Photogenerated Catalysis in Metal–Organic Systems. The Importance of Photoinduced Electron Transfer in the Metal-Mediated Valence Isomerizations of Strained Organic Molecules

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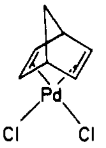
Several highly strained organic molecules were irradiated at 405 nm in the presence of $PdCl_2(\eta^4\text{-NBD})$ (NBD is norbornadiene). Both quadricyclene and 2-carbomethoxyquadricyclene undergo photoinduced valence isomerization with quantum yields that are substantially above unity. In contrast, 2,3-dicarbomethoxyquadricyclene and 4-carbomethoxyhomocubane are much less reactive. A correlation exists between the isomerization quantum yields and the oxidative half-wave potentials of the ground-state organic molecules. The results are consistent with a redox-chain mechanism in which electron transfer from the organic substrate to photoexcited $PdCl_2(\eta^4\text{-NBD})$ plays a prominent role.

Introduction

In a recent article,[1] we reported that irradiation of the square-planar d^8 complex $PdCl_2(\eta^4\text{-NBD})$ (1) in the presence of the highly strained hydrocarbon quadricyclene (Q) results in valence isomerization of the latter to norbornadiene (NBD) with quantum yields that can exceed 10^2 (reaction 1). This novel behavior was attributed to the operation of a redox-chain mechanism in which the initiation step involves reductive quenching of a Pd-to-NBD charge-transfer excited state of 1 by Q (reaction 2). The resulting quadricyclene radical cation, Q^+, undergoes rapid and irreversible rearrangement to its more stable isomer NBD^+ (reaction 3).[2] Since oxidation of Q by NBD^+ (reaction 4) is thermodynamically favorable,[3] Q^+ is regenerated and can reenter the cycle. Recombination of either of the radical cations with the reduced Pd complex or a trace impurity (reaction 5) results in chain termination.



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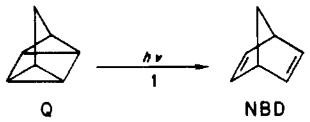
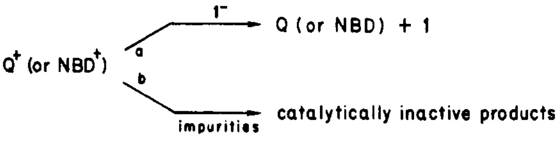


(1)

$$1 \overset{h\nu}{\rightleftharpoons} 1^* \xrightarrow{Q} 1^- + Q^+ \qquad (2)$$

$$Q^+ \longrightarrow NBD^+ \qquad (3)$$

$$NBD^+ + Q \longrightarrow NBD + Q^+ \qquad (4)$$



(5)

The observation that the tripartite interactions of light, 1, and Q result in photogenerated catalysis[4] of valence isomerization prompted us to investigate the generality of this behavior among other strained organic molecules. In this report, we compare the reactivities of Q, the substituted quadricyclenes QR and QR_2, and the homocubane derivative HCR (Figure 1) upon exposure to light in the presence of 1. The results reveal a correlation between the quantum efficiency of isomerization and the ease of oxidation of the organic compound. This finding and related observations are discussed within the context of the redox-chain mechanism described above (reactions 2–5).

Experimental Section

(a) Reagents. Norbornadiene (Aldrich) was purified by three successive distillations from potassium metal under a nitrogen atmosphere. Quadricyclene was prepared and purified as described previously.[5] 2-Carbomethoxyquadricyclene (QR)[6] and 2,3-dicarbomethoxyquadricyclene (QR_2)[7] were synthesized by published procedures and gave satisfactory elemental analyses; gas chromatography revealed, however, that each compound contained ~4% of the corresponding substituted norbornadiene (NBDR or $NBDR_2$, Figure 1). Analytically pure 4-carbomethoxyhomocubane (HCR) was prepared according to the route described by Paquette et al.[8a] and exhibited a single peak in its gas chromatogram. The directions of the same group were followed to synthesize two isomers of HCR, a carbomethoxy-substituted norsnoutane, NSTR,[8a] and a carbomethoxy-substituted tricyclic diene, TCDR[8b] (Figure 1). Samples of $PdCl_2(\eta^4\text{-NBD})$[9] and *trans*-$PdCl_2(py)_2$[10] (py is pyridine) were prepared by literature procedures and characterized by elemental analysis and/or electronic spectroscopy. Samples of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ and $[RhCl(\eta^4\text{-COD})]_2$ (COD is 1,5-cyclooctadiene) were purchased from Engelhard Corp. and used as received. Spectrograde methylene chloride was obtained from Aldrich Chemical Co. and used without further purification unless noted otherwise.

