

# Photoelectron-Transfer Catalysis: Its Connections with Thermal and Electrochemical Analogues

M. JULLIARD and M. CHANON\*

Faculté des Sciences de Saint Jérôme, 13397 Marseille, Cedex 13, France

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Michel Julliard received his M.S., Chemical Engineer, and Ph.D. degrees (1973) at the University of Marseilles. Following post-doctoral work at the Industrial Physical and Chemistry School (Paris) he moved to Professor Jacques Metzger's team where he is now CNRS research assistant. His interests include photochemistry in solution, e.g., solar energy applied to synthesis using photonitrosation with NOCl, the first example of aromatic ester photoenolization, photochemical behavior of diaryltriazenes and the connection with their antitumor properties. He is now focusing on redox photochemistry with special emphasis on electrochemical catalytic processes and photosensitized enzymatic reactions.



M. Chanon was born near Roannes (Loire, France) in 1940. He graduated with a Ph.D. in heterocyclic chemistry with J. Metzger in Marseille (1967). He then entered CNRS where he worked until 1973 on steric effects (gear effect, conformational limitations of Taft equations, and steric effects as monitors for the structure of transition states), role of frontier orbitals (correlation EPS–nucleophilic reactivity of C=S), and computer-assisted organic synthesis. From 1970 to 1979, he was assistant editor and coauthor of Vol. 2 of the series "Thiazoles and Derivatives" (Wiley). He moved from CNRS to National Education in 1973 when he was hired as a professor in the ENS of Tunis. In 1977 he returned to Marseille and became involved in the unification of mechanistic features shared by organic, inorganic, and organometallic species, which led him to the demonstration of the pervasive occurrence of activation induced by electron transfer and electron-transfer catalysis (ETC). The present interests of his team are fundamental and applied developments of ETC and applications of microprocessors in chemistry. He has worked in several foreign institutions (1972, Kemi Centrum Lund, Sweden with Prof. J. Sandstrom; summer 1979, University College of London with Prof. M. L. Tobe; summers 1980 and 1981, Indiana State University, Bloomington with Prof. J. K. Kochi.)

## Introduction

Among the deactivation processes available to an excited molecule,<sup>1</sup> electron transfer has had a rather erratic history. It seems that physicists were well aware of this possibility and the so-called Penning ionization was already discussed and understood in 1927.<sup>2-4a</sup>

Biochemists and biophysicists extended the field of application of this basic concept probably before organic<sup>4b</sup> and inorganic chemists.<sup>5</sup> It is strange to realize that in most of the classic books on excited states there is a section dealing with acid–base properties of excited states,<sup>11,12</sup> whereas the redox properties are never discussed as such. That does not mean that photochemists are unaware of the importance of electron transfer. This is verified by the large amount of work treating exciplexes,<sup>13-15</sup> excimers,<sup>16-22a</sup> Marcus inverted region,<sup>23-36</sup> chemically active charge-transfer complexes.<sup>37-41</sup> Therefore, insight that could be gained by comparing the role played by proton transfer and electron transfer in chemistry is mainly hindered by a barrier of words. We have shown in other reports<sup>42-44</sup> that this situation largely originates from the fact that electron-transfer mechanisms, pervasive as they are in chemistry, have nevertheless very seldom been considered as a unique branch of chemistry but rather as specific subdisciplines of inorganic, organic, organometallic, biochemical, macromolecular, and applied chemistry. Fortunately, in photochemistry recent excellent reviews draw attention to the importance of these processes in organic and inorganic or organometallic chemistry.<sup>46-49</sup> The emphasis in the present review is on chain reactions<sup>6-10</sup> initiated by a photoinduced electron transfer. This topic partly overlaps with generalized<sup>43</sup> S<sub>RN</sub>1 mechanism,<sup>50-63</sup> photogeneration of catalysts,<sup>64-75</sup> and some photosensitized processes involving electron transfer.<sup>76</sup> With the IUPAC definition of catalysis:<sup>77a</sup> "a catalytic reaction is a closed sequence of elementary steps similar to the propagation steps of gas phase chain reactions," the border between catalysis and chain reaction is vanishing and, from an operational point of view (design of new processes), we feel it is more important to stress the analogies underlying both catalytic and chain reaction<sup>77b</sup> than to separate them on formal grounds.

## I. Redox Properties of Excited States and Photoelectron-Transfer Reactions

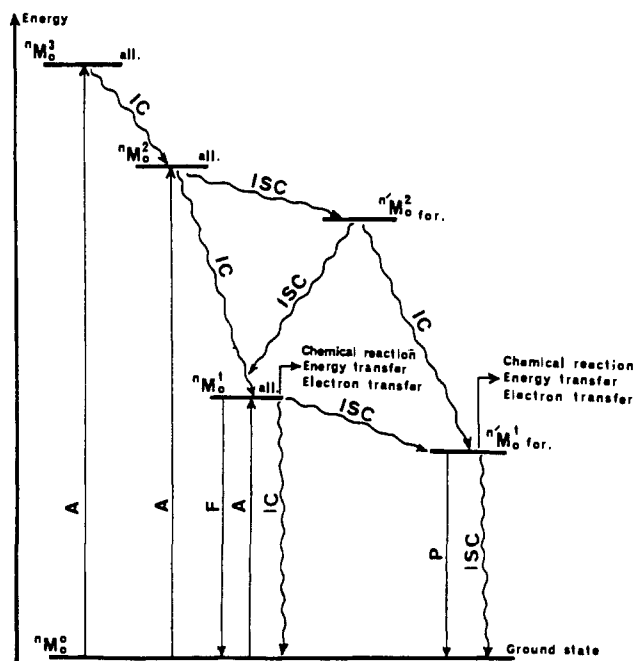
### 1. Background

In contrast to most of the photochemical textbooks that focus either on organic<sup>78-80</sup> or inorganic<sup>73,81,82</sup> molecular species, we will adopt an integrated treatment that covers both types of species. It is indeed important to realize that the changes of redox properties for excited molecules follow the same basic laws of evolution whatever their type, even if the differences in the lifetimes and available multiplicities train some variations in the relative importance of electron-transfer deactivation with respect to other deactivation modes.

### 2. Electron Transfer and Lifetime of Excited States

After absorption of a photon, the molecule is promoted in one of its excited states. The transitions that then occur are summarized in Figure 1.

Spectroscopic transitions between states of different multiplicities are of low probability. This leads to the basic classification: spin-allowed and spin-forbidden transitions. Electronic excited states of the same



**Figure 1.** Energy-level diagram and excited-state processes for a molecule. A = absorption,  $10^{-15}$  s; F = fluorescence,  $10^{-9}$ – $10^{-5}$  s; P = phosphorescence,  $10^{-5}$ – $10^{-3}$  s; IC = internal conversion,  $10^{-14}$ – $10^{-13}$  s; ISC = intersystem crossing,  $10^{-6}$  s;  $nM_i^j$  = state definition of the molecule M,  $i$  = vibronic level,  $j$  = order of the state (for a given multiplicity),  $n$  = multiplicity of the state ( $n \neq n$ ); all. = spin-allowed state; for. = spin-forbidden state.

multiplicity as the ground state are spin-allowed states (e.g., singlet states of organic molecules). Electronic excited states of different multiplicity are called spin-forbidden states (e.g., triplet states of organic molecules). In fluid solution, these two types of states usually have lifetimes longer than  $10^{-9}$ – $10^{-10}$  s. The rates of bimolecular electron-transfer reactions are usually in the range  $10^5$ – $10^{10}$  s $^{-1}$ ,<sup>84,85b</sup> with some very slow ( $10^{-4}$  s) or very fast ( $10^{11}$  s) values. Since the rate of internal conversion is about  $10^{13}$  s $^{-1}$ , one usually considers that internal conversion from the upper spin-allowed excited state to the lower one occurs prior to any other processes (Kasha's rule).<sup>86,87</sup> Consequently, it is the lowest spin-allowed excited state which is generally populated (see, however, ref 88). Spin-forbidden states can be populated via intersystem crossing. As a consequence, wavelength effects are rather rare in the field of organic photochemistry (see exceptions in ref 89). For many organic molecules these two types of lowest excited states have lifetimes longer than  $10^{-9}$ – $10^{-10}$  s, which corresponds to the limit for a normal bimolecular electron transfer.

In the field of transition-metal complexes,<sup>90,91</sup> the lowest spin-allowed excited state generally has a lifetime shorter than  $10^{-10}$  s because of its chemical reactivity and/or fast intersystem crossing to the lowest spin-forbidden excited state.<sup>92</sup> Thus, the only excited state of a transition-metal complex that can be involved in a bimolecular electron-transfer process is, in principle, the lowest spin-forbidden state.

It has long been thought that even this state is very short-lived in fluid solution at room temperature, owing to its large chemical reactivity (dissociation), lack of rigidity, and strong spin-orbit coupling. This was particularly believed when the lowest excited state is metal-centered or ligand-to-metal charge transfer; this

excited state lifetime was thought to be too short to allow the participation of the excited state in bimolecular processes.<sup>48</sup> Nevertheless, polypyridine-chromium(III) complexes,<sup>93</sup>  $UO_2^{2+}$ ,<sup>49</sup>  $Co(en)_3^{3+}$  ( $^1T_{1g}$ ),<sup>94,95</sup>  $Co(phen)_3^{3+}$ ,<sup>96</sup>  $[(CH_3CN)Re(CO)_3phen]^+$ ,<sup>97</sup> and other possible examples (section III2a1a<sup>22b,42,45</sup>) suggest that the postulate "of transition-metal complexes having a too short lifetime to allow intermolecular quenching" has been overused in the past. This is particularly true when a chain reaction amplifies the primary act of photoelectron transfer.<sup>42</sup>

In contrast with the behavior of most organic compounds (see ref 89), however, some photoreactions of transition-metal complexes have wavelength-dependent quantum yields. Generally, these wavelength effects are interpreted in terms of more than one reactive excited state.<sup>70</sup> Moreover, the intermolecular reductive or oxidative quenching of the excited state can only happen if it is fast enough to compete with the intramolecular deactivation modes and with the other types of quenching processes such as ligand substitution reactions, fluorescence, and phosphorescence. In particular, some intra- or intermolecular reactions involving proton transfer<sup>98</sup> or hydrogen transfer<sup>99</sup> may be fast enough to compete with redox quenching. However, except for  $Ru(bpy)_2(CN)_2$ <sup>100</sup> and  $Ru(bpy)_2(bpy-4,4'-(COOH)_2)^{2+}$ ,<sup>101</sup> reactions of this kind are not yet well documented for transition-metal complexes, although they are very common for organic molecules.<sup>102–104</sup>

The next section will show that all excited states are potential redox reagents, since the absorption of light leads to excitation of an electron to a higher level where it is more weakly bound, and at the same time generates an electron hole in a lower level.<sup>44a</sup>

### 3. Photoexcited States Redox Properties

The relative situation of redox potentials  $M/M^-$  and  $M^*/M^-$  (or  $M^+/M$  and  $M^+/M^*$ ), where M is the ground-state molecule and  $M^*$  is the lowest excited-state molecule, is sketched in Figure 2. The situation pictured describes the oxidation of the molecule M. The electrochemical redox potentials of the couples  $M/M^+$ ,  $M^*/M^+$  vs. a reference couple  $Q/Q^-$  are related to the free energy change.

$$\Delta G = \Delta H - T\Delta S$$

When the change in shape, size, and solvation subsequent to electronic excitation is small, the difference between the entropy of the excited state and ground state may be neglected ( $\Delta S \approx 0$ ) and  $\Delta G \approx \Delta H$ . Then, in Figure 2, if  $E_{0-0}$  is the one-electron potential corresponding to the zero spectroscopic energy of the excited state:

$$\Delta H[M \xrightarrow{OE} M^+] - \Delta H[M^* \xrightarrow{BE} M^+] = E_{0-0}[M \xrightarrow{OB} M^*]$$

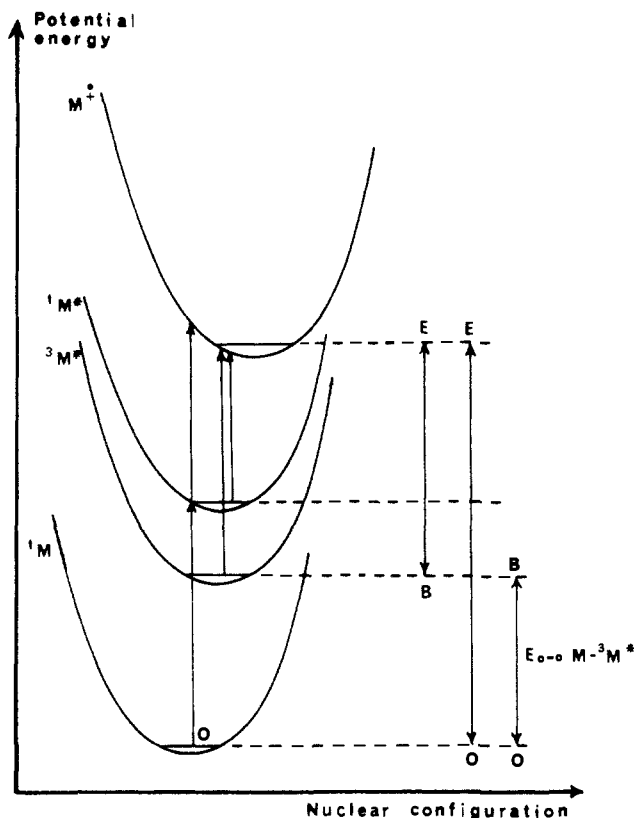
Since  $\Delta G = \Delta H$  and  $\Delta G = -n\mathcal{F}E$  with  $n\mathcal{F} = 1$ ,

$$E^\circ(M^+/M^*) - E^\circ(M^+/M) = -E_{0-0}(M \rightarrow M^*)$$

The  $M^*/M^-$  redox couple can be approximated in the same way. So for any excited state:<sup>48,49,442</sup>

$$E^\circ(M^+/M^*) = E^\circ(M^+/M) - E_{0-0}(M \rightarrow M^*) \quad (1)$$

$$E^\circ(M^*/M^-) = E^\circ(M/M^-) + E_{0-0}(M \rightarrow M^*) \quad (2)$$



**Figure 2.** Schematic representation of the energy change for the excitation and ionization processes of a molecule (from ref 48).  $^1M$  = ground state organic molecule;  $^1M^*$  = lowest singlet excited state;  $^3M^*$  = lowest triplet excited state;  $M^+$  = cation radical.

