Photogenerated Catalysis by Transition-Metal Complexes. Photoacceleration of the Valence Isomerization of Quadricyclene to Norbornadiene in the Presence of $PdCl_2(\eta^4\text{-norbornadiene})$

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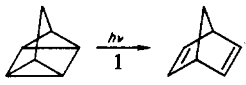
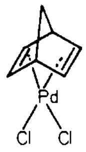
Abstract: Light accelerates the rate at which $PdCl_2(\eta^4\text{-NBD})$ (**1**) catalyzes the valence isomerization of quadricyclene (Q) to norbornadiene (NBD). The observed quantum yield, defined as (mol of NBD produced/mol of photons absorbed), can exceed 10^2 and is dependent upon Q concentration, light intensity, and solvent. Several lines of evidence are consistent with the intermediacy of radical species in the isomerization process. The results are discussed in terms 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.

Transition-metal complexes catalyze the thermal rearrangements of a variety of strained-ring organic molecules.[1] Studies of the kinetics and product distributions of these processes have provided important insights as to the mechanistic roles of the catalyst (both metal and attached ligands), substituents on the organic substrate, and the solvent. Some time ago we reported the qualitative observation that catalysis of the valence isomerization of quadricyclene (Q) to norbornadiene (NBD) by $PdCl_2(\eta^4\text{-NBD})$ (**1**) is accelerated by light (reaction 1).[2] Since photochemical effects in metal-catalyzed ring-opening processes had not been investigated previously, we decided to explore the **1**-Q system in greater detail. A primary aim was to delineate the role(s) played by the metal complex in the overall reaction sequence. Our findings are presented in this report.



(1)

Q NBD



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Experimental Section

Analytically pure **1** was prepared by the procedure of Chatt, Vallarino, and Venanzi.[3] Purified NBD and Q were obtained as described previously.[4] All other chemicals were of at least reagent grade quality and were used as received, except isoamyl nitrite which was distilled under argon.

In a typical photochemical experiment, a nitrogen-purged methylene chloride solution containing 0.5 M Q and 4×10^{-4} M **1** was irradiated[5] with stirring in a 1-cm quartz cell fitted with a ground-glass stopper. The cell was placed in a thermostated holder maintained at 25 ± 0.5 °C. The photolysis apparatus consisted of a 200-W high-pressure mercury-arc lamp whose output was passed through a high-intensity monochromator (19-nm spectral bandwidth). Light intensity was measured by ferrioxalate actinometry.[6] Irradiated samples were analyzed for NBD and Q by gas chromatography. The equipment and operating conditions were very similar to those reported in an earlier study.[7]

Table I. Spectral Assignments for $PdCl_2en$ in Aqueous HCl

λ_{max},[a] nm	ϵ,[a] $M^{-1}\ cm^{-1}$	transition assignment[b]
424	16 ± 7	^{3}LF
375	292 ± 18	^{1}LF
340	105 ± 30	^{1}LF
292	100 ± 70	^{1}LF
253	1490 ± 560	^{1}CT (Cl to Pd)

[a] The λ_{max} and ϵ values are derived from a Gaussian analysis of the observed spectrum (ref 8). [b] ^{3}LF = spin-forbidden ligand field; ^{1}LF = spin-allowed ligand field; ^{1}CT = spin-allowed charge transfer.

Electronic absorption spectra were measured on a Cary 219 spectrophotometer. A Perkin-Elmer MPF-44B spectrofluorimeter was used in the search for luminescence. Proton NMR spectra were obtained with a JEOL FX-90Q spectrometer. Conductance measurements were made with a Yellow Springs Instrument Model 31 conductivity bridge and calibrated cell.

Results and Discussion

(a) Spectral Properties. The electronic absorption spectrum of **1** in CH_2Cl_2 (Figure 1) consists of overlapping bands with maxima at 259, 327, and 398 nm. Reasonable assignments of these features can be made by reference to the spectral analysis of $PdCl_2en$ (**2**) reported by Martin and co-workers[8] (Table I; en is ethylenediamine). Since the gross structural characteristics and ligand-field environments of **1** and **2** are similar, we would expect their ligand-field transitions to occur at comparable energies. Accordingly, we associate the weak, broad band at 398 nm in the spectrum of **1** with one or more spin-allowed ligand-field transitions. The more intense band at 327 nm, on the other hand, has no obvious counterpart in the spectrum of **2**. Since **1** contains a ligand (i.e., NBD) having low-lying π^*-acceptor orbitals whereas **2** does not, we assign the 327-nm band as a spin-allowed Pd-to-NBD charge-transfer transition.[9,10] Support for these assignments is provided by the observation that switching the solvent from CH_2Cl_2 to the more polar CH_3CN causes the 327-nm band to shift to 317 nm, while the 398-nm band is essentially unaffected. Similar blue shifts of metal-to-ligand charge-transfer transitions

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[1] Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

[2] Kutal, C.; Schwendiman, D. P.; Grutsch, P. A. *Sol. Energy* **1977**, *19*, 651.

