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PHOTOCHEMISTRY OF TRANSITION METAL-ORGANIC SYSTEMS

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ABSTRACT

Irradiation of an organic substrate in the presence of a transition metal compound offers a convenient and often highly-selective route to a variety of interesting and useful products. In this article we seek to identify the key ground- and excited-state interactions between the metal and substrate, and thereby gain insight about the factors that predispose the system to a particular reaction path. Such information, in turn, can be of value in the design of new or improved applications based upon this type of process.

INTRODUCTION

Organic molecules can undergo an assortment of fundamentally interesting and synthetically useful transformations when irradiated in the presence of transition metal compounds (refs. 1-3). The generic process is represented by eq. 1, where O and O' denote the original and transformed organic substrates, respectively, and M symbolizes a transition metal compound normally present

$$O \xrightarrow[M]{h\nu} O' \qquad (1)$$

in catalytic amount. Among the families of organic substrates that can engage in this type of process are olefins, aldehydes, ketones, acids, ethers, epoxides, alcohols, nitriles, and various aromatics. This generality also extends to the types of reactions that can be induced; thus, examples of molecular addition (e.g. hydrogenation, hydrosilation), double bond migration, geometric and valence isomerizations, dimerization, polymerization, oxidation, and substitution have been reported.

From a mechanistic standpoint, the transformation shown in eq. 1 retains many of the features of ordinary photochemical (eq. 2) and transition-metal-catalyzed thermal (eq. 3) reactions of organic compounds, but displays some unique characteristics as well. In cases where irradiation serves only to accelerate the rate of the expected thermal process, higher

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$$0 \xrightarrow{h\nu} 0' \qquad (2)$$
$$0 \xrightarrow{M} 0' \qquad (3)$$

chemical yields of product can result, reaction rates are subject to greater control through regulation of light intensity, and thermally-sensitive products are isolated more readily since elevated reaction temperatures can be avoided. Alternatively, the function of M may be to facilitate known photochemical reactions of 0 or perhaps introduce new reaction channels not observed upon irradiation of 0 alone.

While the detailed sequence of steps leading from reactant(s) to product(s) has been delineated in relatively few systems, transformations of the type represented by eq. 1 can be divided operationally into two general categories (ref. 2). The first, which has been termed catalyzed photochemistry, begins with the absorption of light by M (eq. 4), 0 (eq. 5), or a preformed M-0 complex (eq. 6). Product formation then ensues from the interaction of transition metal compound with organic substrate while either or both are in an electronic excited state (denoted by an asterisk). Although the overall process can be catalytic with respect to M, it is stoichiometric in photons and the quantum yield never exceeds unity.

$$M \xrightarrow{h\nu} M^* \xrightarrow{0} 0' + M \qquad (4)$$
$$0 \xrightarrow{h\nu} 0^* \xrightarrow{M} 0' + M \qquad (5)$$
$$M + 0 \rightleftharpoons M\text{-}0 \xrightarrow{h\nu} (M\text{-}0)^* \longrightarrow 0' + M \qquad (6)$$

The second mechanistic category for reactions represented by eq. 1 has been labeled photogenerated catalysis. This type of process involves the light-induced generation of an active ground-state catalyst, C, from M (eq. 7) or 0 (eq. 8). In one or more subsequent thermal reactions, C converts the organic substrate to the final product (eq. 9). Since the catalyst generated by the action of a single photon may result in the production of several molecules of 0', the observed quantum yield of product formation can exceed unity. Other characteristics frequently exhibited by photogenerated catalytic reactions are an induction period, during which the active catalyst is produced, and the continuation of the thermal catalytic cycle after the

$$M \xrightarrow{h\nu} C \qquad (7)$$
$$0 \xrightarrow[M]{h\nu} C \qquad (8)$$
$$C + 0 \longrightarrow C + 0' \qquad (9)$$

cessation of irradiation.

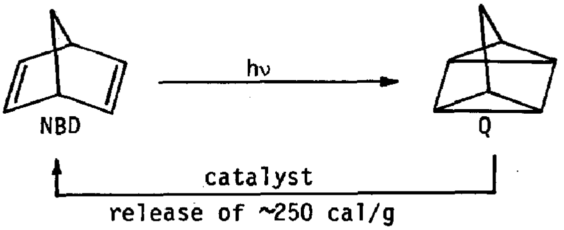
In this article, we shall consider several examples of catalyzed photochemistry and photogenerated catalysis in homogeneous transition metal-organic systems. Our primary aim is to delineate, on a molecular level, the various types of interactions that may occur between M, O, and light. Beside being of fundamental interest, such information facilitates the rational design of practical devices or processes that incorporate eq. 1 as an essential component. Increasing attention is being given to such applications of eq. 1 in the areas of synthesis, catalysis, imaging technology, and the conversion and storage of solar energy (ref. 3).