As the entropy corrections are very difficult to evaluate, eq 1 and 2 can be applied to guess the redox potentials of photoexcited states of molecules. For example, the value of the spectroscopic excited-state energy  $E_{0-0}(M \rightarrow M^*)$  of  $\text{Ru}(\text{bpy})_3^{2+}$  is 2.12 eV, and the ground-state redox potentials (vs. NHE) are

$$E_{1/2}[\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}] = E_{1/2}(M^+/M) = 1.26 \text{ V}$$

$$E_{1/2}[\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+] = E_{1/2}(M/M^-) = -1.28 \text{ V}$$

The redox potentials of the excited complex  $M^*$  can be calculated (cf. Figure 3):

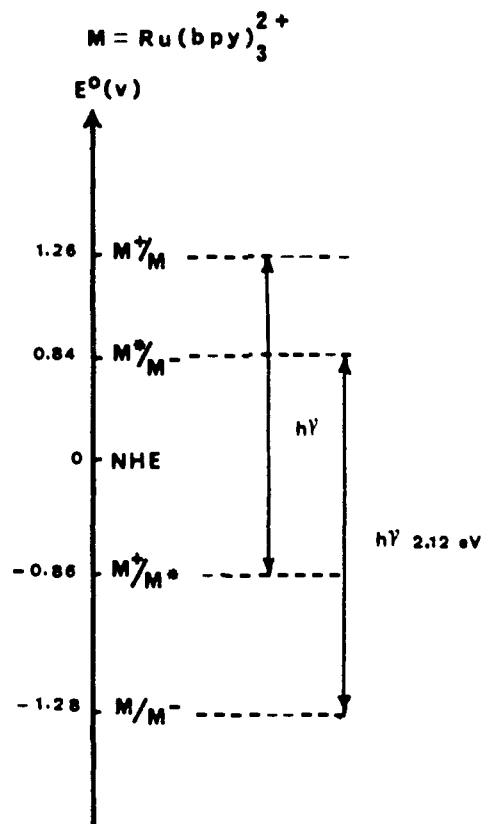
$$E_{1/2}(M^+/M^*) = 1.26 - 2.12 = -0.86 \text{ V}$$

$$E_{1/2}(M^*/M^-) = -1.28 + 2.12 = 0.84 \text{ V}$$

#### 4. Estimation of Redox Potentials for Different Structures

##### a. Organometallic and Inorganic Complexes

The complexes containing aromatic molecules such as bipyridine, phenanthroline, or their derivatives as ligands undergo excited-state electron-transfer reactions. Some features associated with their photochemical and photophysical properties are noteworthy.<sup>48,49</sup> The lowest excited state is generally populated with unitary efficiency regardless of the excitation wavelength. The Stokes shift between absorption and



**Figure 3.** Schematic diagram showing the difference in the redox potentials of the lowest excited state and the ground state of  $\text{Ru}(\text{bpy})_3^{2+}$  complex. Note that the excitation displaces  $M^+/M$  towards the bottom of the scale, whereas  $M/M^-$  is upshifted.

emission from the lowest excited state is generally small. The lifetime of the lowest excited state is generally long enough to allow a bimolecular electron-transfer reaction.

These complexes are marked off from the organic compounds by the crossing of the redox potentials caused by excitation (Figure 3), so that the excited state may often be used either as an electron donor or as an electron acceptor.<sup>49</sup> For example, from the ground-state potential  $E_{1/2}[\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}] = 1.26 \text{ V}$  we have already seen that photoexcitation increases the reducing power by 2.12 V. Similarly, from the ground-state potential  $E_{1/2}[\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+] = -1.28 \text{ V}$ , the oxidizing power is increased by the same value of 2.12 V.

The data concerning some of the other complexes are reported in Table I.

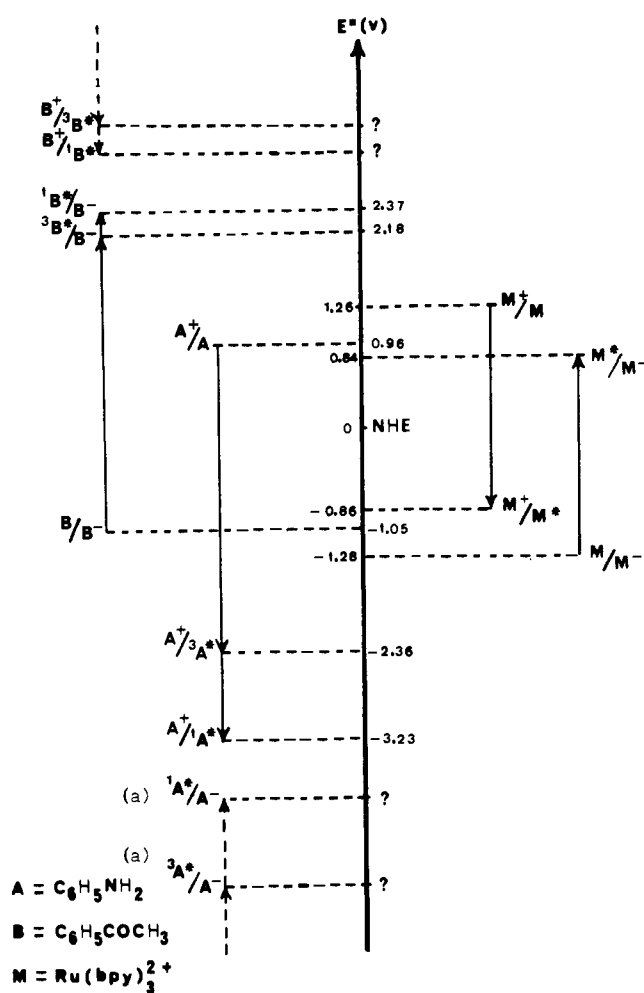
##### b. Organic Molecules

The polarographic half-wave oxidation and/or reduction potentials of the ground-state and the excited-state energies of organic molecules are also provided by eq 1 and 2. In contrast with inorganic complexes, there is generally a greater separation between oxidation states. Therefore, an excited organic molecule usually serves either as an electron donor or as an electron acceptor but not as both (Figure 4). For some classes of compounds, such as azaromatic compounds, aromatic hydrocarbons, and halobenzene derivatives, half-wave oxidation and reduction potentials are well established,<sup>105,106</sup> and one can therefore estimate the redox potentials of their excited states (Table II).

In these series the most drastic changes are displayed by benzene, where the difference between fundamental

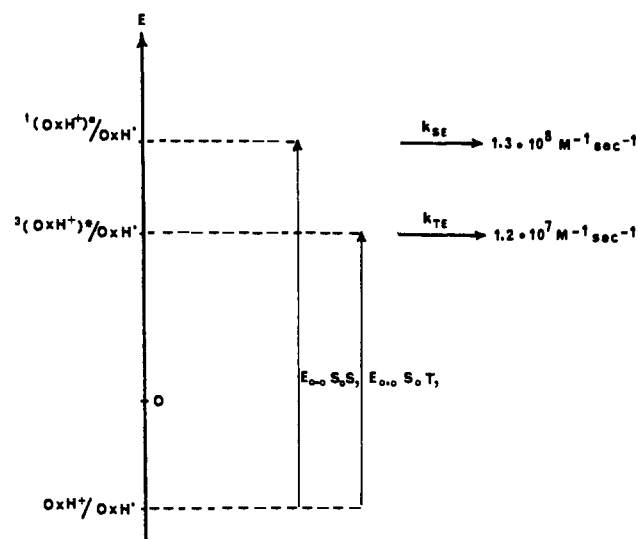
TABLE I. Spectroscopic and Redox Properties of Some Photoexcited Inorganic Complexes<sup>a</sup>

complex	$E_{O-O}$ (M-M*), eV	$\tau$ , $\mu$ s	$E_{1/2}$ (M/M <sup>+</sup> ), V	$E_{1/2}$ (M <sup>*/M</sup> ), V	* $E^\circ$ (M*/M <sup>-</sup> ), V	* $E^\circ$ (M <sup>*/M*</sup> ), V
Cr(bpy) <sub>3</sub> <sup>3+</sup>	1.71	77	-0.25	>1.6	1.46	>-0.1
Cr(phen) <sub>3</sub> <sup>3+</sup>	1.71	108	-0.25		1.46	
Ru(bpy) <sub>3</sub> <sup>2+</sup>	2.12	0.62	-1.28	1.26	0.84	-0.86
Ru(bpy) <sub>3</sub> <sup>2+</sup>	2.12	0.85	-1.35	1.29	0.77	-0.83
Ru(phen) <sub>3</sub> <sup>2+</sup>	2.18	0.81	-1.36	1.26	0.82	-0.92
Ru(phen) <sub>3</sub> <sup>2+</sup>	2.18	0.50	-1.43	1.29	0.75	-0.89
Ru(phen) <sub>3</sub> CN <sub>2</sub>	2.19	1.09	-1.79	1.12	0.40	-1.02
Os(bpy) <sub>3</sub> <sup>2+</sup>	1.85	19	-1.18	0.83	0.67	-1.02
Os(phen) <sub>3</sub> <sup>2+</sup>	1.78	84	-1.21	0.82	0.57	-0.96
Ir(bpy) <sub>3</sub> <sup>3+</sup>	2.81	2.4	-0.76	2.17	2.05	-0.64

<sup>a</sup> From ref 48.

**Figure 4.** Schematic diagram showing the difference in the redox potentials of the lowest excited state and ground state of Ru(bpy)<sub>3</sub><sup>2+</sup>, aniline, and acetophenone. In this figure, the organic compounds whose reduction (oxidation) is not experimentally accessible in the ground state are nevertheless indicated in the excited state to keep in mind that for particular cases an organic compound may in its excited state be both oxidizing and reducing despite the fact that one of these properties is absent in the ground state. (a) These arrows should be shifted upward depending upon the value of what is considered as the lower limit of reduction potential.

and excited states redox potentials can amount to values as large as 4.7 V. This value approximately equals the whole scale of redox potentials of ground-state molecules. In such cases, it should be realized that light excitation actually creates a short-lived local electrode in the studied sample. These differences of reduction potential are still more telling if it is recog-



**Figure 5.** Schematic diagram showing the difference in the redox reactivity of singlet and triplet state of oxonine (Reprinted with permission from ref 109. Copyright 1979, Pergamon Press Ltd.). OXH<sup>+</sup> = oxonine, (OXH<sup>+</sup>)<sup>\*</sup> = photoexcited oxonine, OXH<sup>-</sup> = one-electron semireduced oxonine.

nized that the rate constants for electron transfer from radical anion of aromatic compounds to diaryl disulfide (ArSSAr) in THF<sup>107</sup> vary from 0.015 to  $2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  when the reduction potential of the aromatic compound changes from -1.04 to -1.91 V (vs. SCE) (see section I6). Finally, in the case of organic molecules it must be emphasized that the excited singlet state is, as a rule, more oxidant than the corresponding triplet state. This follows from the energy difference between the two states that affect their redox potentials.<sup>108</sup> An illustration is provided by the photobleaching of oxonine with ethylenediaminetetraacetic acid (EDTA): the rate of electron transfer to its excited triplet state ( $k_T = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) is 1 order smaller than the one measured for its singlet state ( $k_S = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>109,110</sup> (see Figure 5).

The reactivity of the photoexcited singlet and triplet state of acridine orange with a series of electron donors similarly showed the excited singlet state to be more reactive.<sup>83,111</sup> This should no longer hold true with good donors, because both become diffusion limited.

## 5. Thermal and Photochemical Electron-Transfer Processes

Several reviews<sup>112-118</sup> or monographs<sup>84,119-121</sup> deal with the topic of thermal electron-transfer mechanisms. To keep our integrated treatment we follow the original

TABLE II. Spectroscopic and Redox Properties of Some Photoexcited Aromatic Hydrocarbons<sup>a</sup>

compound	$E_S$ , eV	$E_T$ , eV	$E_{1/2}^{\text{red}}$ (M <sup>•</sup> /M <sup>-•</sup> ), V	$E_{1/2}^{\text{ox}}$ (M <sup>•</sup> /M <sup>•+</sup> ), V	singlet state S <sub>1</sub>		triplet state T <sub>1</sub>	
					$E^\circ$ (M <sup>•</sup> /M <sup>-•</sup> ), V	$E^\circ$ (M <sup>•</sup> /M <sup>•+</sup> ), V	$E^\circ$ (M <sup>•</sup> /M <sup>-•</sup> ), V	$E^\circ$ (M <sup>•</sup> /M <sup>•+</sup> ), V
benzene	4.71	3.65	-2.56	2.42	2.15	-2.29	1.09	-1.23
fluorobenzene	4.67	3.66	-2.45	2.64	2.22	-2.03	1.21	-1.02
chlorobenzene	4.61	3.58	-2.40	2.61	2.21	-2.00	1.18	-0.97
bromobenzene	4.55	3.50	-2.11	2.52	2.44	-2.03	1.39	-0.98
anthracene	3.27	1.84	-1.71	1.33	1.56	-1.94	0.13	-0.51
biphenyl	4.16	3.00	-2.34	2.15	1.82	-2.01	0.66	-0.85
naphthalene	3.93	2.64	-2.29	1.78	1.64	-2.15	0.35	-0.86
phenanthrene	3.59	2.69	-2.20	1.74	1.39	-1.85	0.49	-0.95
triphenylene	3.62	2.96	-2.22	1.79	1.40	-1.83	0.74	-1.17

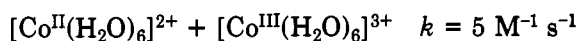
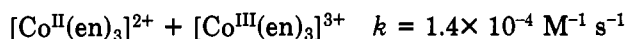
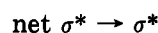
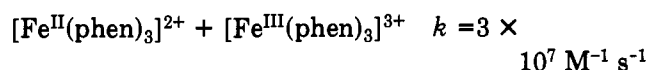
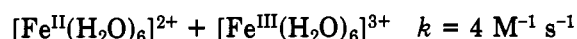
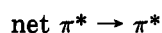
<sup>a</sup> From ref 44a. The reduction potentials were measured in DMF or CH<sub>3</sub>CN vs. SCE. The oxidation potentials were measured in DMF or acetonitrile vs. SCE. The values were corrected vs. NHE by adding 0.24 V. <sup>b</sup> Professor Gerson kindly drew our attention to the fact that probably a better evaluation<sup>105b</sup> of benzene reduction potential is -3.29 V. We lay stress the fact that their values are approximate only and also that much caution should be exercised in extrapolating them indiscriminately to various solvents.<sup>49b</sup>

outer-sphere/inner-sphere distinction introduced by Taube,<sup>122</sup> but we have extended it<sup>44b</sup> to cover particular cases of organometallic<sup>123a</sup> and organic reactivity.<sup>124,125</sup> An interesting dimension, in transition-metal complexes, is brought by the possibilities of high spin ↔ low spin transitions before or after electron transfer.<sup>85a</sup>

### a. Outer-Sphere Electron Transfer

An outer-sphere mechanism characterizes a reaction in which electron transfer takes place from a reductant to an oxidant without formation of bond between them, or if any bond forms<sup>126</sup> it plays no direct role in the act of electron transfer.<sup>120</sup> The rate constants for thermal outer-sphere electron-transfer processes span a wide range of values, and the symmetries of orbitals involved in the electron transfer play a definite role<sup>84b,127</sup> (cf. ref 128).

Example:

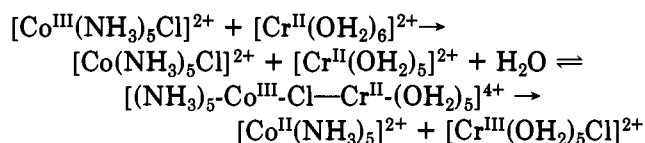


The elementary steps implicated in a thermal outer-sphere electron-transfer mechanism are:<sup>84c</sup> (1) Formation of a precursor complex. (2) Activation of the precursor, electron transfer, and relaxation to the successor complex. (3) Formation of products from the successor complex. The outer-sphere photoelectron transfers are usually not dissected into these steps; their rates may vary appreciably from diffusion control to 10.<sup>29</sup>

### b. Inner-Sphere Electron Transfer

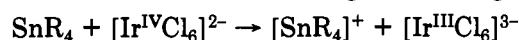
Besides this first mechanism, two other classes of electron transfer are possible: inner-sphere with and without ligand exchange.

An electron-transfer mechanism is said to be inner-sphere if it can be experimentally proved that a bridge through which electron transfer occurs is established between the oxidant and the reductant that are forming. The lifetime of the formed supermolecule is long enough to allow several vibrational equilibrations (usually  $t_{1/2} \approx 10^{-13}$  s). We must emphasize that the inner-sphere electron transfer with ligand exchange mechanism is the best known because it is the easiest to evidence. (For a good treatment of the experimental means to choose between thermal outer-sphere and inner-sphere electron transfer, see ref 129.) In this mechanism, one ligand of one reactant (usually the reductant) must be capable of being replaced by a bridging ligand in a facile substitution process.