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

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

[5] In all photochemical runs, **1** was the sole absorbing species in solution.

[6] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

[7] Sterling, R. F.; Kutal, C. *Inorg. Chem.* **1980**, *19*, 1502. A 6-in. length of stainless-steel tubing packed with Chromosorb G HP (80–100 mesh) was placed between the injector port and the main portion of the gas-chromatographic column. This precolumn trap removed nonvolatile Pd-containing species which accumulated upon repeated sample injections. Better reproducibility resulted when the trap was repacked after every 6–8 injections. Control experiments indicated that thermal reversion of Q to NBD in the gas chromatograph was negligible.

[8] Martin, D. S.; Robbins, G. A.; Rush, R. M. *Inorg. Chem.* **1980**, *19*, 1705.

[9] Similar reasoning has been used to assign metal-to-olefin charge-transfer transitions in $PtCl_3(C_2H_4)^-$: Chang, T.-H.; Zink, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 287.

[10] Spin-forbidden ligand field and Pd-to-NBD charge-transfer transitions should be of low intensity and are most likely hidden under the 398-nm band.

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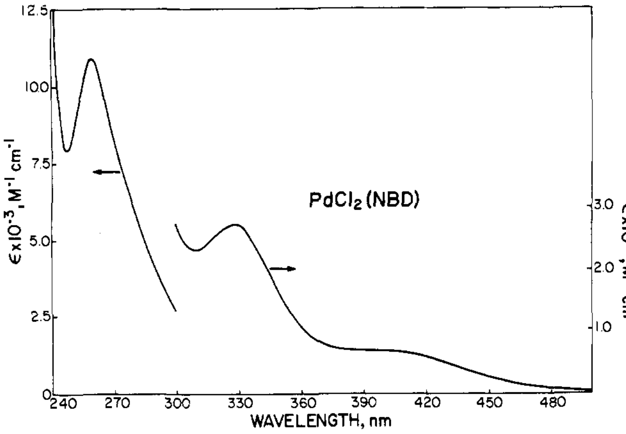

Figure 1. Electronic absorption spectrum of $PdCl_2(\eta^4\text{-NBD})$ in CH_2Cl_2.

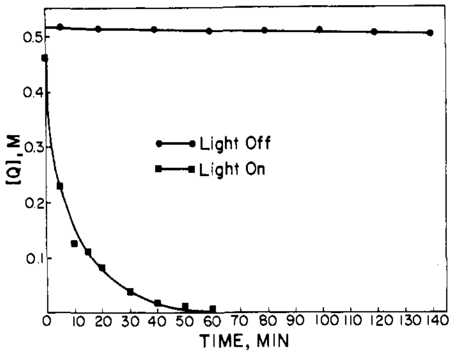

Figure 2. Effect of 313-nm light on the isomerization of Q to NBD in the presence of $PdCl_2(\eta^4\text{-NBD})$; solvent is CH_2Cl_2.

in polar solvents are well documented, whereas ligand-field bands generally are much less sensitive to the environment.[11] The origin of the very intense band at 259 nm in the spectrum of **1** is less certain. It could result from a spin-allowed Cl-to-Pd charge-transfer transition or possibly a second Pd-to-NBD charge-transfer transition.

No luminescence was detected from a room-temperature solution of **1** in CH_2Cl_2 upon excitation with 313-nm light. Repeating the measurement on a sample containing Q yielded the same negative result.