(b) Equipment and Procedures. Electronic absorption spectra were recorded on a Cary 15 spectrophotometer. The photolysis apparatus consisted of a 200-W high-pressure mercury-arc lamp whose output was passed through a Bausch and Lomb high-intensity monochromator (300-nm blaze, 1350 grooves/mm).

In a typical photochemical experiment, a solution containing the transition-metal compound and organic substrate was placed

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[1] Borsub, N.; Kutal, C. *J. Am. Chem. Soc.* **1984**, *106*, 4826. See also: Yasufuku, K.; Takahashi, K.; Kutal, C. *Tetrahedron Lett.* **1984**, *25*, 4893.

[2] Haselback, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583. Roth, H. D.; Manion Schilling, M. L.; Jones, G., II *J. Am. Chem. Soc.* **1981**, *103*, 1246. Ragavachari, K.; Haddon, R. C.; Roth, H. D. *Ibid.* **1983**, *105*, 3110.

[3] Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113.

[4] Photogenerated catalysis has been defined as the light-induced generation of a ground-state catalyst from a catalytically inactive precursor. Salomon, R. G. *Tetrahedron* **1983**, *39*, 485.

[5] Borsub, N.; Chang, S.-C.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 538.

[6] Koser, G. F.; Yu, S.-M. *J. Org. Chem.* **1973**, *38*, 1755.

[7] Cristol, S. S.; Snell, R. C. *J. Am. Chem. Soc.* **1958**, *80*, 1950.

[8] (a) Paquette, L. A.; Ward, J. S.; Boggs, R. A.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 1101. (b) Paquette, L. A.; Boggs, R. A.; Ward, J. S. *Ibid.* **1975**, *97*, 1118.

[9] Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.

[10] Burmeister, J. L.; Basolo, F. *Inorg. Chem.* **1964**, *3*, 1587.

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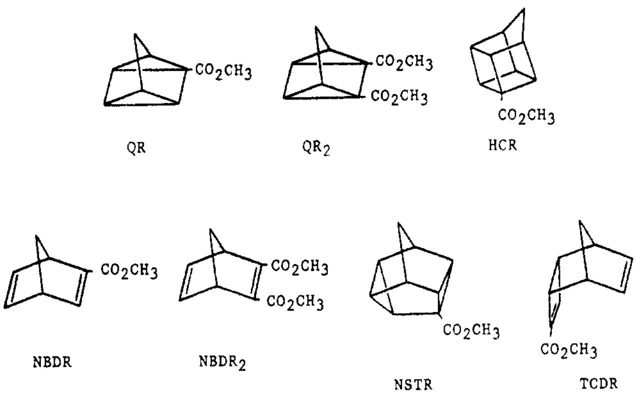

Figure 1. Structures of various compounds employed in this study.

in a 1-cm rectangular quartz cell, deoxygenerated with a slow stream of nitrogen gas for 20 min, and then irradiated at room temperature while being stirred. An accompanying dark sample was run to determine the extent of any thermal reaction. Light intensity was measured by ferrioxalate actinometry.[11]

Irradiated and dark samples were analyzed by gas chromatography on a Varian 2700 instrument equipped with a flame ionization detector. All chromatographic columns were stainless steel and had a 0.085-in. inner diameter. The following operating conditions (column length, packing, temperature) were employed to separate the indicated isomeric mixtures: NBD/Q-6 ft, 5% OV-101 on Chromosorb G, 90 °C; NBDR/QR-3 ft, 5% OV-101 on Chromosorb G, 70 °C; $NBDR_2/QR_2$-3 ft, 5% OV-101 on Chromosorb G, 120 °C; TCDR/HCR/NSTR-5 ft, 15% polymethyl phenyl ether on Chromosorb W, 170 °C. Relative retention times for the various isomers are as follows: NBD (1.0)/Q (2.9); NBDR (1.0)/QR (3.5); $NBDR_2$ (1.0)/QR_2 (2.3); TCDR (1.0)/HCR (1.2)/NSTR (1.3).

It was necessary to remove 1 from samples of QR and QR_2 prior to analysis, since the complex or its decomposition product(s) catalyzed thermal rearrangements of the strained organic compounds in the gas chromatograph. This separation was accomplished by shaking a 1-mL aliquot of the sample solution with 2 mL of a saturated aqueous solution of potassium cyanide. The resulting two-phase system consisted of an aqueous layer containing Pd cyanide complexes and a nonaqueous layer containing QR or QR_2. The former layer was discarded, while the nonaqueous portion was dried over Na_2SO_4 and then analyzed by gas chromatography.