It is generally accepted that for some inorganic substrates, a substantial acceleration of the rate of electron transfer is observed (which may reach 10<sup>10</sup>) on going from outer-sphere to inner-sphere mechanism for similar reactions<sup>84d</sup> (for exceptions, see ref 121b and 130). Nevertheless, Balzani states in a review on photoelectron-transfer reactions<sup>48</sup> that the inner-sphere with ligand-transfer process cannot be faster than ligand substitution reactions and is unlikely to occur within the lifetime of the photoexcited molecule (see, however, section I5c).

Another mechanism which could be of far wider occurrence than usually believed<sup>121c</sup> involves an inner-sphere electron transfer without ligand exchange.<sup>131,132</sup>



It is presently difficult to evaluate the scope of applicability of this mechanism because several reactions described as outer-sphere examples could in fact possess an inner-sphere character. This can be experimentally evidenced by showing that the rate of electron transfer is faster (other reasons have been given for reaction rates faster than those expected from the Marcus treatment<sup>133,134</sup>) than expected from the Marcus approach,<sup>135-137</sup> and that steric effects hindering the encounter between oxidizing and reducing species de-



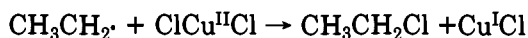
crease the rate of reaction in contrast with what is observed for typical outer-sphere electron transfers. From a photochemical point of view, this inner-sphere mechanism should be suspected every time that charge-transfer complexes or exciplexes are involved (although exciplexes can react following other channels that electron transfer<sup>123b,929</sup>).

No example of photoelectron transfer by the inner-sphere mechanism seems to be reported in the inorganic field, but the relative situation of the  $S_H2$  and inner-sphere with ligand exchange mechanisms must be underscored.

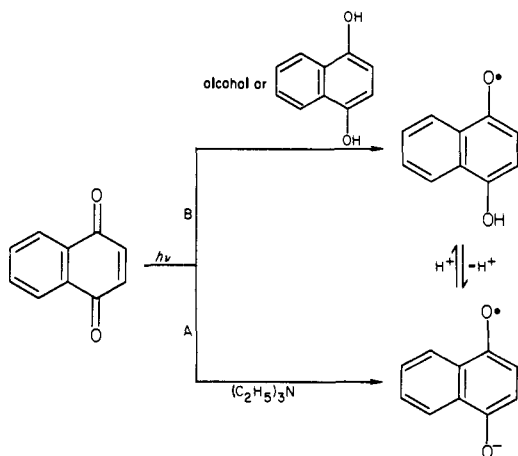
### c. $S_H2$ Mechanism

The question is: "Could the  $S_H2$  reactions be included in the general class of inner-sphere electron transfers?" If the answer is positive, many photoinduced free-radical chain reactions would become part of the photoelectron-transfer catalysis. In fact, in books covering the field of organic, inorganic, and organometallic mechanisms, we found repeated attempts to convince readers to adopt a unified view of this question.

Kosower<sup>138a</sup> was probably the first to make a proposition in this direction stressing the analogy between inner-sphere electron transfer with atom transfer and  $S_H2$  mechanisms. Ingold<sup>139</sup> devoted a small place in his book on homolytic substitutions to reactions of the type:



Littler<sup>124</sup> then proposed the inclusion of "the large category of reactions between radicals and saturated molecules in which a hydrogen, halogen, or other atom is abstracted" in the group of "bonded electron transfers" (inner-sphere electron transfer with atom transfer<sup>120</sup>). Ebersson<sup>140</sup> recently made the same proposition, and recent reports<sup>149</sup> apparently adopt this view. If we follow this nomenclature, the large class of hydrogen abstraction by excited states of  $\text{C}=\text{O}$  become inner-sphere electron-transfer reactions, and the dilemma of outer-sphere vs. inner-sphere electron-transfer mechanism pervades the field of photochemistry.<sup>141</sup> Flash photolysis electron spin resonance spectroscopy has been cleverly used to tackle this problem.<sup>142</sup>



Electron transfer (path A) dominates in the presence of triethylamine in the primary reaction of the triplet 1,4-naphthoquinone with the amine as the electron donor, and Roth<sup>143-145</sup> concluded that the net hydrogen

abstraction in this case is a two-step process. In contrast, a combined CIDEP and CIDNP study of the photolysis of *p*-benzoquinone in 2-propanol was in agreement with the predominating hydrogen-abstraction mechanism (path B).<sup>146</sup> This latter case may be regarded as an inner-sphere electron-transfer mechanism between photoexcited quinones and alcohols or 1,4-dihydronaphthoquinone that is formed. *In this review, however, we shall not treat thoroughly these cases of "inner-sphere" photoinduced electron-transfer catalysis, because the foregoing nomenclature has not yet gained wide acceptance among photochemists.*

To summarize, besides the outer-sphere photoelectron transfer, two main classes of mechanism are possible: (1) The inner-sphere photoelectron-transfer mechanism with ligand exchange including most of the  $S_H2$  displacement reactions.<sup>139</sup> (2) The inner-sphere photoelectron-transfer mechanism without ligand exchange (see section I5d). The latter is necessarily stepwise as the intermediate complex proceeds to the products with only a difference of electron location at the end of the reaction. The stoichiometry is exactly the one provided by outer-sphere photoelectron transfer, but the rate is far higher. Fukuzumi and Kochi<sup>1232</sup> have proposed that there is a continuum of situations between outer-sphere and inner-sphere mechanisms (see also ref 130).

### d. Ground-State Charge-Transfer Complex and Electron Transfer

A charge-transfer complex results from a combination of an electron donor and an electron acceptor.<sup>147</sup> The donor and the acceptor may be molecules, molecules-ions, atoms, or atoms-ions. Mulliken's description<sup>148a-h</sup> of weak donor-acceptor complexes suggests that the zero-order ground state is stabilized by some resonance contribution from a zero-order excited state describing transfer of an electron from D to A:

$$\psi_{\text{N}}(\text{A},\text{D}) = a\psi_0(\text{A},\text{D}) + b\psi_1(\text{A}^-, \text{D}^+) \quad a > b \quad (3)$$

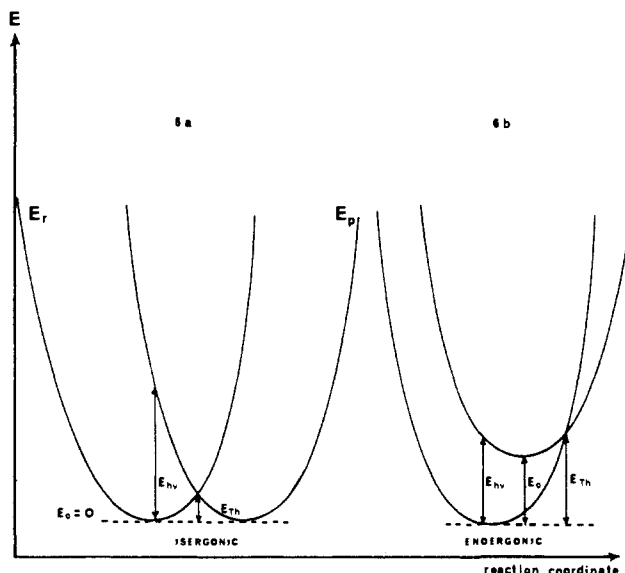
$\psi_{\text{N}}$  = wave function of the ground state

$$\psi_{\text{E}}(\text{A},\text{D}) = a^*\psi_0(\text{A}^-, \text{D}^+) - b^*\psi_1(\text{A},\text{D}) \quad a^* > b^* \quad (4)$$

$\psi_{\text{E}}$  = wave function of the excited state

The molecular orbital theory describes the interaction of D and A in terms of mixing the HOMO of appropriate symmetry for D with the LUMO of A. The dative wave function  $\psi_1$  corresponds to a structure of the complex where one electron has been completely transferred from the donor to the acceptor. In general, this term is relatively small because of the large separation of A and D. It must be emphasized that the contribution of the charge-transfer structure in the ground state is usually not important,<sup>156</sup> i.e.,  $b/a$  in eq 3 is small.

Some experimental criteria characterize the presence of a charge-transfer complex between a donor and an acceptor:<sup>37</sup> The most striking characteristic is a new light-absorption band (or bands). This band, usually evidenced in the UV or visible regions, may however be missed<sup>200</sup> if the charge transfer induces an important chemical activation<sup>157a</sup> or may be absent although other data suggest charge-transfer complex.<sup>157b</sup>



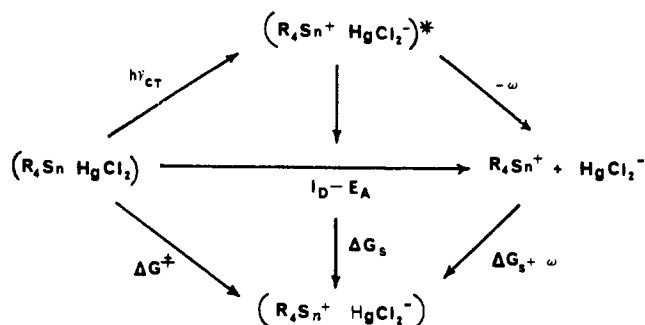
**Figure 6.** Potential energy diagram for electron-transfer reaction.  $E_0$  = overall energy change,  $E_{hv}$  = Franck-Condon maximal of the optical transition,  $E_{Th}$  = activation energy of the thermal electron transfer.

A relationship between the energy of the charge-transfer transition ( $h\nu_{CT}$ ) and the ionization potential ( $I_p$ ) of the donor exists,<sup>158</sup> but it should not be strictly linear<sup>159</sup> even though linearity is found for many cases. Equation 5 may be derived where  $C_1$  and  $C_2$  are con-

$$h\nu_{CT} = I_p - C_1 + \frac{C_2}{I_p - C_1} \quad (5)$$

stants related to electron affinity of the acceptor, electrostatic interactions in the ground and excited states, and resonance energies. Moreover, the charge-transfer band frequency for the ground-state complexes between charged species (e.g., pyridinium iodide) is strongly solvent sensitive.<sup>160a-d</sup>

In a charge-transfer complex the electron-transfer process may not take place by thermal activation, but rather through photoactivation. Then the question arises: Are the rates of thermal electron transfer and optical electron transfer correlated? The answer can be partly found in the inorganic counterpart of charge-transfer absorption: the intervalence transfer absorption<sup>121d,164</sup> displayed by the mixed-valence compounds.<sup>151,152,165</sup> This phenomenon has been evidenced in solid state and in solutions of salts containing the same element in two oxidation states or two elements forming a redox couple. The best known example is that of Prussian Blue ( $KFe[Fe(CN)_6] \cdot H_2O$ ) obtained when solutions of Fe(II) salts react with ferricyanide solutions ( $K_2Fe(CN)_6$ ) or when Fe(III) salts react with ferrocyanide. With some exceptions,<sup>121e,166</sup> chemistry associated with the intramolecular electron transfer has seldom been reported for mixed-valence complexes: they are stable whatever the position of the electron. This contrasts with results reported in the organic and organometallic field.<sup>37-40</sup> A unified model for both charge-transfer complexes and mixed-valence complexes has been proposed by Chiu.<sup>167</sup> The theoretical treatment of these complexes complements those of charge-transfer complexes by giving the quantitative relations to be expected between the rates of photochemical and thermal electron transfer.<sup>168-171a</sup> Ap-



**Figure 7.** General scheme showing the interrelationships among the electronic ( $I_D$  and  $E_A$ ), the charge transfer ( $h\nu_{CT}$ ), and the solvation ( $\Delta G_s$ ) to the activation process of electron transfer from mercury(II) halide to alkyltin compounds (reprinted with permission from ref 172a).  $\Delta G^\ddagger$  = activation free energy for the electrophilic cleavage,  $\Delta G_s$  = solvation free energy change,  $h\nu_{CT}$  = charge-transfer transition energy of the alkyltin-mercury(II) complex,  $\omega$  = interaction energy in the excited ion pair,  $I_D$  = ionization potential,  $E_A$  = electronic affinity.

proximate potential energy surfaces may be constructed whose profile for a self-exchange reaction (isoergonic) is shown in Figure 6a. The occurrence of a photoelectron-transfer process when the reactants are in their equilibrium configuration needs a large input of energy ( $E_{hv}$ ) during the time required for the electronic transition, because the products can only be obtained in a very high energy state at the equilibrium configuration of the reactants. In a thermal electron-transfer process, the adjustment of the inner coordination shells of the two reactants of the outer solvation shells to some nonequilibrium configuration are required prior to electron transfer. The zero-order surface will intersect at those nuclear configurations for which  $E_R = E_P = E_{th}$ . Thus, for a one-electron transfer proceeding by an outer-sphere mechanism, it is predicted that the Franck-Condon maximum of the optical transition and the activation energy of the thermal electron transfer are closely related. In the particular case of an isergonic electron transfer the approximate<sup>152</sup> equation is

$$E_{hv} = 4E_{th} \quad (6)$$

For many electron-transfer reactions, the overall energy change  $E_0$  (Figure 6b) is not zero, but for small values of  $E_0$ , again  $E_{hv}$  and  $E_{th}$  are related.<sup>168</sup>

$$E_{hv} = 4E_{th} - E_0 \quad (7)$$

On the other hand, an activation free energy relationship has been proposed by Fukuzumi<sup>172a</sup> for the electrophilic mercury(II) cleavage of a tetraalkyltin series. The  $\Delta G^\ddagger$  free energy is separated into three effects: electronic, steric, and solvation as shown in Figure 7.

$$\Delta G^\ddagger = \Delta I_D + \Delta E + \Delta G_r^s \quad (8)$$

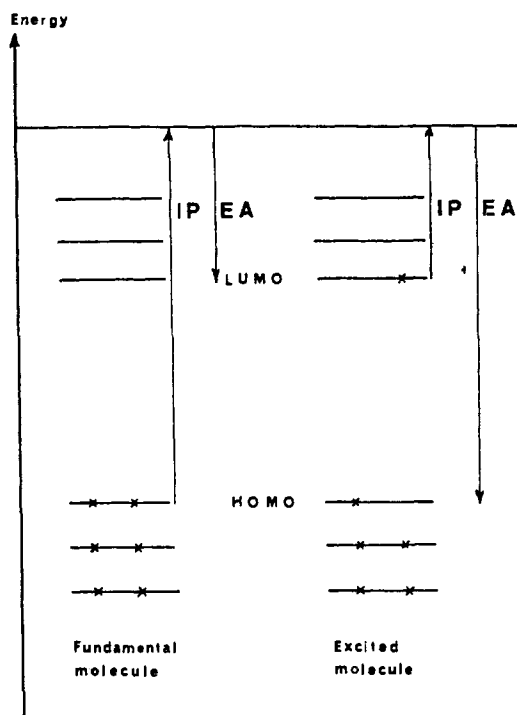
An equivalent linear free energy relationship is expressed as

$$\Delta G^\ddagger = \Delta h\nu_{CT} + \Delta G_r^s \quad (9)$$

where  $\Delta h\nu_{CT}$  is the relative transition energies of the alkyltinmercury(II) complex and  $\Delta G_r^s$  is the solvation change.

Solvation of the ion pair leads to diminution of the activation free energy, generally in parallel with the polarity of the solvent.<sup>49b</sup> These formulations emphasize the strong similarity between the charge-transfer





**Figure 8.** Schematic orbital diagram showing the decrease of the ionization potential and the increase of the electron affinity upon excitation of a molecule.

excited states, i.e., the photochemically excited-state ion pair  $[R_4Sn^+ HgCl_2^-]^*$  and the transition state in the electrophilic cleavage by mercury(II).