EXAMPLES OF CATALYZED PHOTOCHEMISTRY

Systems conforming to eq. 4

The interaction of an electronically-excited compound with a ground-state substrate that results in a photochemical reaction of the latter has commonly been termed photosensitization. The archetype of M in the photosensitization process of eq. 4 is $\mathrm{Ru(bipy)}_3^{+2}$ (bipy is 2,2'-bipyridine). This transition metal complex possesses a charge transfer excited state that can undergo one or more of the following interactions with a variety of substrates: (i) electronic energy transfer, (ii) reductive electron transfer, (iii) oxidative electron transfer. The relative importance of i-iii depends upon a combination of factors, the principal ones being the ground-state redox potentials and the excited-state energies of the reactants. Examples of each of these interactions and strategies that make use of $\mathrm{Ru(bipy)}_3^{+2}$ as a photosensitizer in solar-driven water-splitting cycles can be found in a number of excellent reviews (ref. 4-7).

Another type of solar energy storage cycle is based upon the interconversion of the organic valence isomers, norbornadiene (NBD) and quadricyclene (Q), eq. 10. Despite possessing several attractive features (ref. 8), this system suffers from a lack of absorption in the wavelength region of available solar radiation. Early work by Hammond and co-workers (ref. 9) established that the photoisomerization of NBD to Q could be accomplished through the agency of organic triplet sensitizers such as acetophenone or benzophenone. The mechanism of sensitization consists of

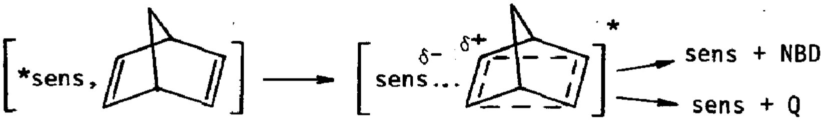


(10)

the following sequence of events: (i) photoexcitation of the sensitizer to its singlet excited state, ^{1}sen; (ii) intersystem crossing from ^{1}sen to the triplet state, ^{3}sen; (iii) electronic energy transfer from ^{3}sen to the $(\pi - \pi^*)$ triplet state of NBD, ^{3}NBD; (iv) reaction of ^{3}NBD to form Q (ref. 10). For sensitizers with triplet energies exceeding that of NBD (i.e., > 70 kcal), energy transfer is an exothermic process that can occur with near unit efficiency in optimal cases. In these systems, however, even a modest energy separation between ^{1}sen and ^{3}sen will place the onset of the singlet absorption band of the sensitizer well below 400 nm. Consequently, only a small fraction of the solar spectrum will be effective in driving the photoisomerization reaction. While the use of sensitizers having lower-energy ^{1}sen states can ameliorate this absorption problem, eventually, a point is reached where the energy of ^{3}sen falls below that of ^{3}NBD. In this endothermic regime, energy transfer can occur only if the sensitizer and/or NBD acquires enough thermal energy from the surroundings to overcome the deficiency in excited state energy. Nonetheless, the overall sensitization efficiency can still be appreciable in such cases provided that ^{3}sen is sufficiently long-lived to allow the thermal activation process to compete with decay to the ground state. This ability to compensate for lack of excited state energy with thermal energy ("thermal upconversion") is most attractive, since it provides a means of extending the useful wavelength range of a sensitizer farther into the solar spectral region (ref. 11).

Recent studies (ref. 12, 13) from our laboratory provide evidence that Cu(prophos)BH$_4$ (prophos is bis(1,3-diphenylphosphino)propane) undergoes thermally-activated energy transfer to NBD. This Cu(I) compound possesses a long-lived (4.2 μsec at 25°C) excited state which is emissive in fluid solution. Quenching of the emission by NBD is accompanied by the efficient production of Q and, significantly, the two processes occur with identical kinetics. The simplest explanation of this behavior is that emission and sensitization originate from the same excited state of Cu(prophos)BH$_4$. Since the energy of this state is estimated to be 64-65 kcal, sensitization via energy transfer to the triplet state of NBD is endothermic by 5-6 kcal.

Another possible sensitization mechanism can be envisioned in which electron-transfer interactions play a prominent role. In the sequence shown in eq. 11, the NBD molecule functions as an electron donor to the photoexcited sensitizer, *sens, and as a result, experiences bonding changes which facilitate



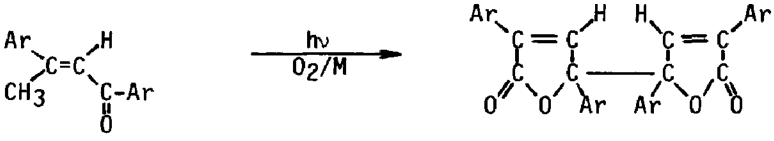
(11)

its rearrangement to Q. Both Ir(bipy-N,N')$_2$(bipy-C,N')$^{+2}$ and Rh(phen)$_3$$^{+3}$ (phen is 1,10-phenanthroline) have been cited as possible examples of redox sensitizers (ref. 14).