(b) Photochemical Studies. Figure 2 illustrates the dramatic effect of light on the valence isomerization of Q to NBD in the presence of catalytic amounts of **1**. A 0.5 M solution of Q in methylene chloride is more than 50% isomerized following 5 min of irradiation at 313 nm, whereas an identically prepared dark sample undergoes only about 1% conversion in 1 h. The photochemical process is characterized by a very high catalyst turnover (e.g., >1000 mol of NBD produced per mol of **1**). Moreover, photoisomerization is remarkably clean as evidenced by the excellent mass balance between reactant and product (Figure 3). Samples analyzed at different times following photolysis gave no indication of post-irradiation effects. This result establishes that the lifetime of any photogenerated catalytic species must be shorter than our shortest sampling time (37 s).[12]

Table II contains a compilation of quantum yield (ϕ) data obtained under a variety of experimental conditions. The key results can be summarized as follows: (1) ϕ greatly exceeds unity and decreases with increasing light intensity (runs A–C); (2) ϕ is relatively insensitive to changes in the wavelength of irradiation (runs B and G); (3) ϕ increases with increasing Q concentration (runs C and D); (4) addition of free NBD has little effect upon ϕ(runs A and E); (5) ϕ drops sharply as the solvent is changed from CH_2Cl_2 to CH_3CN (runs A and F); (6) ϕ decreases upon addition of a free radical scavenger such as isoamyl nitrite (runs G and H) or 1,2,4-trimethoxybenzene.[13]

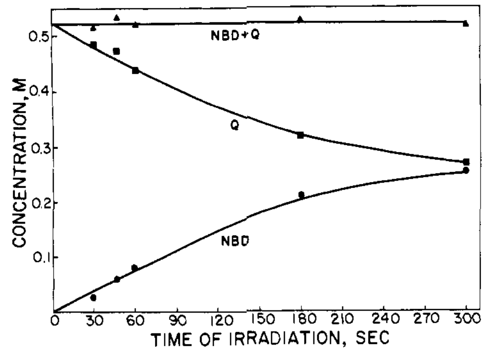

Figure 3. Mass balance during the 313-nm photoisomerization of Q to NBD in the presence of $PdCl_2(\eta^4\text{-NBD})$; solvent is CH_2Cl_2.

(c) Thermal Studies. While most of our studies were aimed at delineating the role of **1** in the photochemical isomerization of Q to NBD, we briefly examined the behavior of the Pd complex during the corresponding thermal isomerization process. Some interaction between **1** and Q occurs as evidenced by changes in the electronic absorption spectrum over a period of several hours following the mixing of the two components.[14] This behavior cannot be attributed to the formation of ionic species such as $PdCl(\eta^4\text{-NBD})(\text{solvent})^+$, since the equivalent conductance of a CH_2Cl_2 solution of 4×10^{-4} M **1** is very small (<0.2 ohm^{-1} cm^2) before and after the addition of Q. Moreover, proton NMR measurements on CH_2Cl_2 solutions containing 2×10^{-3} M **1** and 0.2 M Q provide no clear indication of Q-assisted loss of coordinated NBD or the generation of any new Pd-containing species. While we are uncertain as to the origin of the spectral change that occurs upon mixing **1** and Q, it is important to note that this change is not accelerated by light. Thus it can be concluded that either (i) the thermal and photochemical isomerization reactions of Q proceed by different mechanisms or (ii) the spectral change arises from a competing thermal process that is unrelated to isomerization.

(d) Mechanistic Interpretations. The observation that ϕ greatly exceeds unity constitutes prima facie evidence that the irradiation of **1** generates an active thermal catalyst for the isomerization of Q to NBD.[15] The simplest explanation for the similarity of the 313 and 405-nm quantum yields (Table II, runs B and G) is that a single excited state of **1** participates in the catalyst-forming step. Since ligand-field and metal-to-ligand charge-transfer states are energetically accessible at these wavelengths, we need to consider the likely consequences of populating each type of state.

If the photoactive state were ligand field in character, we would expect heterolytic cleavage of a metal–ligand bond to be an important photochemical process (reaction 2).[16] The resulting Pd species (e.g., **3** and/or **4**), having a high degree of coordinative unsaturation, could initiate isomerization by attacking the electron-rich cyclopropane rings of Q (reaction 3).[1] Regardless of the exact details of this latter process, the quantum yield results require that the photogenerated catalyst convert a large number of Q molecules to NBD prior to being deactivated (reaction 4a). Two lines of evidence appear to be inconsistent with this type of mechanism. First, added NBD has little effect upon the quantum yield (Table II, runs A and E). Such behavior is contrary to the expectation that the diene would capture the coordinatively un-

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[11] Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. Lees, A. J.; Adamson, A. W. *Ibid.* **1982**, *104*, 3804.