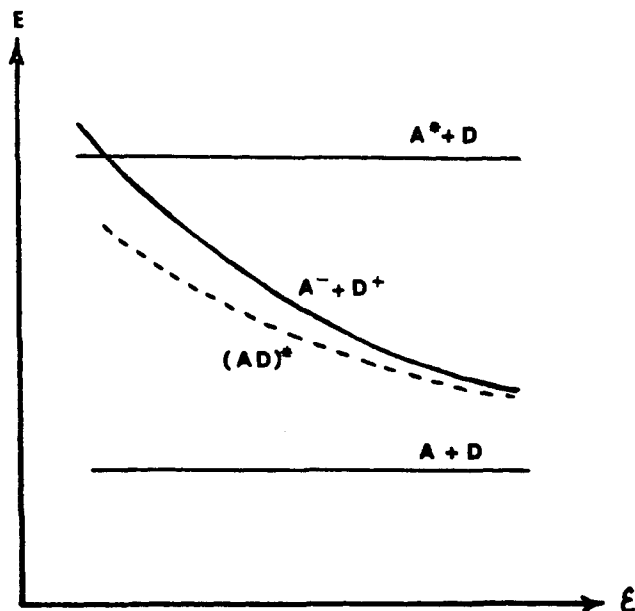
Numerous other examples exist in the literature showing varying degrees of correlation between the rate constants and the ionization potentials or electron affinities of one or more of the reactants.<sup>173</sup> Thus, the charge-transfer formulation provides a straightforward basis from which a unified view<sup>172b</sup> of electron-transfer reactions may evolve.

Prof. L. Ebersson<sup>140</sup> kindly mailed us a preprint of his paper dealing with the application of Marcus theory to rates of electron transfer in chemistry. All the rate constants calculated from Marcus theory for this kind of electron-transfer mechanism are underestimated. As most of the presently reported cases seem to form a charge-transfer complex<sup>37-40</sup> before electron transfer, we propose, as a working hypothesis, to include charge-transfer complexes as precursors of inner-sphere transition states. (A recent Ebersson paper<sup>153</sup> proposes another explanation for this underestimation. In any case, it may be of interest to gather all electron transfers dealing with EDA couples because of Balzani's suggestion<sup>462a</sup> concerning the indirect involvement of excited states in electron-transfer paths for CTC and specific Endicott's treatment of these cases.<sup>462b</sup>)

#### e. Electron Transfer via Exciplex Dissociation

An electronically excited state is both a better oxidant and a better reductant than the ground state. Then one can assume that this behavior closely parallels the fact that the excitation of an electron from a low-energy (HOMO) to a high-energy orbital (LUMO) reduces the ionization potential and increases the electronic affinity of a molecule, as can be seen from Figure 8.

Thus, in some cases, an electronically excited molecule is able to form a charge transfer complex with one



**Figure 9.** Dependence of an exciplex potential energy on solvent dielectric constant (Reprinted with permission from ref 179. Copyright 1979, Pergamon Press, Ltd.). A = electron acceptor, D = electron donor,  $A^*$  = excited acceptor,  $(AD)^*$  = exciplex,  $A^- + D^+$  = ion pair.

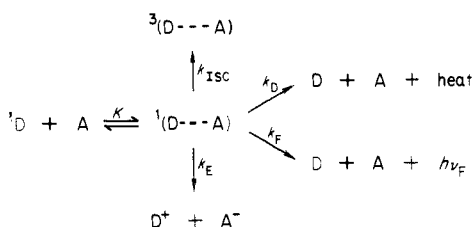
or several other molecules, whereas it could not do it in its ground state. These types of excited molecular complexes are the so-called "excimer" (complexation between same species) and "exciplex" (complexation between different species).<sup>174-178</sup> By analogy with Mulliken description of ground-state charge-transfer complexes, exciplexes can be described as resonance hybrids of locally excited and charge-transfer configuration:

$$\psi(A,D)^* = a\psi(A^*,D) + b\psi(A^-,D^+) \quad (10)$$

Potential energy surfaces for hypothetical nonpolar ( $a > b$ ) and polar ( $b > a$ ) exciplexes can be drawn.<sup>179</sup> The energy of the charge-transfer configuration and hence the exciplex is highly dependent upon the solvent polarity, as shown schematically in Figure 9. Thus, polar exciplexes are known to dissociate into non-fluorescent radical ions in polar solvents.<sup>180</sup> As a result, the net chemical reaction between the components of the exciplex is an electron transfer. The solvated ion pair which is formed at first must then dissociate into solvent-separated ions, but it is often difficult to prevent the back recombination of the ions which then leads to an inefficient overall reaction.<sup>181</sup> Moreover, systems where excimer or exciplex emission was observed were often photochemically unreactive.

A dilemma exists: Does excited-state complex formation occur on the way to electron-transfer products or is it just an energy wasting but spectroscopically observable dead end?

Caldwell<sup>182,183</sup> clearly showed by analyzing the kinetics of formation and decay of several phenanthrene-styrene type exciplexes that the thermodynamic behavior of these reactive exciplexes is almost identical with that of the known unreactive ones. Furthermore, the radiative lifetimes of the reactive exciplexes ( $k_f \approx 2-4 \times 10^{-6} \text{ s}^{-1}$  in general)<sup>184</sup> closely matches those determined for the unreactive ones. In fact, why are exciplex emissions still the exception in photoreactions? Since

Scheme I<sup>a</sup>

<sup>a</sup>  $k_D$ ,  $k_F$ ,  $k_E$  = rate of diffusion, fluorescence, and electron transfer, respectively.

data seem only available for organic singlet photo-reactions,<sup>185</sup> let us consider exciplex behavior in the particular case of photoelectron transfer in Scheme I. In the limit of low reversibility ( $k$  important), the lifetime of the exciplex is given by:

$$\tau_C = (k_F + k_{ISC} + k_D + k_E)^{-1} \quad (11)$$

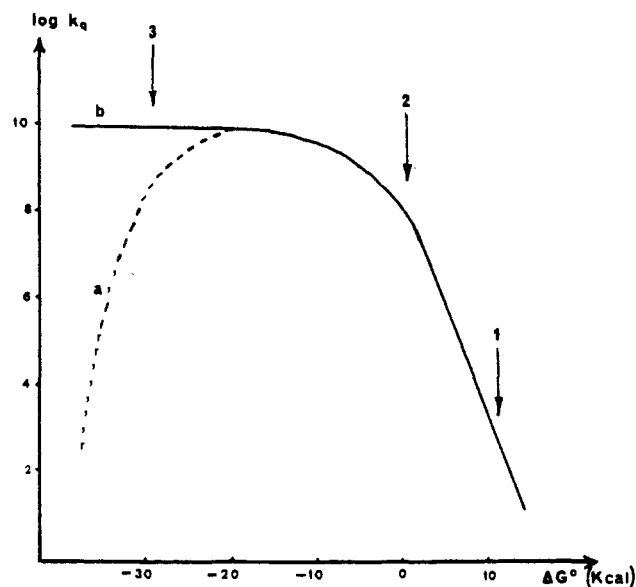
Since values  $k_F \approx 10^6$ – $10^7$  s<sup>-1</sup> and  $k_{ISC} = 10^7$ – $10^8$  s<sup>-1</sup> are not uncommon, it is easy to see that  $k_E \lesssim 10^5$  s<sup>-1</sup> leads to an apparently unreactive exciplex and  $k_E \gtrsim 10^9$  s<sup>-1</sup> leads to so great an electron-transfer process over radiative deactivation that emission is essentially non-competitive. On the contrary, the formation of the fluorescent excited state and intersystem crossing can be two competing processes.<sup>186</sup>

In fact, for simultaneous emission and reaction, the range of  $k_E$  values is limited and the absence of emission seems to be normal in many exciplex photoreactions, and there have been several reports proposing that the exciplex is an intermediate in many photochemical transformations of organic molecules.<sup>40,187,188</sup> Nevertheless the fluorescence, excitation, and absorption spectra and fluorescence decay kinetics of charge-transfer complexes and exciplexes of some hetero-aromatic cations such as 1-azaphenanthrene and some electron acceptors like 1,6-dimethylnaphthalene suggest that the fluorescent state of the exciplex may differ from that of the charge-transfer complex.<sup>190</sup> Furthermore, Lewis<sup>123b</sup> recently proved that singlet-state [2+2] cycloadditions occur more efficiently from relatively nonpolar exciplexes than from highly polar exciplexes or radical ion pairs. The question of actual electron-transfer participation in exciplex reactivity therefore remains open.<sup>49b</sup>

In the field of transition-metal complexes, much less evidence is available for the existence of this type of complex. Documented cases seem to be those of excited metalloporphyrins with nitro aromatic compounds.<sup>191–193</sup> Furthermore, it should be noted that both the structure of transition-metal complexes, which in most cases are "spherical type" molecules, and the nature of the solvents used (which have to be polar because the complexes are usually charged species) are not favorable to the formation of exciplexes (see, however, ref 194 and 195). Nevertheless, Marcantonatos<sup>154a</sup> demonstrated their formation for  $UO_2^+(aq)$  and even reported evidence for triple exciplexes<sup>154b</sup> with this ion.

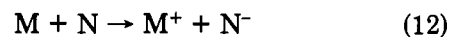
## 6. Kinetic Aspects of Photoelectron-Transfer Processes

The redox properties of excited states allow expectation of some reactions for these excited states that are totally absent in the ground state. As the lifetime of



**Figure 10.** Plot of the logarithm of the experimental quenching constant vs. the free energy change of the electron-transfer reaction for  $Cr(bpy)_3^{3+}$  complex (reprinted with permission from ref 49a. Copyright 1979, Pergamon Press, Ltd.).  $k_q$  = quenching constant,  $\Delta G^\circ$  = free energy change, 1 = weak donor-acceptor couple, 2 = strong donor-acceptor couple, 3 = photoexcited donor-acceptor couple, a = Marcus inverted region (see text), b = Rehm-Weller relationship.

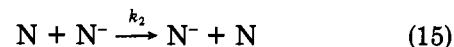
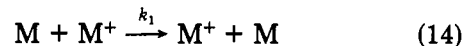
these states is, however, a limiting factor we must now answer the question: How much faster is an electron transfer from/to an excited state than when compared to the one involving the ground state? Figure 10 illustrates the answer. In this figure, the rates of electron transfer are correlated with  $\Delta G^\circ$  associated with the redox couples. Marcus<sup>126,135,136,196,197</sup> and Sutin<sup>114,198</sup> developed a model where they showed that the free energy of activation for a cross reaction



can be expressed by

$$\Delta G_{1,2} = \frac{\Delta G_1 + \Delta G_2}{2} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{8(\Delta G_1 + \Delta G_2)} \quad (13)$$

where  $\Delta G_1$  and  $\Delta G_2$  refer to the free energy of activation for the self-exchange reactions 14 and 15.



When  $\Delta G^\circ \ll 8(\Delta G_1 + \Delta G_2)$ , eq 13 reduces to:

$$\Delta G_{1,2} = \frac{\Delta G_1 + \Delta G_2}{2} + \frac{\Delta G^\circ}{2} \quad (16)$$

Or with  $\lambda = 2(\Delta G_1 + \Delta G_2)$

$$\Delta G_{1,2} = \lambda + \frac{\Delta G^\circ}{2} \quad (17)$$

Under such conditions a linear relationship between the free energies of activation and the standard free energy changes for a series of reactions where  $\lambda$  is constant should hold.  $\Delta G_{1,2}$  reaches a minimum for  $\Delta G^\circ = -\lambda$ , and it should increase when  $\Delta G^\circ$  becomes large and negative. This means that the rate constants of the electron-transfer step for cross-section between

a single reductant M and a homogeneous series of oxidants N should increase up to a maximum and then decrease with increasing oxidation potential of the oxidant. The region in which the rate constant should decrease with increasing  $|\Delta G^\circ|$  value is usually called the "Marcus inverted region". Figure 10 (curve a) illustrates this theory.

Rehm and Weller,<sup>28,29</sup> using the Stern-Volmer relationship and steady-state approximation, proposed the empirical equation:

$$\Delta G_{1,2} = \frac{\Delta G^\circ}{2} + \left[ \frac{(\Delta G^\circ)^2}{2} + \left(\frac{\lambda}{4}\right)^2 \right]^{1/2} \quad (18)$$

and obtained curve b.

These curves nearly coincide for positive or slightly negative  $\Delta G^\circ$  values. Their slopes are approximately linear with a value of  $-(1/(2.303 RT))$  if the Rehm-Weller approach is used.

There has been much work done to determine if it was possible to have an inversion of rate (curve a, Figure 10), but extensive studies<sup>28,29,48</sup> seem to establish that curve b best accounts for the rate of intermolecular electron transfer from an excited state. (For more detailed discussions on the question of non-Marcusian behavior, see ref 155). An interesting application of the Weller treatment is that photochemical excitation can be expected to accelerate the rate of electron transfer far more for weak donor-acceptor redox couples (rate passing from point 1, Figure 10, to diffusion-controlled value) than for strong donor-acceptor couples (rate passing from point 2 to diffusion-controlled value). An illustration of this latter case can be found in a recent paper:<sup>199</sup> the rates of electron transfer from the same phenolate ion to various carbonyl triplets are insensitive to the reduction potentials of these carbonyl triplets. The large oxidation potential of the phenolate ion dominates in determining the free energy change associated with the electron-transfer step so that  $\Delta G$  has always sufficiently large negative values. Then  $k_q$  always approaches the limiting diffusion-controlled value.

Other aspects of the photoelectron transfer rate must be discussed. A first question is: Will an electron transfer be faster if it follows a charge-transfer complex or an exciplex? If it is supposed that charge transfer complexes and exciplexes are the organic counterpart of the inner-sphere photoelectron-transfer intermediates, the electron-transfer rate would have to be higher when an exciplex or a charge-transfer complex is formed between the electron donor and the electron acceptor. This follows from the fact that the partners of the redox reaction are already in the same cage of solvent, and it is no longer correct to speak about diffusion control as a limiting factor. In other words, the precursor complex (sections I5a and I5b) is already formed.

Another approach is to consider that in a charge-transfer complex the adjustment of the donor-acceptor couple geometry together with the arrangement of surrounding solvent molecules is already carried out when the complex is formed. The photochemical activation of charge-transfer complex or the dissociation of an exciplex promotes an electron transfer that cannot be kinetically controlled. Since the complex formation corresponds to a thermodynamically allowed electron-transfer process, the rate constant in this approach would be as fast as in an inner-sphere electron-transfer

mechanism. In fact, a recent picosecond dynamics study of the photoreduction of benzophenone by triethylamine shows that a charge-transfer complex is formed between these reactants within 20 ps.<sup>200</sup> Haim and Sutin recently reported quantitative data on a closely connected problem: rates of optically induced electron within ion pairs.<sup>161</sup>

A second question concerns the favorable requirement of molecular orbital of the donor and the acceptor prior to the electron transfer. Several key ideas apply to molecular orbital symmetry requirement in electron-transfer processes.<sup>84c</sup> Efficient outer-sphere electron transfer requires both molecular orbitals of the donor and receptor to be  $\pi^*$  orbitals, whereas inner-sphere reactions require both molecular orbitals to be  $\pi^*$  or  $\sigma^*$ . If either of these does not meet the symmetry requirements for effective transfer, greater chemical activation, encompassing both structural deformation<sup>162</sup> and electron configuration change, may be required. In such a case, even a strongly thermodynamically favored electron transfer can operate with a rate slower than diffusion controlled. Nevertheless, these requirements are seldom (see ref 128) dealt with for photoelectron-transfer rates probably because only symmetry-allowed transfers are effectively observed. They could, however, play a nonnegligible role to complete the purely thermodynamic contribution (section I3) to redox reactivity difference between singlet and multiplet states.