Systems conforming to eq. 5

There are few authentic examples of catalyzed-photochemical reactions proceeding according to eq. 5. The chief difficulty encountered in assigning this type of mechanism is eliminating the possibility of a ground-state interaction between M and O (i.e. eq. 6). While the absence of new absorption features in the electronic spectrum of a mixture of the two components is commonly cited as evidence against ground-state complexation, this criterion can be misleading if such features are weak or are masked by other absorption bands. The best indicator of a bimolecular interaction between O* and M is the observation (e.g. from luminescence intensity or lifetime measurements) of dynamic quenching of the organic excited state by the metal species.

A possible example of a reaction that conforms to eq. 5 is the metal-catalyzed photooxidation of the α, β-unsaturated ketones, **1**, reported by Sato and co-workers (ref. 15), eq. 12, where Ar is phenyl, p-tolyl, or p-bromophenyl. Irradiation of the organic substrate in the absence of metal

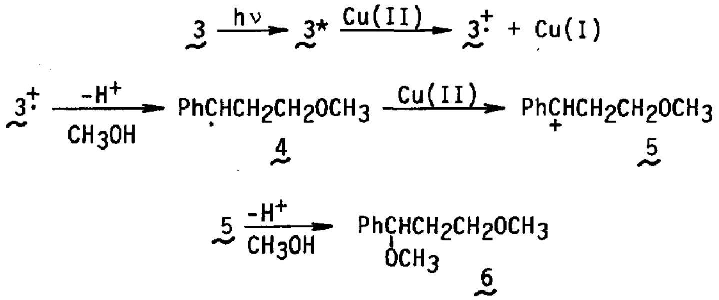


1 **2** (12)

results in cis-trans isomerization about the olefinic bond, whereas oxidation to the dimeric lactones, **2**, predominates in the presence of Cu(II) salts or FeCl$_3$. A spectral study gave no indication of ground-state complex formation between 1 and the metal; in fact, absorption by Cu(II) acted as an inner filter that retarded the reaction. These results were interpreted in terms of a mechanism (eq. 13) in which the metal and/or oxygen react with the photoexcited organic substrate.

$$\begin{tikzcd} \mathbf{1} \arrow[r, "h\nu"] & \mathbf{1}^* \arrow[r, "M/O_2"] \arrow[d] & (\mathbf{1}\text{-M-}O_2)^* \arrow[r] & \mathbf{2} \\ & \text{cis-trans isomerization} & & \end{tikzcd} \qquad (13)$$

More recently, Mizuno and co-workers (ref. 16) have reported that photoinduced nucleophilic attack of methanol on the three-membered ring of phenylcyclopropane, 3, is catalyzed by $Cu(ClO_4)_2 \cdot 6H_2O$. The key steps in the proposed mechanism are summarized in Scheme 1. Electron transfer from photoexcited 3 to Cu(II) generates radical cation $3^{\cdot+}$, which is then attacked by methanol to yield the ring-opened radical, 4. With a sufficiently high concentration of Cu(II), 4 is oxidized to cation 5. Nucleophilic attack of the alcohol on 5 affords the final product, 6.



$$\mathbf{3} \xrightarrow{h\nu} \mathbf{3}^{*} \xrightarrow{Cu(II)} \mathbf{3}^{\cdot+} + Cu(I)$$

$$\mathbf{3}^{\cdot+} \xrightarrow[CH_3OH]{-H^+} \underset{\mathbf{4}}{Ph\underset{\cdot}{C}HCH_2CH_2OCH_3} \xrightarrow{Cu(II)} \underset{\mathbf{5}}{Ph\underset{+}{C}HCH_2CH_2OCH_3}$$

$$\mathbf{5} \xrightarrow[CH_3OH]{-H^+} \underset{\mathbf{6}}{Ph\underset{\substack{|\\ OCH_3}}{C}HCH_2CH_2OCH_3}$$

Scheme 1

Systems conforming to eq. 6

Transformations proceeding by way of a preformed M-O complex (eq. 6) are especially common for olefins in the presence of Cu(I) salts (ref. 17). Complex formation almost always shifts the absorption spectrum of the system to longer wavelengths, presumably due to the introduction of low-lying