[12] That is, we required at least 37 s to remove the sample from the light beam, walk over to the gas chromatograph, and inject an aliquot of the photolyzed solution.

[13] Absorption by the radical scavenger is negligible under the conditions employed in these experiments.

[14] In contrast, a CH_2Cl_2 solution of **1** containing no Q undergoes no discernible spectral changes after sitting in the dark at 25 °C for 13 h or upon being irradiated at 313 nm for 40 min.

[15] In the terminology suggested by Salomon, this type of process is referred to as a photogenerated catalysis: Salomon, R. G. *Tetrahedron* **1983**, *39*, 485.

[16] Ligand-field photolysis of $PtCl_3(C_2H_4)^-$ in aqueous solution, for example, results in the competitive aquation of ethylene and chloride ion: Natarajan, P.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 5599.

$$1 \xrightarrow[\text{(ligand field)}]{h\nu} 1^* \longrightarrow \underset{3}{PdCl_2(\eta^2\text{-NBD})} \text{ and/or } \underset{4}{PdCl(\eta^4\text{-NBD})^+} \quad (2)$$

$$Q \xrightarrow{3/4} NBD \quad (3)$$

$$3/4 \begin{cases} \xrightarrow{a} 1 \\ \xrightarrow[b]{NBD} \text{catalytically inactive products} \end{cases} \quad (4)$$

saturated Pd species (reaction 4b) and thereby lower ϕ. Second, even low concentrations of a radical scavenger inhibit photoisomerization (Table II, runs G and H). Since radicals are not generated in any of the proposed steps, such inhibition is difficult to rationalize.

Another possible catalytic cycle for the conversion of Q to NBD can result from population of the Pd-to-NBD charge-transfer excited state of **1**. In the initiation step, this state is reductively quenched by Q (reaction 5).[17,18] The structurally labile radical cation, Q^+, then undergoes rapid and irreversible rearrangement to its more stable isomer, NBD^+ (reaction 6).[19] Since electron transfer from Q to NBD^+ (reaction 7) is energetically favorable,[18,19] Q^+ is regenerated and can reenter the cycle. Recombination of Q^+ or NBD^+ with the reduced Pd complex or trace impurities results in chain termination (reaction 8).

$$1 \xrightarrow[\text{(Pd-to-NBD charge transfer)}]{h\nu} 1^* \xrightarrow{Q} 1^- + Q^+ \quad (5)$$

$$Q^+ \longrightarrow NBD^+ \quad (6)$$

$$NBD^+ + Q \longrightarrow NBD + Q^+ \quad (7)$$

$$Q^+(\text{or } NBD^+) \begin{cases} \xrightarrow[a]{1^-} Q\text{ (or NBD)} + 1 \\ \xrightarrow[\text{impurities}]{b} \text{catalytically inactive products} \end{cases} \quad (8)$$

Several lines of evidence support a redox-chain mechanism of this type.[20] The repetition of reactions 6 and 7 readily accounts for quantum yields greater than unity. Moreover, the decrease in ϕ with increasing light intensity reflects differences in the kinetics of chain initiation vs. chain termination. Thus the rate of the former process (reaction 5) doubles with a twofold increase in light intensity, whereas the rate of chain termination (reaction 8a) experiences a fourfold enhancement under similar circumstances. Finally, the intermediacy of radical species in the rearrangement of Q to NBD is strongly supported by the inhibitory effect of radical scavengers.

It should be noted that while both **1** and light are required to initiate (reaction 5) the proposed catalytic cycle, the key chain-carrying species (reactions 6 and 7) is the quadricyclene radical cation, Q^+. Consequently, direct generation of Q^+ by electrochemical techniques would be expected to result in the catalyzed conversion of Q to NBD. To test this point, we subjected a 0.1 M solution of Q in methylene chloride to constant potential (1.3 V vs. SCE) oxidation at a Pt electrode and analyzed the amount of NBD produced.[21] The finding that the (mol of NBD produced)/(faradays passed) exceeds unity demonstrates the feasibility of reactions 6 and 7.