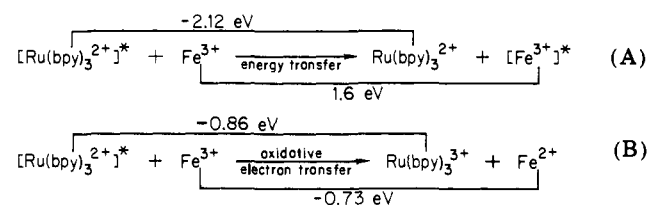
For micellar effects on electron-transfer rates, see ref 163.

## 7. Electron-Transfer vs. Energy-Transfer Processes

Although usually discussed separately and treated using different formalisms, the quenching of an excited state by exchange energy transfer and outer-sphere electron transfer are conceptually related processes.<sup>189</sup>

In both cases, spatial overlap of donor and acceptor orbitals is required, no bond-breaking or -making processes take place, and Franck-Condon restrictions have to be obeyed because the electronic rearrangement (energy transfer) or the net transfer of an electron occurs in a time that is short compared to that required for nuclear motions. Hence Balzani<sup>201</sup> used the thermodynamic theory of ground-state electron transfer (Marcus-Hush theory) to treat in the same way the quenching of excited state by energy transfer or electron transfer. So the question arises: When both processes are thermodynamically allowed, which experiments should be done to recognize the type of quenching occurring?

For example, the  $\text{Ru}(\text{bpy})_3^{2+}$  complex possesses simultaneously the properties of being a good energy donor, a good electron acceptor, and a good electron donor. On irradiation, with  $\text{Fe}^{3+}$  as a quencher, both energy transfer (eq A) and oxidative electron transfer (eq B) are thermodynamically allowed.



In continuous irradiation, the quenching takes place without any permanent chemical change. Moreover,  $[\text{Fe}^{3+}]^*$  is known to be a nonemitting excited state. Thus, one cannot say whether the quenching occurs according to eq A or B. Only a very detailed analysis of the various rate constants has led to the conclusion that electron transfer is probably the major quenching mechanism in this system.<sup>202</sup>

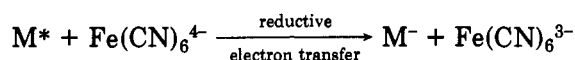
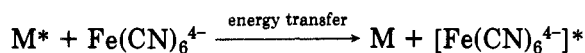
Other systems in which discrimination between thermodynamically allowed energy and electron transfer has been achieved are  $[\text{Ru}(\text{bpy})_3^{2+}]^*$  quenching by  $\text{Cr}(\text{bpy})_3^{3+}$ ,<sup>93</sup>  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ , and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ .<sup>203</sup> Electron-transfer quenching predominates for these examples.

On the contrary, at least 90% of the  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitized decomposition of  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  proceeds by means of a triplet-to-triplet energy-transfer mechanism.<sup>204</sup> Likewise, quenching of excited metalloporphyrins by oxygen which can give rise to both superoxide ion (electron transfer) as well as singlet oxygen (energy transfer) leads to singlet oxygen production.<sup>205</sup>

To summarize, the determination of the type of quenching product (if any) is not sufficient. Electron-transfer products are not a proof per se of an electron-transfer quenching. Thus, in the quenching of the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  by superoxo-bridged dinuclear cobalt(III) complexes, the formation of  $\text{Ru}(\text{bpy})_3^{3+}$  and cobaltous ion is explained to occur partly in an energy-transfer pathway.<sup>206</sup>

The formation of an excited quencher is not a proof of an energy-transfer quenching, because the primary electron-transfer quenching products  $\text{M}^-$  and  $\text{Q}^+$  (or  $\text{M}^+$  and  $\text{Q}^-$ ) could undergo subsequent reaction to yield  $\text{M}$  and  $\text{Q}^*$ .<sup>48</sup> Specific information on the nature of the quenching mechanism can be gained from the comparison between quenching constants of related systems. In particular, plots of  $\log k_q$  ( $k_q$  = quenching constant) vs. the free energy changes for each process help elucidate the quenching mechanism, provided that a series of data is available.

The quenching of  $[\text{Cr}(\text{bpy})_3^{3+}]^*$ ,  $[\text{Ru}(\text{bpy})_3^{2+}]^*$ , and  $[\text{Os}(\text{bpy})_3^{2+}]^*$  by  $\text{Fe}(\text{CN})_6^{4-}$ <sup>207</sup> illustrates this point, since it may take place either by energy transfer or electron transfer.<sup>48</sup>



The plots of  $\log k_q$  vs. the excited-state energy or the reduction potential of the three complexes show that the expected correlation holds only for the ruthenium complex, pointing out a reductive quenching mechanism only for this compound. Nevertheless, we stress the fact that if it is possible to choose between energy-transfer and electron-transfer quenching in a homologous series, the discrimination is difficult in other cases. Balzani states that the available data seem to indicate that when both energy transfer and electron transfer are thermodynamically allowed, electron transfer predominates.<sup>49</sup> He also underscores the fact that for exchange energy-transfer processes, favorable and simultaneous overlap of two orbital pairs (HOMO-HOMO and LUMO-LUMO) of the donor-ac-

ceptor couple) is required, whereas such a criterion is less stringent for electron-transfer process where only one such overlap is required. He concludes: "This may be the reason why electron transfer prevails over energy transfer when both processes are in their highly exergonic region."<sup>201</sup> More experimental data are still necessary to decide if this assumption is generally valid.

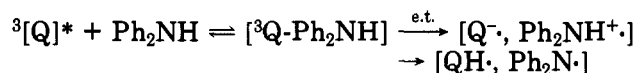
## 8. Electron-Transfer vs. Proton-Transfer Processes

Proton transfer is one of the most common chemical reactions. It is encountered in organic and inorganic chemistry and even more so in biochemistry where all reactions are carried out in aqueous solutions. The reactivity of the proton especially in its hydrated form is so high that most of its reactions are diffusion controlled. Thus, from some studies<sup>208</sup> it has become apparent that  $\text{p}K$  changes of  $-7$  can be readily attained for molecules which become more acidic in the excited state.

Recently, two groups<sup>209,210</sup> have measured the rate of proton ejection from 2-naphthol-6-sulfonate [ $\text{p}K^* = 1.66$ ],<sup>209</sup> 2-naphthol-3,6-disulfonate [ $\text{p}K^* \approx 0.5$ ],<sup>210</sup> and 8-hydroxy-1,3,6-pyrenetrisulfonate [ $\text{p}K^* \approx 0.5$ ].<sup>210</sup> They found  $1.0 \times 10^9 \text{ s}^{-1}$ ,  $1.5 \times 10^{10} \text{ s}^{-1}$ , and  $1.2 \times 10^{10} \text{ s}^{-1}$  values, respectively.

Since the rates of these processes are very high, one can question whether proton transfer may be faster than electron transfer. The use of ultrarapid techniques has led to new developments in the picosecond time range and the answer to the question can be partly given. Photoionization of halides, anions,<sup>211</sup> phenolates and phenol,<sup>212</sup> and ferrocyanide ion<sup>213,214</sup> which possess charge transfer to solvent spectra are very fast (i.e., for phenol, much shorter than the lifetime of the phenol excited state  $\text{S}_1$ ). In the case of phenol, the question arises: Does proton transfer occur before or after electron ejection? The  $\text{pH}$  effect has shown that electron ejection occurs before deprotonation.<sup>212</sup> When benzophenone is photoreduced by triethylamine, the charge-transfer complex formed within 20 ps is subsequently quenched by a proton transfer with a half-life of 15 ps.<sup>200</sup>

Thus, it is sometimes difficult to predict if electron transfer may arise before or after proton transfer when both phenomena are competitive. In such cases, the solvent and the temperature can play a fundamental role as in the competition between electron and hydrogen atom transfer. For example, the kinetics and mechanism of the quenching of the triplet states of 2,6-diphenyl-1,4-benzoquinone (Q) by electron and H atom donors such as diphenylamine (DPA) have been studied.<sup>216</sup> In polar solvents ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$ ), the formation of cation radicals of the amines is recorded because an electron transfer was occurring. In weakly polar solvents, a triplet exciplex is formed,<sup>217</sup> but quenching by DPA also leads to the formation of diphenylamine radical. Thus, quenching was described by



The dependence of the yield of  $\text{Ph}_2\text{N}^{\cdot}$  on temperature was studied, and it was experimentally established that

it decreases when the temperature decreases.

Finally, if electron transfer frequently plays a predominant role in many biological reactions, the transfer of proton<sup>218</sup> is also widely occurring. Proton translocation processes are involved in a picosecond regime in such natural processes as visual transduction,<sup>219</sup> which can account for the formation of bathorhodopsin.<sup>220-222</sup> It must be underscored that these proton transfers (theoretically faster than known intermolecular electron transfers) are intramolecular and that intramolecular electron transfer in 6-[(4-methylphenyl)amino]-2-naphthalenesulfonic acid *N,N*-dimethylamide excited state is also occurring on a picosecond scale.<sup>223</sup> Let us close this section by recalling that a protonated substrate accepts an electron far faster than it would do in its free form.

### 9. Quantum Yields of Intermolecular Photoelectron Transfer

In some textbooks, the primary photochemical process is incorrectly considered to be the absorption of the radiation. Thus, some confusion in the photochemical literature exists concerning the right use of the two key terms, "primary process" and "quantum yield". For that reason, the development here will adopt the definitions of Porter, Balzani, and Moggi.<sup>224</sup>

They call *primary step* any one of the elementary transformations of an excited state of the molecule that absorbs light, the absorption step itself being also a primary step among others. Thus, a *primary process* ends with a primary step. In Figure 1, A, IC, ISC, F, P, energy transfer, electron transfer, and chemical reaction of the excited state are primary processes.

Furthermore, the words "efficiency" and "quantum yield" must be clearly distinguishable terms. The first is to be reserved for describing the relative importance of one step among all the steps which depopulate a given excited state, and the second is to be used only when reference is made to the number of absorbed photons.

The *primary quantum yield* is the number of molecules that undergo a given primary process per photon absorbed by the ground-state molecules of that species. In contrast, the *overall quantum yield* is the ratio of the total amount of a given photoinduced phenomenon observed experimentally to the total amount of light absorbed by the system.

#### a. General Expression of the Overall Quantum Yield

The most general expression seems to be a product of probabilities such as eq 19.<sup>225</sup> In the particular case

$$\Phi_o = \Phi_p \times Y_i \quad (19)$$

of bimolecular electron transfer,  $\Phi_o$  (overall quantum yield) represents the probability that absorption of light will lead to electron-transfer final products,  $\Phi_p$  (primary quantum yield) is the probability that a photon absorbed then induces electron transfer leading to metastable intermediate or ion pair, and  $Y_i$  is the probability that these primary intermediates will proceed to stable final products.

If several excited states lead to the same product *i*, then the right-hand side of eq 19 becomes a summation over all reactive states.

It should be remembered that  $\Phi_p$  may be viewed as the product of two efficiencies as shown in eq 20. In-

$$\Phi_p = \phi_{ES} \times \phi_R \quad (20)$$

deed,  $\phi_{ES}$  is the efficiency for the population of the requisite excited state from the early populated spin-allowed excited state, and  $\phi_R$  is the efficiency of electron transfer from this requisite excited state.

Let us discuss probable variations in  $\phi_{ES}$ ,  $\phi_R$ , and  $Y_i$  efficiencies.

(1)  $\phi_{ES}$ . In direct irradiation experiments,  $\phi_{ES}$  is unity if the spin-allowed excited state populated by the wavelength being used is responsible for the electron-transfer reaction. If the reaction occurs from the lowest spin-allowed excited state and if a higher spin-allowed excited state is formed initially,  $\phi_{ES}$  depends on the efficiency of internal conversion (this process is often 100% efficient). When a spin-forbidden state is involved,  $\phi_{ES}$  is equal to the intersystem crossing efficiency  $\phi_{ISC}$ .

$$\phi_{ES} = \phi_{ISC} = (k_{IC}\zeta_{nM2})(k_{ISC}\zeta_{nM1}) \quad (21)$$

When the excited state of interest is formed by photosensitization,  $\phi_{ES}$  depends on the competition between excitation transfer to the acceptor (rate  $k_T[Q]$ ) and other decay processes of the sensitizer (rate  $1/\zeta_s$ ).

$$S^* + Q \xrightarrow{k_T} S + Q^*$$

$$\phi_{ES}(Q^*) = \frac{\phi_{ES}(S^*) \times k_T[Q]}{1/\zeta_s + k_T[Q]} \quad (22)$$

$\phi_{ES}(S^*)$  = efficiency for the population of the sensitizer excited state.  $\phi_{ES}(Q^*)$  = efficiency for the population of the acceptor excited state.  $\zeta_s$  = lifetime of  $S^*$ .

Note here that the value of  $\phi_{ES}(Q^*)$  can vary from zero to unity depending on the nature of the sensitizer (which affects  $\zeta_s$  and  $k_T$ ) and on the concentration of the acceptor. Therefore, the primary quantum yield and rate for a nonreversible photosensitized electron-transfer reaction do depend on the concentration of the quencher *Q* but not linearly. In contrast, the reciprocal of the quantum yield is a linear function of  $[Q]^{-1}$ .

$$\phi_{ES}(Q)^{-1} = \frac{1}{\phi_{ES}(S^*)k_T[Q]\zeta_s} \quad (23)$$

(2)  $\phi_R$ . The probability of electron-transfer reaction between the excited state and a molecule *M* depends on the rate of the transfer and of the lifetime of the excited state. The concentration of the substrate *M* influences the value of  $\phi_R$  until there is enough *M* present so that the excited state can react with it (eq 24). *M* can be another molecule of reactant in its

$$\phi_R = k_M[M]\zeta_{ES} \quad (24)$$

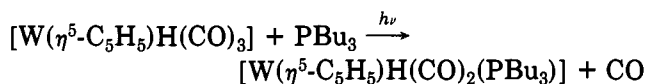
ground state (case of excimer).

For low concentrations of *M*, the primary quantum yield is proportional to  $[M]$ . If  $Y_i$  is constant, the reciprocal of the overall quantum yield is a linear function of  $[M]^{-1}$  (eq 25).

$$\Phi_o^{-1} = \phi_{ES}^{-1}Y_i^{-1} \left[ 1 + \frac{1}{k_M[M]\zeta_{ES}} \right] \quad (25)$$

(3)  $Y_i$ . In photoinduced electron-transfer reactions,

reactive intermediates such as radical ions or exciplexes are common. Their further reactions including reversion to ground state of reactants or initiation of catalytic cycle determine the actual yields and overall quantum yields of products. The most important consequence of this behavior is that in many reactions, the overall quantum yield  $\Phi_0$  is determined only by  $Y_i$  and depends only slightly on excited-state rate parameters, if at all. It must be emphasized that contrary to  $\Phi_p$ , which is always  $\leq 1$ ,  $Y_i$  can reach very high values in the case of photocatalytic cycles or chain reactions. On the contrary, one can imagine situations where even with a mean value for  $Y_i$  (e.g.,  $Y_i \approx 10$ ), a low primary quantum yield (e.g.,  $\Phi_p < 0.1$ ) owing to reversible excited-state electron-transfer reaction<sup>226</sup> may lead to an overall quantum yield  $\Phi_0 < 1$ . Indeed, chain reactions with very low primary quantum yield may be found in literature. Thus, photolysis of  $[W(\eta^5-C_5H_5)H(CO)_3]$  promotes substitution of  $PBu_3$  for CO.