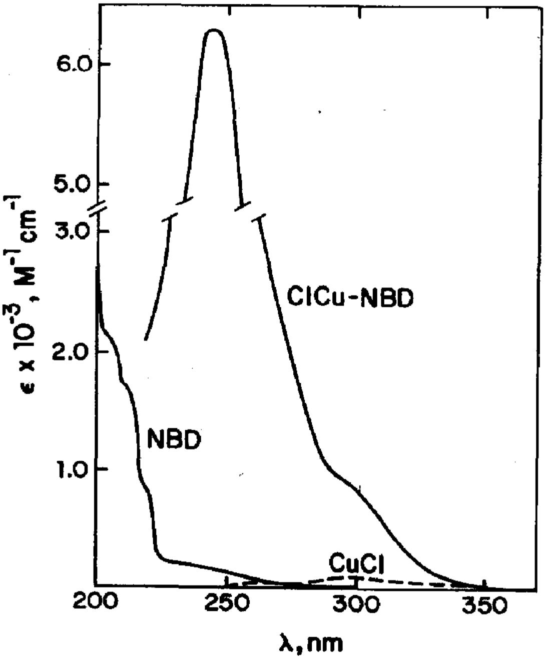
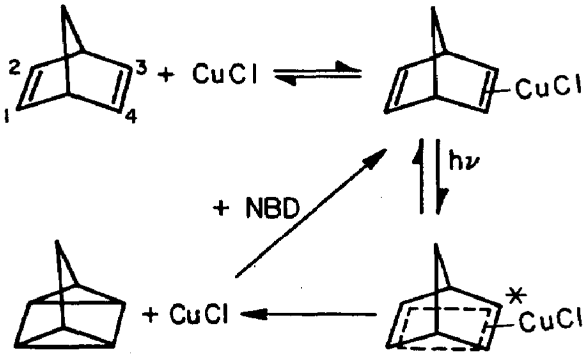


Fig. 1. Spectral change upon mixing CuCl and NBD in ethanol (ref. 17).

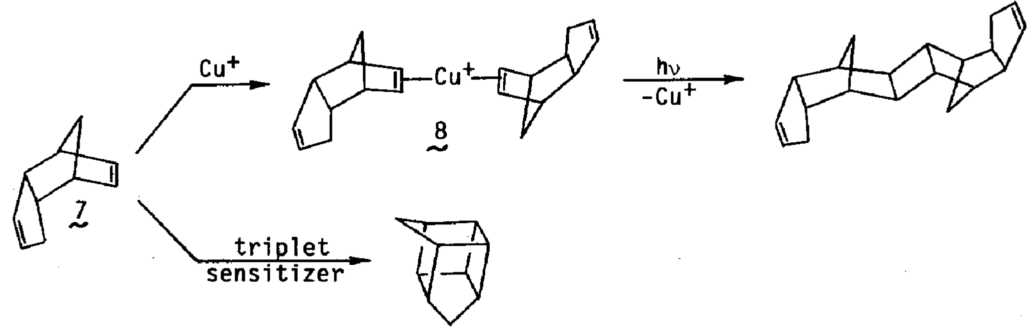
metal-olefin charge transfer states. Moreover, the attractive possibility exists that the complex provides a sterically and/or electronically favorable path to the product which is inaccessible to the uncoordinated olefin.

The spectral change that occurs upon mixing CuCl and NBD is depicted in Figure 1 (ref. 17). Although the individual components are weakly-absorbing above 300 nm, they form a 1:1 complex having an intense Cu-NBD charge transfer band that overlaps the high-energy end of the solar spectrum. Photoexcitation of the complex with 313-nm light affords Q with a quantum yield of 0.3-0.4. The essential details of the mechanism of this process are depicted in Scheme 2 (refs. 18, 19). Irradiation into the charge-transfer absorption band of the complex may, depending upon the direction of electron flow, populate the lowest unoccupied (charge transfer to NBD) or depopulate the highest occupied (charge transfer to Cu) π -type orbital predominantly localized on NBD. In either case, the resulting redistribution of electron density weakens the bonding between carbon atoms C_1-C_2 and C_3-C_4 while enhancing that between C_1-C_4 and C_2-C_3. These photoinduced changes produce a reactive species which can relax back to NBD or complete the structural rearrangement necessary to form Q. Since Q has little affinity for Cu(I), the photoactive complex is regenerated in a fast thermal step and the entire cycle can be repeated.