Results

Since transition metals catalyze the thermal rearrangements of a wide variety of strained-ring organic molecules,[12] we determined the extent to which such processes occur in the systems investigated in this study. Solutions of a metal complex and organic substrate were maintained at 24 ± 0.5 °C in the dark for a period of 1 h and then analyzed by gas chromatography. Under these conditions, negligible (<2%) isomerization occurs for Q, QR, QR_2, and HCR in the presence of 1. Similarly, HCR remains unchanged in solutions containing *trans*-$IrCl(CO)(PPh_3)_2$ or $[RhCl(\eta^4\text{-COD})]_2$.

Table I summarizes the results obtained upon irradiating each of the strained organic molecules in the presence of 1. The quantum yield (ϕ) data refer to valence isomerization processes and were determined at 405 nm. Also listed are the half-wave oxidation potentials ($E_{1/2}$) of the organic substrates. Though the data base is limited, it reveals an interesting inverse correlation between ϕ and $E_{1/2}$. Thus the easily oxidized Q molecule rearranges to NBD with exceptionally high quantum efficiency. The presence of the electron-withdrawing carbomethoxy group in QR raises the oxidation potential relative to Q but also causes a sharp reduction in the quantum yield for isomerization to the corresponding substituted norbornadiene (NBDR). Nonetheless, the finding that ϕ exceeds unity establishes the operation of a photogenerated catalytic cycle in the 1–QR system. Further increases in $E_{1/2}$ caused by the incorporation of a second CO_2CH_3 group, as in QR_2, or by a change to the homocubane structure, as in HCR, renders the organic substrate unreactive toward photoinduced rearrangement.

Table I. Quantum Yields for Photoisomerization of Strained-Ring Compounds in the Presence of 1[a]

compd	concn, M	$E_{1/2}$, V vs. SCE[b]	ϕ
Q	0.39	0.91[c]	230
QR	0.44	1.2[d]	3.0
QR_2	0.45	1.64[c]	<0.06[e]
HCR	0.06	2.0[d]	<0.06[e]

[a] Irradiations performed at 405 nm; solvent was CH_2Cl_2. [b] Since the one-electron oxidations of these strained molecules are irreversible, the $E_{1/2}$ values are not thermodynamic quantities. Rather, the assumption is made that the cited values (which are shifted kinetically from the reversible potentials) are in the same relative order as the true thermodynamic potentials.[3] [c] Taken from ref 3. [d] Calculated from data in ref 3 by addition of 0.3 V to the $E_{1/2}$ value of the parent hydrocarbon. This increment represents the average electron-withdrawing effect of the CO_2CH_3 group (e.g., $E_{1/2}(QR_2) - E_{1/2}(Q) = 0.73$ V). [e] Since no measurable isomerization occurs, this value reflects our limits of detection. The compound also is unreactive upon irradiation at 366 and 313 nm.

Table II. Quantum Yields for Photoisomerization of QR to NBDR[a]

run	[QR], M	light intensity, (einsteins· s^{-1}) x10^9	ϕ
A	0.22	6.80	1.3
B	0.29	7.00	1.6
C	0.36	6.90	1.7
D	0.45	7.00	3.0
E	0.36	3.18	3.3
F	0.37	26.8	1.4
G	0.37	31.8	1.3
H	0.37	7.70	2.2[b]
I	0.39	7.35	<0.06[c]

[a] Unless indicated otherwise, the following experimental conditions were employed: irradiation at 405 nm, [1] = 6 × 10^{-4} M, CH_2Cl_2 as solvent. [b] The CH_2Cl_2 solvent was distilled from P_2O_5 prior to use. [c] *trans*-$PdCl_2(py)_2$ replaced 1 as the light-absorbing transition-metal complex.

A more detailed photochemical investigation of the 1–QR system is summarized in Table II. Several important features should be noted: (1) ϕ increases with increasing QR concentration (runs A–D); (2) ϕ decreases with increasing light intensity (runs C, E–G); (3) rigorous exclusion of water from the system has little effect upon ϕ (run H);[13] (4) QR is unreactive when irradiated in the presence of *trans*-$PdCl_2(py)_2$ (run I). In addition to these results, we found no evidence of post-irradiation effects in samples analyzed over a period of 3 h following photolysis. Moreover, the satisfactory mass balance obtained upon prolonged irradiation indicates that isomerization of QR to NBDR proceeds with high (>85%) chemical yield.

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(11) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(12) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(13) This result discounts the possibility that a trace amount of water in the solvent functions as a proton donor in the acid-catalyzed thermal rearrangement of QR; e.g., see ref 3.

In a series of exploratory studies, the d^8 complexes *trans*-$IrCl(CO)(PPh_3)_2$ and $[RhCl(\eta^4\text{-COD})]_2$, both of which are reported to contain low-lying metal-to-ligand charge transfer excited states,[14] were irradiated at 313, 366, and 405 nm in the presence of HCR for periods of 30–120 min. In all cases, light caused no discernible reaction of the organic substrate.