The overall quantum yield varies from 0.6 to 30, and estimated chain length of about 2000 supports a primary quantum yield of about 0.015.<sup>227</sup>

Therefore, a  $\Phi_0$  value smaller than one is not an absolute criterion, and one can admit the possibility of photoelectron-transfer catalysis with overall quantum yield of near unity. (See also ref 231.)

In the photosubstitution of *p*-nitrocumyl chloride with sodium azide, which is proven to proceed by the  $S_{RN}1$  mechanism, Wade found at 366 nm an overall quantum yield value  $\Phi_0 = 1.1$ .<sup>228</sup>

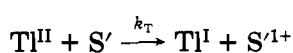
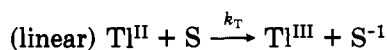
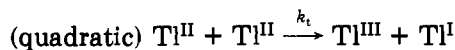
Moreover, one can assume that if the experimental value of the overall quantum yield exceeds its theoretical value on the basis of a bimolecular reaction, a catalytic cycle may be postulated as in the photo-racemization of 1,1'-binaphthyl<sup>229</sup> (see section III5b).

Nevertheless, higher values of  $\Phi_0$  are the best criterion for involvement of a chain reaction, as in the photo-stimulated reaction of iodobenzene with diethyl phosphite ion<sup>230</sup> or the  $CH_3CN$  ligand substitution by  $PPh_3$  with light-induced electron transfer between  $[(CH_3CN)Re(CO)_3phen]^+$  and  $PPh_3$ <sup>231</sup> where the overall quantum yield for substitution varies from 8 to 24.

### b. Kinetic Expression of the Overall Quantum Yield

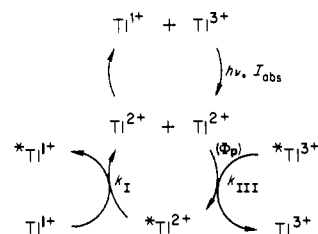
We shall see in section III the variety of chain reactions proceeding by a photoinduced or photosensitized electron transfer. Several equations were developed that are consistent with the experimental overall quantum yields and whose dependence on reactant concentrations and adsorbed light intensity is complex.

The first and more illustrative example is the  $Tl^{II}-Tl^{III}$  electron exchange.<sup>232,233</sup> The proposed mechanism is given in Scheme II ( $Tl^{III}$  being the absorbing species) with the possible termination reactions:



(S = solvent)

### Scheme II<sup>a</sup>



<sup>a</sup> \*Tl = labeled Tl.

For such an exchange reaction involving quadratic termination of chains, the variation of  $\Phi_0$  may be expressed by

$$\Phi_0 = \Phi_p \left[ \frac{k_{III}[Tl^{III}]k_I[Tl^I]}{k_{III}[Tl^{III}] + k_I[Tl^I] + 2(k_t I_{abs} \Phi_p)^{1/2}} \times \left( \frac{1}{\Phi_p k_t I_{abs}} \right)^{1/2} + \frac{k_{III}[Tl^{III}] + k_I[Tl^I] + (k_t I_{abs} \Phi_p)^{1/2}}{k_{III}[Tl^{III}] + k_I[Tl^I] + 2(k_t I_{abs} \Phi_p)^{1/2}} \right] \quad (26)$$

The second term in this relation cannot exceed unity. Overall quantum yields exceeding unity arise from the first term, which depends on a balance between propagation and termination rates and the absorbed light intensity. For a linear chain termination, the expression of  $\Phi_0$  would be:

$$\Phi_0 = \Phi_p \left[ \frac{k_I[Tl^I]}{k_{III}[Tl^{III}] + k_I[Tl^I] + k_T} + \frac{k_I[Tl^I]k_{III}[Tl^{III}]}{k_T(k_{III}[Tl^{III}] + k_I[Tl^I] + k_T)} \right] \quad (27)$$

The general conclusion is made that for a linear chain termination exchange reaction, the overall quantum yield  $\Phi_0$  is independent of absorbed light intensity, whereas for quadratic chain termination  $\Phi_0$  is proportional to  $I_{abs}^{-1/2}$ . Experiments showed that chain termination is largely quadratic disproportionation of  $Tl(II)$ , but at low light intensities a linear termination reaction is important.<sup>233</sup>

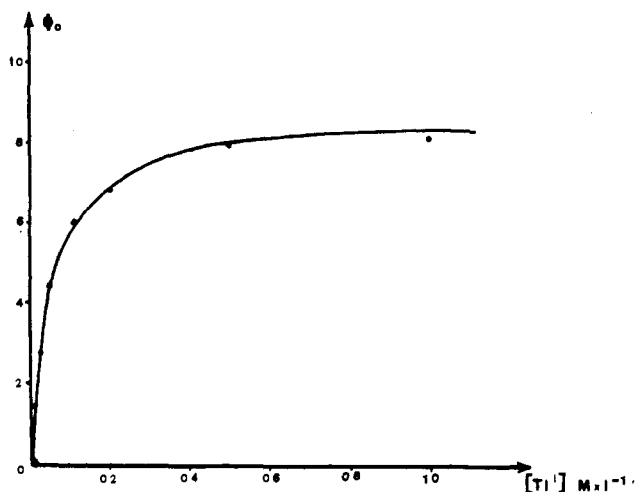
(1) *Dependence of  $\Phi_0$  on  $Tl(I)$  Concentration.* Figure 11 shows the variation of  $\Phi_0$  for constant values of  $[Tl^{III}]$  and  $I_{abs}$ . Its values are approximately a linear function at low  $[Tl^I]$  and approach a limiting plateau value at high  $[Tl^I]$ . Then  $k_{III}[Tl^{III}] + k_I[Tl^I] \gg 2(k_t I_{abs} \Phi_p)^{1/2}$  such that eq 26 simplifies to the form:

$$\Phi_0 = \Phi_p \left[ \frac{k_{III}[Tl^{III}]k_I[Tl^I]}{k_{III}[Tl^{III}] + k_I[Tl^I]} \times \frac{1}{(k_t I_{abs} \Phi_p)^{1/2}} + 1 \right] \quad (28)$$

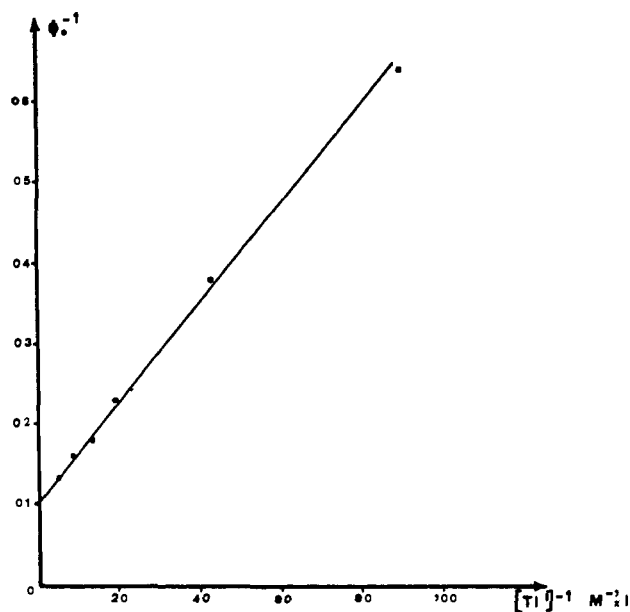
Consequently, extrapolation of the plot in Figure 11 to the value of  $\Phi_0$  at  $[Tl^I] = 0$  yields an estimate of the primary quantum yield  $\Phi_p = 0.1$ , since in eq 28  $\Phi_0$  tends to  $\Phi_p$ . Equation 28 transforms to:

$$\frac{1}{\Phi_0 - \Phi_p} \approx \frac{1}{\Phi_p} = \left( \frac{k_t I_{abs}}{\Phi_p} \right)^{1/2} \left( \frac{1}{k_{III}[Tl^{III}]} + \frac{1}{k_I[Tl^I]} \right) \quad (29)$$





**Figure 11.** Variation of the overall quantum yield  $\Phi_0$  with  $[Tl^I]$ .  $[Tl^{III}] = 0.005 \text{ M}$ ,  $I_{\text{abs}} = 1.6 \times 10^{-5} \text{ E} \times \text{l}^{-1} \times \text{min}^{-1}$ . Extrapolation of the plot to the value of  $\Phi_0$  at  $[Tl^I] = 0$  yields an approximate estimate of the primary quantum yield  $\Phi_p$ .

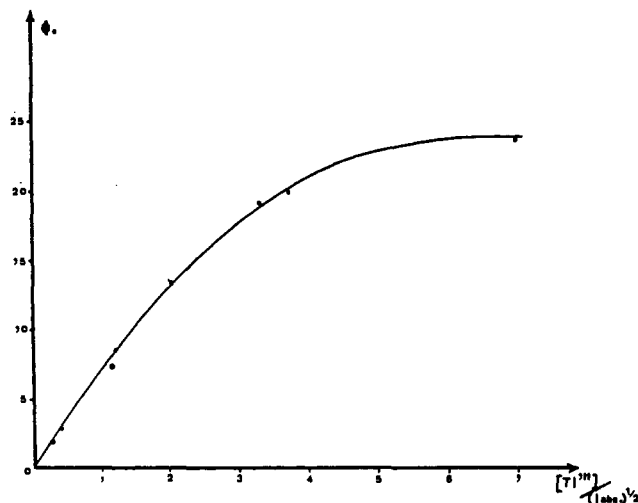


**Figure 12.** Variation of  $1/\Phi_0$  with  $1/[Tl^I]$ .  $[Tl^{III}] = 0.005 \text{ M}$ ;  $I_{\text{abs}} = 1.6 \times 10^{-5} \text{ E} \times \text{l}^{-1} \times \text{min}^{-1}$ . From this plot, slope/intercept =  $k_{III}[Tl^{III}]/k_I$  yielding the ratio  $k_{III}/k_I$ .

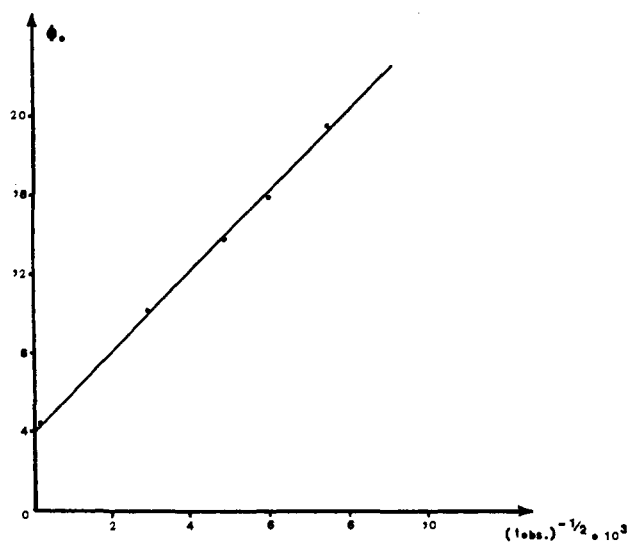
Since the value of  $\Phi_p$  is substantially less than the value of  $\Phi_0$ , Figure 12 shows that at constant  $[Tl^{III}]$  and  $I_{\text{abs}}$  values,  $1/\Phi_0$  is proportional to  $1/[Tl^I]$  for a 1000-fold variation in  $[Tl^I]$ . From this plot, slope/intercept =  $k_{III}[Tl^{III}]/k_I$ , yielding the rate ratio  $k_{III}/k_I$ .

(2) *Dependence of  $\Phi_0$  on Tl(III) Concentration.* At constant  $[Tl^I]$ ,  $\Phi_0$  varies with increasing  $[Tl^{III}]$  in a similar functional manner as with  $[Tl^I]$  in the previous section. However,  $Tl^{III}$  is the principal light-absorbing species, and variation in  $[Tl^{III}]$  also involves variation in  $I_{\text{abs}}$ . So a proper test of eq 28 is provided by the variation of  $\Phi_0$  with  $[Tl^{III}]/(I_{\text{abs}})^{1/2}$ , as shown in Figure 13. As predicted by eq 28,  $\Phi_0$  varies linearly at low  $[Tl^{III}]$  and approaches a plateau value at high  $[Tl^{III}]$ . The intercept at  $[Tl^{III}] = 0$  yields again the  $\Phi_p$  value. A plot of  $1/\Phi_0(I_{\text{abs}})^{1/2}$  vs.  $1/[Tl^{III}]$  as required by eq 29 is linear and also yields the ratio  $k_{III}/k_I$ .

(3) *Dependence of  $\Phi_0$  on Absorbed Light Intensity.*



**Figure 13.** Variation of the overall quantum yield  $\Phi_0$  with  $[Tl^{III}]/I_{\text{abs}}^{1/2}$ .  $[Tl^I] = 0.005 \text{ M}$ . The limiting slope of this curve at low  $[Tl^{III}]$  yields the rate relation  $k_{III}\Phi_p^{1/2}/k_I^{1/2}$ . The intercept at  $[Tl^{III}] = 0$  yields  $\Phi_p$ .



**Figure 14.** Variation of the overall quantum yield  $\Phi_0$  with absorbed light intensity  $I_{\text{abs}}^{-1/2}$ . A light intensity variation accounts for an important quadratic termination of  $Tl^{II}$ .

In principle, the variation of the overall quantum yield with light intensity should be related to quadratic chain termination reaction. At high  $[Tl^I]$  corresponding to "plateau" conditions in Figure 11, eq 28 reduces to the form:

$$\Phi_0 = \Phi_p \left( 1 + \frac{k_{III}[Tl^{III}]}{(k_t I_{\text{abs}} \Phi_p)^{1/2}} \right) \quad (30)$$

Then a plot of  $\Phi_0$  versus  $I_{\text{abs}}^{-1/2}$  would be linear, as in Figure 14. The slope of this line yields the rate ratio  $k_{III}/(k_t \Phi_p)^{1/2}$  and the intercept again the primary quantum yield  $\Phi_p$ . A reduced slope and anomalous intercept may suggest that some linear termination is occurring simultaneously.