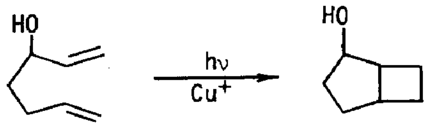


Scheme 2

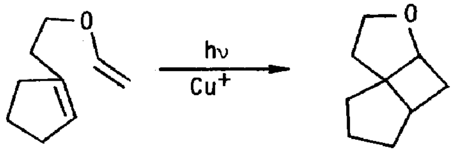
A particularly dramatic example of the influence of ground-state complex formation on olefin photoreactivity is provided by the behavior of endo-dicyclopentadiene, 7 (ref. 20). The intramolecular cycloaddition of 7 when irradiated in the presence of high-energy triplet sensitizers contrasts sharply to the intermolecular cycloaddition process (dimerization) that is favored in the presence of $Cu(F_3CSO_3)$ (eq. 14). The latter pathway reflects the formation of a 1:2 Cu(I)-7 complex, 8, in which the metal is coordinated preferentially to the more strained bond of the diene. In essence, the copper serves as a template for the photochemical ring-forming reaction. Salomon and co-workers have employed this strategy of olefin complexation to Cu(I) in several specific, high-yield syntheses of bicyclic (e.g. eq. 15) and multicyclic (e.g. eq. 16) ring systems (refs. 21, 22).



(14)

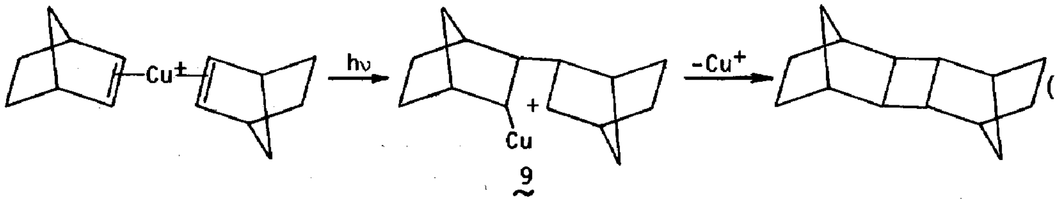


(15)



(16)

Although there is general agreement that Cu(I)-catalyzed photocycloadditions of olefins proceed by way of a ground-state copper-olefin complex, the detailed sequence of steps leading from this species to final product(s) may vary depending upon the nature (type of excited state populated, presence of other ligands coordinated to copper, structure of olefin, solvent polarity) of the system. In some cases, two coordinated olefin moieties may undergo a concerted photochemical reaction which results in ring formation (ref. 23). Alternatively, photoexcitation of a Cu(I)-bis(olefin) complex may give rise to a carbenium ion intermediate, 9, as illustrated for the dimerization of norbornene (eq. 17). This type of process, termed photocupration, is also thought to be responsible for a series of novel



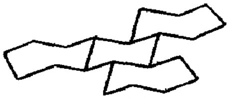
(17)

rearrangement and fragmentation reactions that result upon irradiation of methylenecyclopropanes in the presence of $Cu(F_3CSO_3)$ (ref. 24, 25). A third pathway for cycloaddition, applicable to five, six, and seven-membered cycloalkene systems, involves initial cis-trans photoisomerization about a coordinated olefinic bond to yield the highly-strained trans-cycloalkene (ref. 26). This reactive species then undergoes a concerted thermal cycloaddition with one (or more) additional olefin molecule(s). Mackor and co-workers (refs. 27, 28) invoked such a pathway to explain the novel Cu(F_3CSO_3)-catalyzed cyclotrimerization of cis-cycloheptene, cis-C_7 (Scheme 3). In the only photochemical step, a coordinated cis-C_7 rearranges to the corresponding trans isomer, trans-C_7. Several equilibria are then established, the net result of which is the formation of (F_3CSO_3)Cu(trans-C_7)$_3$. Cyclotrimerization of the trans-C_7 molecules within this complex occurs in a concerted thermal process to yield **10**.

$$(F_3CSO_3)Cu(\underline{cis}\text{-}C_7)_3 \xrightarrow{h\nu} (F_3CSO_3)Cu(\underline{trans}\text{-}C_7)(\underline{cis}\text{-}C_7)_2$$

$$3(F_3CSO_3)Cu(\underline{trans}\text{-}C_7)(\underline{cis}\text{-}C_7)_2 \longrightarrow (F_3CSO_3)Cu(\underline{trans}\text{-}C_7)_3 + 2\ (F_3CSO_3)Cu(\underline{cis}\text{-}C_7)_3$$

$(F_3CSO_3)Cu(\underline{trans}\text{-}C_7)_3 + 3\ \underline{cis}\text{-}C_7 \longrightarrow$



10

$+ (F_3CSO_3)Cu(\underline{cis}\text{-}C_7)_3$

Scheme 3

EXAMPLES OF PHOTOGENERATED CATALYSIS

Catalysis resulting from ligand loss

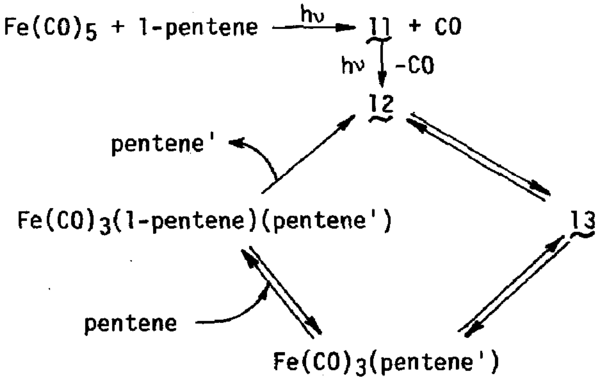
Numerous examples of photogenerated catalysis in metal-organic systems have been reported. Quite commonly, the absorption of light by the transition metal compound induces dissociation of one or more ligands. The resulting coordinatively-unsaturated species then adds the organic substrate and, in some cases, other potentially reactive molecules (H_2, O_2, etc.) present in the system. Further reaction within the coordination sphere of the metal leads to the final product.