Discussion

Photogenerated catalysis of valence isomerization has now been observed in two metal–organic systems: 1–Q and 1–QR. Evidence supporting the operation of a redox-chain mechanism (reactions 2–5) in the first case has been summarized elsewhere.[1] The present study has yielded new information that, in our view, reinforces this earlier assignment and in addition, strongly suggests that a redox-chain pathway is responsible for the photochemical behavior of *all* of the strained-ring molecules listed in Table I. It is this theme of a common mechanism that we wish to develop in the ensuing discussing.

Perhaps the most compelling evidence in favor of a redox-chain mechanism is the inverse correlation between ϕ and $E_{1/2}$ found in Table I. Minimally, this behavior strongly supports the importance of electron transfer in the overall mechanistic sequence. On a more detailed level, it is consistent with the proposed chain initiation step (e.g., reaction 2) in which reductive quenching of an excited state of 1 by the organic substrate produces the catalytically active radical cation species (e.g., Q^+). That is, reductive quenching should compete less and less favorably with other excited-state deactivation processes as the organic quencher becomes increasingly difficult to oxidize.[15] As a result, fewer radical cations are generated and the overall quantum yield for isomerization decreases accordingly.

Additional support for the operation of a redox-chain mechanism is provided by the photochemical behavior of the 1–QR system summarized in Table II. In analogy to reaction 2, we propose that reductive quenching of 1^* by QR generates the primary photoproducts 1^- and QR^+. The radical cation can then enter a cycle in which it is consumed via rearrangement to the more stable isomer $NBDR^+$ (as in reaction 3) and regenerated via thermal oxidation of QR by $NBDR^+$ (as in reaction 4).[16] Several repetitions of this two-step cycle readily accounts for isomerization quantum yields above unity. The observed rise in ϕ with increasing QR concentration follows from the bimolecular kinetics of electron transfer between $NBDR^+$ and QR. Similarly, the inverse dependence of ϕ upon light intensity reflects increased competition from bimolecular chain termination processes (as in reaction 5a) as higher concentrations of 1^- are produced photochemically.

Examination of the electronic absorption spectrum of 1[1] reveals that both ligand field and Pd-to-NBD charge-transfer excited states are populated upon 405-nm excitation. In our previous study[1] of the 1–Q system, we identified the latter type of state as the one more likely to be involved in the key reductive quenching step (reaction 2) that initiates photogenerated catalysis. This assignment, for which considerable precedent exists,[17] can now be reevaluated in light of new information contained in Table II. In particular, it should be noted that the photogenerated catalytic behavior observed when QR is irradiated in the presence of 1 ceases when 1 is replaced by *trans*-$PdCl_2(py)_2$ (compare runs D and I). Significantly, the Pd-to-py charge-transfer excited states in *trans*-$PdCl_2(py)_2$ are energetically well separated from some lower lying liquid field states,[18] and only the latter are populated upon excitation at 405 nm. The finding that QR is unreactive under these conditions therefore lends credence to our earlier conclusion that ligand field excited states in Pd(II) complexes play no role in initiating redox-chain cycles.

Finally, there are several possible explanations for the lack of reactivity of HCR upon being irradiated in the presence of *trans*-$IrCl(CO)(PPh_3)_2$ or $[RhCl(\eta^4\text{-COD})]_2$. It may be, for example, that the low-lying metal-to-ligand charge-transfer excited states in these complexes have reduction potentials below 2 V vs. SCE and thus are unable, on energetic grounds, to be reductively quenched by HCR. Other possibilities include a short excited-state lifetime of the metal complex and rapid back-electron transfer between the primary photoproducts of reductive quenching. Additional studies are required to evaluate the importance of these various factors.

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Registry No. 1, 12317-46-3; Q, 278-06-8; QR, 24161-47-5; QR_2, 714-53-4; HCR, 40317-63-3.

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[14] Geoffroy, G. L.; Isci, H.; Litrenti, J.; Mason, W. R. *Inorg. Chem.* **1977**, *16*, 1950. Epstein, R. A.; Geoffroy, G. L.; Keeney, M. E.; Mason, W. R. *Ibid.* **1979**, *18*, 478.

[15] Correlations between the rates of excited-state quenching and the energetics of quencher–quenchee electron transfer are well established: Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.

[16] Oxidation of QR by $NBDR^+$ should be favorable by ~0.5 V.[3]

[17] For example, see: Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

[18] For details of the absorption spectrum of *trans*-$PdCl_2(py)_2$, see: Balch, A. L.; Petridis, D. *Inorg. Chem.* **1969**, *8*, 2247.