To conclude, the kinetic expressions and treatment proposed by Stranks and Yandell<sup>232,233</sup> may be applied to many photoinduced electron-transfer chain reactions proceeding in liquid phase. It permits evaluating the primary quantum yield  $\Phi_p$ , the rate constants of some

TABLE III. Kinetic Expressions of the Overall Quantum Yield for an Intermolecular Photoelectron-Transfer-Catalyzed Reaction (See also ref 235b)

kinetic quantum yield equation	usable in case of ground-state CTC	usable with underscored conditions	possible variations	possible treatment	information gained	ref
$\Phi_0 = \Phi_p \left[ \frac{k_{III}[\text{Ti}^{III}][k_1[\text{Ti}^I] + 1]}{k_{III}[\text{Ti}^{III}] + k_1[\text{Ti}^I] + (k_t I_{\text{abs}} \Phi_p)^{1/2}} + 1 \right]$	no	$k_{III}[\text{Ti}^{III}] + k_1[\text{Ti}^I] \gg 2(k_t I_{\text{abs}} \Phi_p)^{1/2}$ , $[\text{Ti}^I] = \text{constant}$	$\Phi_0$ vs. $[\text{Ti}^I]$ , $\Phi_0$ vs. $[\text{Ti}^{III}] / (I_{\text{abs}})^{1/2}$	extrapolation of $\Phi_0$ at $[\text{Ti}^I] = 0$ , intercept at $[\text{Ti}^{III}] = 0$	$\Phi_p$ value	232
$\frac{1}{\Phi_0} = \left( \frac{k_t I_{\text{abs}}}{\Phi_p} \right)^{1/2} \left( \frac{1}{k_{III}[\text{Ti}^{III}]} + \frac{1}{k_1[\text{Ti}^I]} \right)$	no	$[\text{Ti}^{III}] = \text{constant}$ , $I_{\text{abs}} = \text{constant}$ , $\Phi_p \ll \Phi_0$	$1/\Phi_0$ vs. $1/[\text{Ti}^I]$	slope/intercept = $(k_{III}/k_1)[\text{Ti}^{III}]$	ratio $k_{III}/k_1$	232
$\Phi_0 = \Phi_p \left( 1 + \frac{k_{III}[\text{Ti}^{III}]}{(k_t I_{\text{abs}} \Phi_p)^{1/2}} \right)$	no	$[\text{Ti}^I] = \text{high}$	$\Phi_0$ vs. $1/(I_{\text{abs}})^{1/2}$	slope = $k_{III}/(k_t \Phi_p)^{1/2}$ , intercept = $\Phi_p$	$k_{III}/k_t$ and $\Phi_p$ value	232
$\Phi = \Phi_1 + \frac{k_1 \Phi_1^{1/2} [\text{PtBr}_6^{2-}]}{(k_t I_{\text{abs}})^{1/2}}$	no	$(k_t I_{\text{abs}} \Phi_1)^{1/2} \ll k_1 [\text{PtBr}_6^{2-}]$ , $k_2 [\text{Br}^-] \gg k_1 [\text{PtBr}_6^{2-}]$	$\Phi$ vs. $[\text{PtBr}_6^{2-}]$ , $\Phi$ vs. $(I_{\text{abs}})^{1/2}$	slope = $k_1 (\Phi_1/k_t)^{1/2}$ , intercept = $\Phi_1$ , linear dependence	$k_1/k_t$ and $\Phi_1$ values quadratic termination step	234
$f \text{ CT} = \frac{q}{P[\text{DEP}]} + \frac{1}{P}$	yes	fraction of light $f$ CT absorbed by the ground-state charge-transfer complex must be known	$f$ CT/ $\Phi$ vs. $1/[\text{DEP}]$	slope/intercept	$q/P$ and $P$	230
$\Phi_r = k_{ra} [\text{Ph}_3\text{C}^{\cdot-}]^{1/2} \left( \frac{k_{et}}{(k_d + k_{et}) I_{\text{abs}} k_{rr}} \right)^{1/2}$	no	$k_e \gg k_{ra} [\text{Ph}_3\text{C}^{\cdot-}]$ , $k_c \gg k_{rr} [\text{Ph}_3\text{C}^{\cdot-}]$	$\Phi$ vs. $I_{\text{abs}}$	linear dependence or not	nonchain or chain	235

TABLE IV. Summary of Parameters to be Measured and Information Gained for an Intermolecular Photoelectron-Transfer-Catalyzed Reaction

measured parameter	determination method	information gained
overall quantum yield $\Phi_0$ and primary quantum yield $\Phi_p$	Actinometry	
ratio $k_{III}/k_I$	direct (time-resolved spectroscopy) $\Phi_0$ variation vs. $(I_{\text{abs}})^{-1/2}$ (intercept) $\Phi_0$ variation vs. [absorbing species]/ $(I_{\text{abs}})^{1/2}$ (intercept) $\Phi_0$ variation vs. [reactant] (intercept)	catalytic cycle efficiency, $Y_i$
ratio $k_{III}/k_t$	$\Phi_0^{-1}$ variation vs. [reactant] $^{-1}$	rate-determining exchange
ratio $k_{III}/k_t$	$\Phi_0$ variation vs. $(I_{\text{abs}})^{-1/2}$	chain length

steps of the catalytic cycle, and the type (linear or quadratic) of the termination chain reactions.

It should be emphasized that in organic photoinduced electron transfer such as  $S_{RN}1$  reactions, the chain carrier is an organic ion radical, and quadratic chain-termination reactions are strongly disfavored since this type of intermediate is not known to dismutate. Thus, the surrounding solvent molecules may undergo linear chain-termination reaction with it. As a consequence,  $\Phi_0$  would not depend on  $I_{\text{abs}}$ . Moreover, photoinduced chain reactions triggered by excitation of a ground-state charge-transfer complex differ from those induced by direct excitation. The overall quantum yield of the former depends on the concentration of the substrate, whereas that of the latter may be constant.

### c. Quantum Yield Kinetic Analysis Related to Previous Section

The foregoing quantum yield analysis may be illustrated with respect to some other examples such as the photostimulated reaction of iodobenzene with diethyl phosphite ion,<sup>230</sup> the photoinduced chain exchange of  $\text{PtBr}_6^{2-}$  with  $\text{Br}^-$ ,<sup>234</sup> the photomethylation of the triphenylmethyl anion by dimethyl sulfoxide,<sup>235a</sup> and the photodebromination of 5-bromo-2-methoxy-pyrimidine.<sup>235b</sup> The overall quantum yield equations developed in these papers together with those of Stranks and Yandell are summarized in Table III. The main points on which one can focus to gain information are summarized in Table IV.

If the overall and primary quantum yields are known, then the catalytic cycle efficiency  $Y_i$  may be calculated and the photochemist can answer the basic question: Is my photoelectron-transfer reaction a catalytic one?

A good review on measurements of quantum yields may be found in Vol. 4 of the collection "Creation and Detection of Excited States".<sup>171b</sup>

## II. Photoinduced Electron-Transfer Catalysis. Various Kinds and Relations with Other Processes

### 1. Activation Induced by Electron Transfer

In the preceding sections we have shown that pho-

TABLE V. Examples of Paramagnetic Structural Blocks Highly Prone to Decomposition but of Finite Lifetime

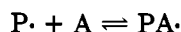
starting <sup>d</sup>	type of activation <sup>a</sup>	structural block	products <sup>b</sup>	ref
<b>1. Neutral</b>				
RSO <sub>2</sub> Cl	+	RSO <sub>2</sub> ·	R· + SO <sub>2</sub> , LA (π)	242
RCO <sub>2</sub> X	-	RCO <sub>2</sub> ·	R· + CO <sub>2</sub> , LA (π)	243
RCOX	+	RCO·	R· + CO, LA (π) LB (σ)	244a
PhN=NSO <sub>2</sub> Ph	+	PhN=N·	Ph· + N <sub>2</sub>	215, 244b
R(CF <sub>2</sub> CF <sub>2</sub> ) <sub>n</sub> CF <sub>3</sub>	+	R(CF <sub>2</sub> CF <sub>2</sub> ) <sub>n</sub> CF <sub>2</sub> ·	RCF <sub>2</sub> CF <sub>2</sub> · + CF <sub>2</sub> =CF <sub>2</sub> , LA (π)	138b
		CH <sub>3</sub> C(=O)CH <sub>2</sub> ·	CH <sub>3</sub> · + O=C=CH <sub>2</sub> , LA (π)	247
	+		Bu <sub>3</sub> Sn· +	248
				249
			t-Bu· + t-BuC≡N	245
				250
		·CH <sub>2</sub> CH <sub>2</sub> Hg <sup>I</sup> CH <sub>3</sub>	Hg <sup>I</sup> CH <sub>3</sub> + CH <sub>2</sub> =CH <sub>2</sub> , LB (π)	251
			CH <sub>3</sub> · +	252
			CH <sub>3</sub> · + (CH <sub>3</sub> ) <sub>3</sub> COP(CH <sub>3</sub> ) <sub>2</sub> , LB (σ)	253
			(CH <sub>3</sub> ) <sub>3</sub> C· + (CH <sub>3</sub> ) <sub>3</sub> P=O, LA (π)?	253
AlH <sub>4</sub> <sup>-</sup>	-	AlH <sub>4</sub> ·	H· + AlH <sub>3</sub> , LA (π)	254
η <sup>5</sup> -(C <sub>5</sub> H <sub>5</sub> )Fe <sup>II</sup> η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	+	η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> Fe <sup>I</sup> η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ·	η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> Fe <sup>I</sup> + C <sub>6</sub> H <sub>6</sub>	255
		Mn(CO) <sub>5</sub> ·	Mn(CO) <sub>4</sub> · + CO, LA (π) LB (σ)	246, 256
		Re(CO) <sub>5</sub> ·	Re(CO) <sub>4</sub> · + CO	246, 257
		η <sup>5</sup> -CpMo(CO) <sub>3</sub> ·	η <sup>5</sup> -CpMo(CO) <sub>2</sub> · + CO <sup>e</sup>	227
		Ni <sup>I</sup> L <sub>3</sub> X·	NiL <sub>2</sub> X· + L	258
NO <sub>3</sub> <sup>-</sup> K <sup>+</sup>	+	NO <sub>3</sub> <sup>·</sup>	NO + O <sub>2</sub>	259
ClO <sub>4</sub> <sup>-</sup>	+	ClO <sub>4</sub> ·	ClO <sub>2</sub> + O <sub>2</sub>	260
<b>2. Positively Charged<sup>c</sup></b>				
(SiMe <sub>3</sub> ) <sub>3</sub> C-C≡C-C(SiMe <sub>3</sub> ) <sub>3</sub>	-	(SiMe <sub>3</sub> ) <sub>3</sub> C-C≡C-C(SiMe <sub>3</sub> ) <sub>3</sub> <sup>+</sup> ·		261
	-		Br· +	262
R <sub>4</sub> Sn	-	R <sub>4</sub> Sn <sup>+</sup> ·	R· + R <sub>3</sub> Sn <sup>+</sup> , LA (π)	132
NFCl <sub>2</sub>	-	NFCl <sub>2</sub> <sup>+</sup> ·	F· + ·NCl <sub>2</sub> , LA (π)	263a
Cr(CO) <sub>6</sub>	-	Cr(CO) <sub>6</sub> <sup>+</sup> ·	Cr(CO) <sub>5</sub> <sup>+</sup> + CO	264, 265
<b>3. Negatively Charged</b>				
RX	-	RX <sup>-</sup> · (see section III2a and for ArSC(S)SAr <sup>-</sup> · see ref 487)		
O-O	-	O-O <sup>-</sup> · (see section III)		
		IOH <sup>-</sup> ·	I· + OH <sup>-</sup> ·	266
		Br <sub>2</sub> <sup>-</sup> ·	Br· + Br <sup>-</sup> ·	267

<sup>a</sup> + reductive activation; - oxidative activation. <sup>b</sup> LA = Lewis acid, LB = Lewis base; followed by the symmetry of the supposed "active" orbital. <sup>c</sup> More examples may be found in ref 268. <sup>d</sup> When nothing in this column, the structural block has not yet been generated by electron-transfer activation. <sup>e</sup> More examples of metal carbonyl in ref 269. <sup>f</sup> The mechanistic chemistry of explosives<sup>259</sup> probably abounds in such examples. Other examples of radical decomposition may be found in ref 263b.

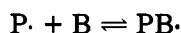
tochemical excitation may induce intermolecular electron transfer. The next question to deal with now is: How does this electron transfer affect the reactivity of the donor and that of the acceptor?

Because of the dispersion of data involving electron-transfer reactions, the various aspects of the activation associated with the act of electron transfer are not well realized despite their considerable importance. In the

first paper of this series<sup>42</sup> we showed that this activation may change reactivity patterns by figures as high as 15 powers of 10 (Table 4 in this reference). This implies that a rich field of investigation could be *the study of symmetry-sensitive reactions (Woodward-Hoffman rules)*<sup>236,237a</sup> in the presence of strong oxidizing or reducing agents or in the presence of redox photosensitizers.<sup>237b</sup> Furthermore, these changes display a remarkable variety: dissociative as well as associative modes operate, and for both modes oxidative and reductive activation are feasible. A particular aspect of dissociative activation is the strong increase of acidity associated with oxidation of groups such as NOH, COOH, CONH<sub>2</sub>, CH<sub>2</sub>OH, etc. Isomerizations and enantiomerizations (section III5) may be viewed according to the cases either as partial or total dissociative activation. Table V gives several kinds of highly dissociative structural units that may originate from a stable fragment by a simple electron transfer. Although these examples are noncatalytic, they illustrate the widespread occurrence of such an activation. This table should also draw attention to a very important *new kind of interaction in mechanistic chemistry: namely, paramagnetic species + generalized acids or bases.*<sup>238-240</sup> The latter was shown to be general in organic chemistry<sup>241</sup> but demands a wider generalization:



A = diamagnetic acid



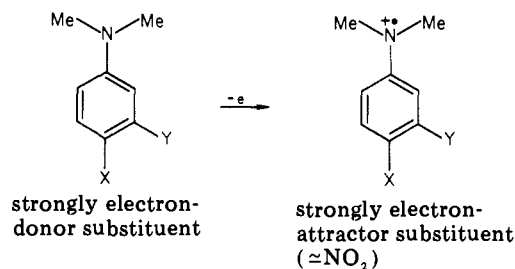
B = diamagnetic base

P = paramagnetic species

We have left aside the case of intramolecular electron-transfer<sup>270</sup> activation, but many photochemical reactions involving charge-transfer transition provide unambiguous examples of such an activation.<sup>271-273</sup> In these cases the activation induced in the structural unit where electron population has been "transferred" by interaction with light is large enough to induce a chemical event before the fast return to the ground state. If a parallel were to be drawn between electron- and proton-transfer catalysis, these examples would compare with intramolecular proton catalysis.<sup>274</sup> Along the same line, some inorganic chemists are not opposed to a formulation of thermal homolysis (S<sub>H</sub>1) as an intramolecular electron transfer.<sup>270</sup> We will not deal with chain reactions induced according to this mode, as they have been excellently reviewed in the past.<sup>8,9</sup> Associative activation may also be either reductive or oxidative, and we shall treat various examples of it later (section III6b).

A remarkable aspect of this activation originates from its *umpolung character*:<sup>277</sup> mixtures of donors or of acceptors (a particular case being the pure product in an inert solvent) may be activated by addition of appropriate oxidizing or reducing reagents.<sup>278</sup> An obvious extension is to activate these mixtures by photochemical excitation; this is an especially valuable trick if a catalytic reaction<sup>42</sup> follows the initial umpolung act.

Far-reaching aspects of this activation are substituent effects umpolung<sup>279</sup> or superenhancement following the act of single electron transfer.



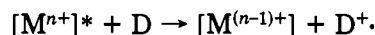
Therefore, substituents usually viewed as having a deactivating effect on a given reaction can be transformed into activating ones by oxidizing or reducing them. It would be interesting to know if good activating substituents could be transformed very temporarily (*hν* excitation) into superactivating ones (e.g., NR<sub>2</sub> → NR<sub>2</sub><sup>•+</sup> or NO<sub>2</sub> → NO<sub>2</sub><sup>•+</sup>) able to induce the apparition of totally new mechanistic pathways and intermediates. This aspect deserves its own review and largely extends beyond the scope of the present paper, but it must be stressed that a related and important consequence of this activation deals with the enhancement of leaving-group abilities by oxidation or reduction. For example, it is usually thought that the generation of vinyl cations<sup>280</sup> demands the presence of a superleaving group such as trifluoromethanesulfonate (triflate) or nonafluorobutanesulfonate (nonaflate). Less usual excellent leaving groups could be obtained by oxidation (intra- or intermolecular) of vinylic substituents provided that the structural environment confers to the oxidation a strong character of localization on Y and/or that Y is stabilized.<sup>281,282</sup>



The photochemical reaction of vinyl iodides,<sup>283a</sup> or of 2-nitrofurans<sup>284</sup> where the intermediacy of vinyl cations has been proposed, could be viewed as the result of such an effect. It follows from this remark that oxidative electron-transfer activation of substituted aromatic compounds may smoothly pass from the associative mode to the dissociative one by a progressive change of substituents. The reductive activation of leaving groups is well documented in section III2a.