Metal carbonyls are the paradigm of this type of behavior. For example, Wrighton and co-workers (refs. 29,30) reported that irradiation of $Fe(CO)_5$, $Fe_3(CO)_{12}$, or $Ru_3(CO)_{12}$ in the presence of linear pentenes results in double bond migration and cis-trans isomerization to yield a mixture of isomeric products close to the thermodynamic ratio. Quantum yields for disappearance of the original organic substrate exceed unity and are lowered upon addition of free CO. In a recent pulsed-laser study of the $Fe(CO)_5$/1-pentene system, Grant and co-workers (ref. 31) found that the overall reaction takes place in two distinct stages: (1) an induction period, during which the rate increases with time; (2) a steady-state period, in which the rate decreases monotonically as the system approaches equilibrium substrate concentrations. Such behavior is consistent with the photochemical formation of a $Fe(CO)_4$(1-pentene) complex, 11, in the initial stage of irradiation (eq. 18). The induction period can

$$Fe(CO)_5 + \text{1-pentene} \xrightarrow{h\nu} \underset{11}{Fe(CO)_4\text{(1-pentene)}} + CO \qquad (18)$$

be associated with the complete conversion of $Fe(CO)_5$ to this stable catalyst precursor, and inhibition by CO follows straightforwardly from the reversal of eq. 18. Further loss of CO from 11, presumably via photochemical dissociation, then generates the active thermal catalyst $Fe(CO)_3$(1-pentene), 12. A likely pathway for double bond migration and cis-trans isomerization involves conversion of this coordinatively-unsaturated species to the π-allyl hydride intermediate, 13 (eq. 19). A catalytic cycle that incorporates 11, 12, and 13 is presented in Scheme 4, where pentene' represents an isomer of 1-pentene.

12 13 (19)

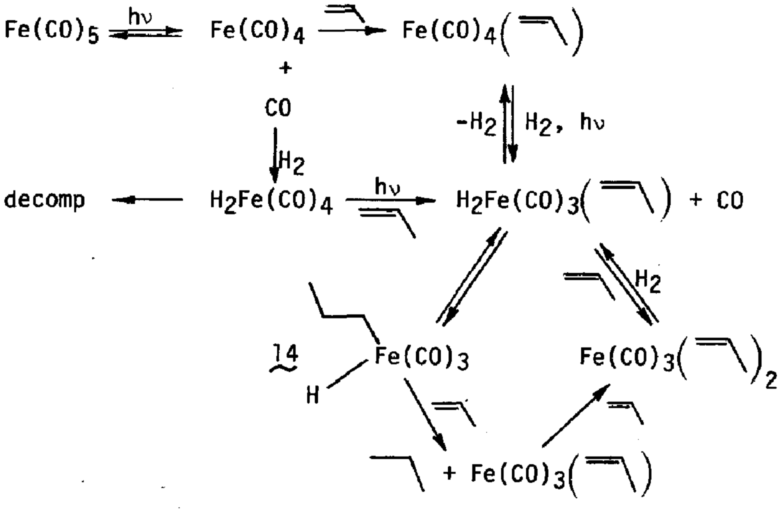


Scheme 4

In systems containing the trinuclear clusters, $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ (ref. 30), it has been established that irradiation causes fragmentation of the cluster framework. Moreover, the isomeric ratio of 2-pentenes obtained in experiments with $Fe(CO)_5$ matches quite closely that found with $Fe_3(CO)_{12}$.

These observations suggest that photodeclusterification of $Fe_3(CO)_{12}$ and (perhaps) $Ru_3(CO)_{12}$ yields catalytically-active mononuclear carbonyl fragments similar to those proposed in Scheme 4. This conclusion cannot be generalized to all clusters, however, as evidenced by the report (ref. 32) that irradiation of $Ru_3(CO)_9(PPh_3)_3$ in the presence of 1-pentene yields a cluster (of unknown composition) as the active isomerization catalyst.