It is informative to compare our results with those obtained in studies of the Q-to-NBD rearrangement induced by organic sensitizers.[22] While the mechanism of sensitization in these latter systems involves electron transfer from Q to the photoexcited sensitizer (as in reaction 5) followed by rearrangement of Q^+ (reaction 6), quantum yields above unity have never been observed. Such behavior suggests that recombination of the photogenerated radical cation/anion pair (as in reaction 8a) competes favorably with oxidation of Q by NBD^+ (reaction 7). In contrast, the exceptionally high ϕ values found for **1** (Table II) are indicative of some type of inhibition of this recombination process. One possibility is that 1^- decomposes rapidly and irreversibly to a species which is ineffective as a scavenger for Q^+ or NBD^+. The observation of an irreversible reduction wave in the cyclic voltammogram of **1** at ca. −1 V vs. SCE is consistent with this suggestion.[23]

Table II. Quantum Yields (ϕ) for the Photoisomerization of Q to NBD in the Presence of **1**

run	light intensity, (einstein·s^{-1}) × 10^8	ϕ^a	conditions^b
A	0.50	$3.8 \pm 0.4 \times 10^{2c}$	
B	1.36	2.0×10^2	
C	4.1	1.1×10^2	
D	4.1	4.0×10^1	[Q] = 0.2 M
E	0.50	$3.7 \pm 0.2 \times 10^2$	1 M NBD added
F	0.48	5.8×10^1	solvent is CH_3CN
G	1.27	2.2×10^2	irradn at 405 nm
H	1.27	6.2×10^1	irradn at 405 nm, 7.4 × 10^{-3} M isoamyl nitrite added

^{a}Quantum yield is defined as (mol of NBD produced/mol of photons absorbed). ^{b}Unless indicated otherwise, the following experimental conditions were employed: 5-min irradiation at 313 nm, [**1**] = 4 × 10^{-4} M, [Q] = 0.5 M, CH_2Cl_2 as solvent. ^{c}Where quoted, uncertainty values represent mean deviation.

The only apparent inconsistency between our results and the proposed redox-chain mechanism is the decrease in quantum yield that occurs upon switching the solvent from CH_2Cl_2 to CH_3CN. Since the latter is more polar, we would expect it to favor the formation and separation of the chain-carrying ions and thus enhance ϕ.[20] While the observed behavior could reflect a complicated solvent dependence of reactions 5–8, we cannot entirely discount the occurrence of alternative mechanisms involving uncharged radical intermediates.[24] This possibility will be explored in future studies in which evidence for photogenerated radicals will be sought by electron-spin resonance techniques.

In closing, we wish to note that photogenerated transition-metal catalysis of ring-opening processes in strained organic molecules offers several potential advantages over the corresponding catalyzed thermal reactions. These include (1) significant rate enhancements at ambient temperatures, (2) the ability to control rates by altering light intensity, and (3) access to reaction pathways that yield products not observed thermally. Advantages 1 and 2 are realized in the present study, whereas advantage 3 has yet to be attained.

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Registry No. 1, 12317-46-3; **2**, 15020-99-2; NBD, 121-46-0; Q, 278-06-8.

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[17] Considerable precedent exists for bimolecular electron-transfer reactions of metal-to-ligand charge-transfer excited states: Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. Ahn, B.-T.; McMillin, D. R. *Inorg. Chem.* **1981**, *20*, 1427.

[18] Reductive quenching is facilitated by the low oxidation potential of Q; $E_{1/2}^{ox}$ (in CH_3CN) = 0.91 V vs. SCE. For comparison, $E_{1/2}^{ox}$ = 1.56 V for NBD. Gassman, P.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

[19] For a recent discussion of the structures and relative energies of NBD^+ and Q^+, see: Ragavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110.

[20] For examples of photoinitiated redox-chain processes in strictly organic systems, see: Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265. Mukai, T.; Sato, K.; Yamashita, Y. *Ibid.* **1981**, *103*, 670. Jones, G.; Becker, W. G.; Chiang, S.-H. *Ibid.* **1983**, *105*, 1269.

[21] Details of the electrocatalytic conversion of Q to NBD will be reported elsehwhere.

[22] See: Jones, G.; Becker, W. G. *Chem. Phys. Lett.*, **1982**, *85*, 271 and references cited therein.

[23] The cyclic voltammogram of **1** was obtained in CH_3CN at a scan rate of 50 mV/s.

[24] In their study[25] of the Q-to-NBD rearrangement induced by organic singlet sensitizers, Jones et al. also observed smaller quantum yields upon switching from a nonpolar to a polar solvent. They attributed this behavior to the formation of different photogenerated intermediates (polarized collision partners vs. solvent-separated ion pairs) in the two environments. Our results do not permit us to test this proposal in the **1**-Q system.

[25] Jones, G.; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805.