solvent effects (average of 2 runs)			
Fresh catalyst	benzene	1.8×10^{-4}	2.4
Fresh catalyst	o-xylene	1.1×10^{-4}	1.5

TABLE 2

KINETIC DATA FOR THE CONVERSION OF QUADRICYCLANE TO NORBORNADIENE BY PALLADIUM(II) CHLORIDE CATALYSTS

	Solvent	k(sec.$^{-1}$ (g./l.)$^{-1}$)	k_M(sec.$^{-1}$ (g.-atom metal/l.)$^{-1}$)
a) $[(C_6H_5)_3P]_2PdCl_2$			
	xylene[a]	5.4×10^{-2}	3780
	benzene[b]	1.2×10^{-2}	80
b) Polystyrene-anchored phosphine palladium(II) chloride with 0.70% Pd			
Fresh catalyst	xylene	2.0×10^{-5}	0.31
First nine points		3.1×10^{-5}	0.47
Last nine points		1.3×10^{-5}	0.20
First recycle	xylene	1.5×10^{-5}	0.23
Second recycle	xylene	1.6×10^{-5}	0.24
Third recycle	xylene	0.41×10^{-5}	0.062
Fourth recycle	xylene	0.18×10^{-5}	0.028
Fresh catalyst after norbornadiene equilibration	xylene	1.4×10^{-4}	0.21
c) Polystyrene-anchored phosphine palladium(II) chloride with 1.1% Pd			
Fresh catalyst	benzene	8.0×10^{-5}	0.78

[a] 0.1 M quadricyclane, 2.7×10^{-4} M Pd.

[b] 0.5 M quadricyclane, 6.2×10^{-5} M Pd.

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