Photogenerated catalysis of olefin hydrogenation, hydrosilation, and hydroformylation reactions by mononuclear or polynuclear metal carbonyls has received considerable attention (refs. 33-36). Here again, photoinduced loss of CO to yield a coordinatively-unsaturated species appears as a key step in the mechanisms of these transformations. In the hydrogenation cycle summarized in Scheme 5 (ref. 29), for example, initial photodissociation of CO from $Fe(CO)_5$ facilitates the formation of $H_2Fe(CO)_4$ and/or $Fe(CO)_4$(olefin), which then undergo additional CO loss to produce $H_2Fe(CO)_3$(olefin). Further reactions of this complex are purely thermal in nature. Thus migratory insertion of the olefin into the Fe-H bond yields **14**, which then reductively eliminates the alkyl group and remaining hydride.



Scheme 5

While generation of catalytically-active species via photoinduced ligand loss has found greatest application among carbonyl-containing complexes, this strategy can also be employed with complexes possessing other types of leaving groups. For instance, Faltynek (ref. 37) has reported that irradiation of $RhCl(PR_3)_3$ (R=phenyl or butyl) yields an active catalyst, $RhCl(PR_3)_2$, for the hydrosilation of olefins (eq. 20). Interestingly, the rate of the catalytic process is markedly enhanced in the presence of oxygen. This behavior reflects the photochemical oxidation of PR_3 to the poorly-coordinating phosphine oxide,

$$RhCl(PR_3)_3 \xrightarrow{h\nu} RhCl(PR_3)_2 + PR_3 \xrightarrow[\text{olefin}]{HSiR_3} \text{hydrosilation} \qquad (20)$$

$P(O)R_3$. Since the latter type of ligands are less likely to bind to the metal than their phosphine counterparts, higher concentrations of the catalytically-active $RhCl(PR_3)_2$ can be generated in aerated systems.

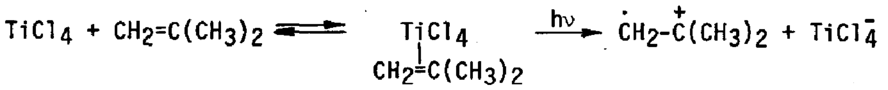
Catalysis resulting from redox processes

Generation of a thermally-active catalyst can also result from photoinduced electron transfer. A clever example of this type of process capitalizes on the well-known intramolecular decomposition of $CoBr(NH_3)_5^{+2}$ (eq. 21) that results upon excitation into the Br-to-Co charge-transfer absorption band (ref. 38). One of the photoproducts, aquated Co^{+2}, functions as a catalyst

$$CoBr(NH_3)_5^{+2} \xrightarrow{h\nu} Co^{+2} + 5NH_3 + Br\cdot \qquad (21)$$

for the oxidative decolorization of the red dye Alizarin S by hydrogen peroxide (ref. 39). A number of photodecompositions of Co(III) complexes that lead to color changes have found use in unconventional (i.e. silver-free) photographic processess (ref. 3).

Photoredox reactions frequently are employed to initiate polymerization of organic molecules. Marek has proposed (ref. 40) that photoinduced charge-transfer within the ground-state complex formed between $TiCl_4$ and isobutylene results in the production of cation radicals (eq. 22). These

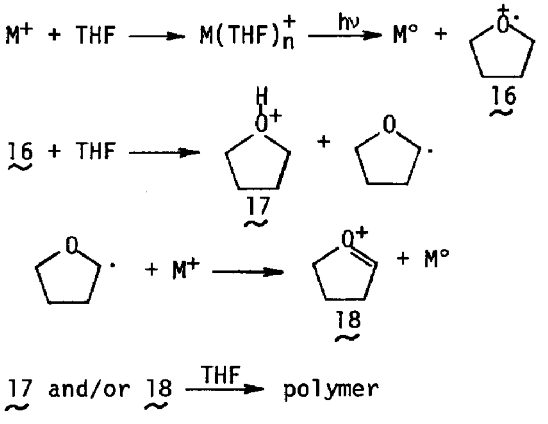


$$TiCl_4 + CH_2{=}C(CH_3)_2 \rightleftharpoons \begin{array}{c} TiCl_4 \\ | \\ CH_2{=}C(CH_3)_2 \end{array} \xrightarrow{h\nu} \dot{C}H_2\text{-}\overset{+}{C}(CH_3)_2 + TiCl_4^- \qquad (22)$$

$$2\ \dot{C}H_2\text{-}\overset{+}{C}(CH_3)_2 \longrightarrow \underset{\mathbf{15}}{\overset{+}{C}(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}(CH_3)_2} \xrightarrow{CH_2=C(CH_3)_2} \text{polymer} \qquad (23)$$

species undergo rapid dimerization to form the bication, **15**, which then initiates polymerization of isobutylene (eq. 23). A similar mechanism has been suggested for the photoinitiated copolymerization of isobutylene with isoprene in the presence of VCl_4 (ref. 41). In related work (ref. 42), Woodhouse, Lewis, and Marks found that irradiation of dilute tetrahydrofuran

(THF) solutions of Ag(I), Cu(I), Cu(II), or Tl(I) salts having suitable noncoordinating anions (e.g. PF_6^-) results in the formation of polytetrahydrofuran. As summarized in Scheme 6, light-induced ligand-to-metal charge transfer within a ground-state complex generates the reduced metal and the tetrahydrofuran cation radical, 16. The latter species reacts further to yield intermediates, 17 and 18, known to initiate cationic polymerization.



Scheme 6

Recently, we investigated (ref. 43, 44) the dramatic acceleratory effect (see Figure 2) of light on the valence isomerization of quadricyclene to norbornadiene in the presence of $PdCl_2(\eta^4\text{-NBD})$, 19 (eq. 24). The observed

$$Q \xrightarrow[19]{h\nu} NBD \qquad (24)$$

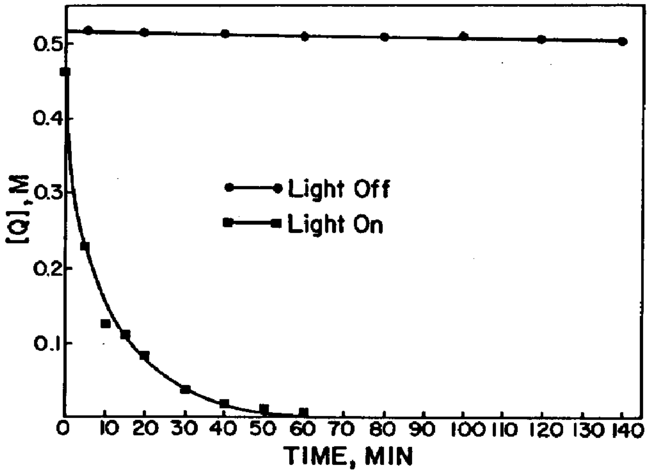


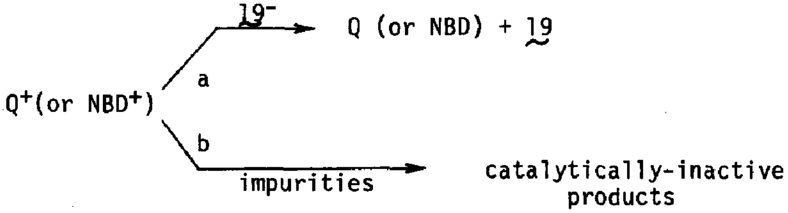
Fig. 2. Effect of 313-nm light on the isomerization of Q to NBD in the presence of $PdCl_2(\eta^4\text{-NBD})$ (ref. 43).

quantum yield can exceed 10^2 and is dependent upon Q concentration, light intensity, and solvent composition. 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 19 by Q (eq. 25). The resulting quadricyclene radical cation, Q^+, undergoes rapid and irreversible rearrangement to its more stable isomer, NBD^+ (eq. 26). Since oxidation of Q by NBD^+ (eq. 27) is thermodynamically favorable, Q^+ is regenerated and can reenter the cycle. Recombination of either of the radical cations with the reduced Pd complex or a trace impurity (eq. 28) results in chain termination.

$$19 \xrightarrow{h\nu} 19^* \xrightarrow{Q} 19^- + Q^+ \qquad (25)$$

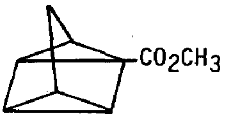
$$Q^+ \longrightarrow NBD^+ \qquad (26)$$

$$NBD^+ + Q \longrightarrow NBD + Q^+ \qquad (27)$$

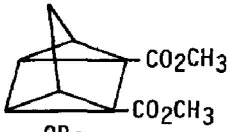


(28)

Supporting evidence for the operation of a redox-chain mechanism was obtained from a comparative study (ref. 45) of the reactivities of Q and its substituted derivatives, QR and QR_2, upon being irradiated in the presence



QR



QR_2

of 19. As seen from the data in Table 1, an inverse correlation exists between the quantum yield for isomerization (ϕ) and the ground-state oxidation potential (E^{ox}) of the organic substrate. Such behavior is fully consistent with the proposed chain initiation step (eq. 25) in which reductive quenching of photoexcited 19 by the organic substrate yields 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. As a result, fewer radical cations are generated and the overall quantum yield for isomerization decreases accordingly.

TABLE 1

Quantum yields for photoisomerization of quadricyclenes in the presence of 19[a]

compound	concentration, M	E^{ox}, V vs. SCE	Ø
Q	0.39	0.91	230
QR	0.44	1.2	3.0
QR_2	0.45	1.64	<0.06

[a] Irradiations performed at 405 nm; solvent was CH_2Cl_2.

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