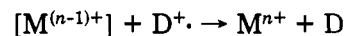
When the relative contributions of vibrational and electronic excitation vs. intrinsic structural reactivity of radical cations<sup>285</sup> and radical anions<sup>286-288</sup> generated in the gas phase have been more cleanly delineated, a batch of other examples of activation induced by electron transfer will appear.

In a recent review Whitten<sup>46</sup> states the basic problem to be surmounted for application of the enhanced redox properties of photoexcited states. While processes such as:



M = metal complex but can be generalized, D = donor

can occur with very high rates and efficiency, they are generally followed by energy-wasting back-reactions:



which also usually occur with high rate and efficiency. Therefore, the overall result is "no net chemical reaction". Much recent work has been devoted to

finding ways to circumvent back reactions (charge separation at solid-aqueous interfaces,<sup>289</sup> micelles,<sup>290</sup> liposomes,<sup>291</sup> microemulsions,<sup>292-294</sup> and polyelectrolytes<sup>295</sup>). This has been done either by reducing the rate of back reactions or by removing rapidly one of the products formed in the primary step. A natural way of removal is obviously very fast reaction different from this wasting energy back reaction. It follows that the very large figures connected with electron-transfer activation (associative or dissociative) lie at the heart of the reactivity induced by photochemically induced electron transfer. Even when very large figures are not sufficient to completely overcome the back reaction, the small amount of created reactive species may trigger a chain reaction<sup>42</sup> and/or appropriate sensitizers can carry on several cycles of reactions leading to an overall chemical transformation.

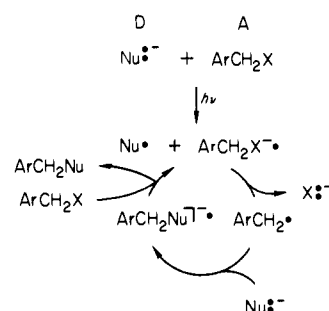
## 2. Various Classes of Photoinduced Electron-Transfer Catalysis and Their Connections with Thermal and Electrochemical Processes

One outstanding fact of electron-transfer catalysis is its actual interdisciplinary character: the classifications are therefore important because they allow comparisons between apparently unconnected fields to be drawn, but they are also somewhat artificial. For this reason we shall not follow a unique classification throughout the review but rather situate it with respect to different already existing classifications. In the present section we shall strongly rely upon the Wrighton<sup>296</sup> approach of photocatalysis, but in section III we shall return to a more chemical classification of reactions: liquid phase, gas phase, solid phase, and inside each of the subsections adopt the classical way of describing mechanistic features.<sup>297</sup> Nevertheless, at the end of section III we shall suggest a classification that we believe is of heuristic value for the design of new catalytic reactions.

The photochemical classification returns to Wrighton's definition<sup>74</sup> of photocatalysis: "Photocatalysis is the photogeneration of a catalyst from a thermally inert precursor such that substrate transformations result which are both catalytic with respect to the number of photons absorbed and with respect to the actual catalyst." From this definition we can recognize three main classes of photoinduced electron transfer catalysis, only two of them being truly photocatalytic.

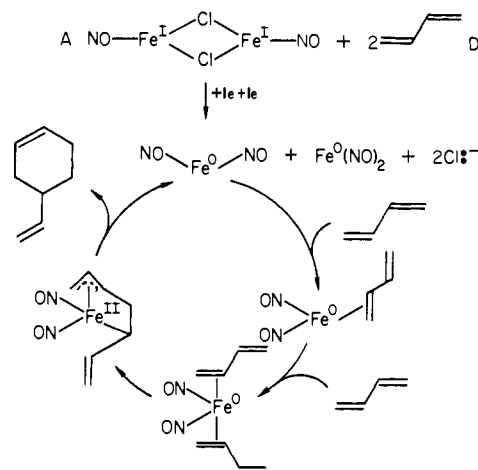
### a. Class I of Photoelectron-Transfer Catalysis (Chain Dominant)

In the first one illustrated by Scheme III<sup>42</sup> the absorption of light induces an electron transfer from the donor to the acceptor at a faster rate<sup>168</sup> than this one would have had if only a thermal excitation had been available for the process. At this point the fact that the electron transfer occurs through a CTC, an exciplex, or from apparently uncorrelated molecules is of no concern for us. The only relevant information is that this electron transfer occurs as an initiating step followed by a chain reaction. To close the chain, light is not required, and for a theoretical chain reaction without termination steps the quantum yield would therefore tend toward infinite values. This class of reaction corresponds to a special case of photocatalysis where

Scheme III<sup>a</sup>

<sup>a</sup> Nu = nucleophile, ArCH<sub>2</sub>X = any aromatic substrate able to accept one electron from Nu under *hν* excitation.

Scheme IV

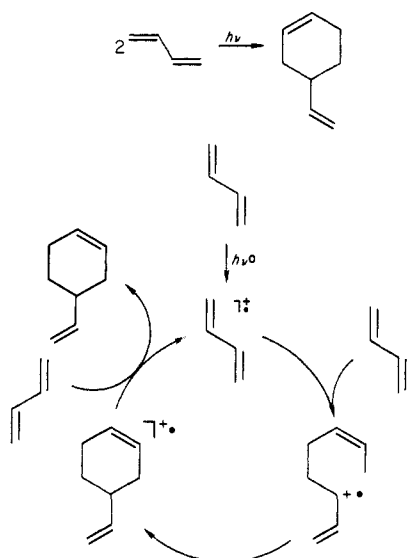


the source of catalyst is the substrate itself. The rate of production of this catalyst may, however, be increased by artificial stimulation (light changing redox relationship in the DA couple or cathode (anode) inducing increased flow of electrons).

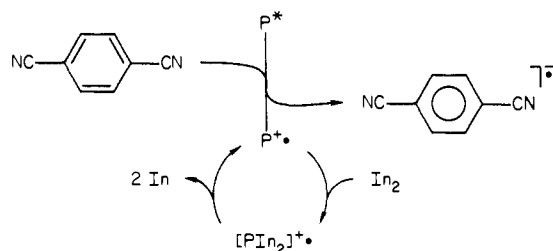
### b. Class II (Catalysis Dominant)

In class II photoelectron-transfer catalysis the role of light is to transform an inert procatalytic substance present in the medium into a catalyst: this catalyst then does its work without further need of photons to carry on the reaction (in the theoretical situation when no termination step occurs). The process is therefore truly photocatalytic: its difference from class I is that the procatalyst is not one of the reagents but rather is an external or a mixture of external agents added in catalytic amounts. This class has been well recognized in electrochemistry;<sup>298-305</sup> for lack of space we shall not treat in this review the photoelectron-transfer generation of acidic or basic catalysts.<sup>307-309</sup>

Let us take an electrochemical example<sup>275,305,310,311</sup> to illustrate class II electron-transfer catalysis and its relations with class I (Scheme IV). In electrochemistry the reduction  $\text{Fe}^{\text{I}} \rightarrow \text{Fe}^{\text{0}}$  is provided by the cathode and consumes only a small amount of faradays per molecule of transformed butadiene because the last step regenerates  $\text{Fe}^{\text{0}}$ . Let us suppose that the photochemical excitation of butadiene transforms it into a reducing reagent (D) strong enough to do the work (reduce A) that the cathode has done in the foregoing experiment; then we would have had a dimerization of butadiene photoinduced by electron-transfer catalysis. This would

Scheme V<sup>a</sup>

<sup>a</sup> Possibly via an exciplex.

Scheme VI<sup>a</sup>

<sup>a</sup> P = phenanthrene, In = indene, In<sub>2</sub> = dimer of the indene.

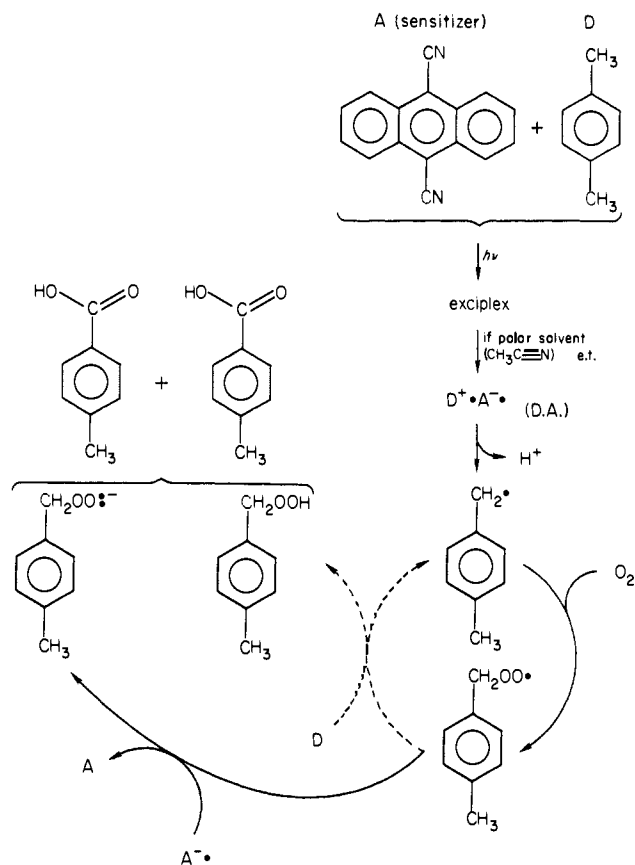
have been a typical class II electron-transfer catalytic process because an external reagent was needed to induce the change in starting mixture of DA, DD, or AA (D = donor, A = acceptor) couple; therefore, inactive DA couples activated by entrainment<sup>314,315</sup> pertain to class II electron-transfer catalysis as do also radical chain reactions initiated by radicals (provided that S<sub>H</sub>2 is viewed as an inner sphere electron transfer). These later cases will not be treated here because most of them are already gathered in classic books on chain reactions.<sup>6-10,317a</sup> It should be realized however that the links between thermal, photochemical, electrochemical, and sonochemical techniques have still to be exploited for obtaining better yields for many of them.

A still more drastic scenario would simply have consisted of the transformation shown in Scheme V. We give these various scenarios to show that when the simple DA interaction does not directly initiate an electron-transfer catalysis of class I, there are still many tricks left to trigger such a kind of catalysis.

The redox photosensitized cleavage of indene dimers using aromatic hydrocarbon-dicyanobenzene system illustrates this class II with a photochemical system (Scheme VI).<sup>312</sup>

### c. Class III (Redox Photosensitization)

An example of the third class of photochemical ETC is met when a photosensitizer in an excited state gives (or takes) an electron to (or from) the substrate and when this electron transfer induces an activation in

Scheme VII<sup>a</sup>

<sup>a</sup> ---- = minor pathway, (D.A.) = dissociative activation.

the substrate. This one, then, chemically evolves (associatively or dissociatively) to the products, via subsequent steps. In one of them the sensitizer regains (or releases) the electron that it had given (or taken) in the initiation step. Therefore, the sensitizer is ready again to do its work of initiating the cyclic set of reactions by another electron transfer. However, to start another set of elementary steps, another photon is needed: therefore, for these cases there will be at least one photon consumed for every molecule of product formed. The recent paper on the photosensitized oxygenation of alkylbenzenes<sup>316</sup> illustrates this in Scheme VII.

Small amounts of sensitizer (1%) suffice to perform the reaction whose mildness of conditions (room temperature) contrasts with those reported for direct free-radical oxidation<sup>317b</sup> or for metal salt catalyzed oxidations.<sup>318,319</sup> Herein lies a general principle of electron-transfer catalysis important for photochemistry: Most of the reactions catalyzed by metal salt complexes and where the initiation step is an electron transfer could be made to work photochemically with catalytic amounts of the appropriate sensitizer. The role of the light is just to transform the sensitizer-reagent couple into a new species whose redox properties match or even challenge those presented by the metal salt complex. The search for the right sensitizer is not always obvious: in the foregoing example rose bengal and methylene blue do not sensitize the reaction. Furthermore, the sensitizer must be able to stand several cycles without decomposition; otherwise, the connotation of catalytic process is lost. In this respect, reactions such as the photooxidation of leucoethyl



TABLE VI. Spectroscopic and Redox Properties of Some Organic Photoexcited Sensitizers<sup>a</sup>

compound	$E_{O-O}$ (M-M*), <sup>a</sup> eV		$E_{1/2}$ <sup>b</sup> (M/M*), <sup>b</sup> V vs. SCE	$E_{1/2}$ (M <sup>+</sup> /M), <sup>b</sup> V, vs. SCE	solvent	pH	$E$ (M*/M <sup>-</sup> ), <sup>c</sup> V		$E$ (M <sup>+</sup> /M*), <sup>c</sup> V	
	S <sub>1</sub>	T <sub>1</sub>					S <sub>1</sub>	T <sub>1</sub>	S <sub>1</sub>	T <sub>1</sub>
acetophenone	3.42	3.20	-1.29		H <sub>2</sub> O	4.65	2.13	1.91		
acetophenone	3.42	3.20	-1.85		CH <sub>3</sub> CN		1.57	1.35		
4-methoxyacetophenone	3.51	3.11	-1.50 (MP)		DMF		2.01	1.61		
anthraquinone		2.71	-0.94	1.21	CH <sub>3</sub> CN			1.77		-1.50
propiophenone		3.23	-1.40		EtOH 20/H <sub>2</sub> O 80	7.5		1.83		
benzaldehyde	3.34	3.12	-1.15		H <sub>2</sub> O	4.65	2.19	1.97		
benzaldehyde	3.34	3.12	-1.35		EtOH	7.6	1.99	1.77		
benzaldehyde	3.34	3.12	-1.93		DMF		1.41	1.19		
benzoic acid	4.42	3.40	-2.17		DMF 95/H <sub>2</sub> O 5		2.25	1.23		
methyl benzoate	4.42	3.41	-2.29		DMF		2.13	1.12		
1-naphthol	3.96	2.54		0.63						-3.33 -1.91
phenol	4.47	3.54		0.63	<i>i</i> -PrOH 50/H <sub>2</sub> O 50					-3.84 -2.91
carbazole	3.68	3.05		1.16	CH <sub>3</sub> CN					-2.52 -1.89
anisole	4.47	3.50		1.76	?					-2.71 -1.74
aniline	4.19	3.32		0.87	CH <sub>3</sub> CN					-3.32 -2.45
pyridine		3.67		2.12	CH <sub>3</sub> CN					-1.55
acenaphthene	3.82	2.57	-2.55	1.25	CH <sub>3</sub> CN		1.27	0.02	-2.57	-1.32
anthracene	3.31	1.82	-1.41	1.09	CH <sub>3</sub> CN		1.90	0.41	-2.22	-0.73
anthracene	3.31	1.82	-1.93		DMF		1.38	-0.11		
9,10-diphenylanthracene	3.16	1.81	-1.94	1.22	CH <sub>3</sub> CN		1.22	-0.13	-1.94	-0.59
benzene	4.77	3.66		2.30	CH <sub>3</sub> CN				-2.47	-1.36
chrysene	3.43	2.45		1.40					-2.03	-1.05
naphthalene	3.99	2.64		1.54	CH <sub>3</sub> CN				-2.45	-1.10
1-methoxynaphthalene	3.87	2.59		1.38	CH <sub>3</sub> CN				-2.49	-1.21
phenanthrene	3.59	2.68		1.50	CH <sub>3</sub> CN				-2.09	-1.18
perylene	2.85	1.52		0.85	CH <sub>3</sub> CN				-2.00	-0.67
pyrene	3.33	2.09		1.16	CH <sub>3</sub> CN				-2.17	-0.93
<i>cis</i> -stilbene	4.11		-2.07		DMF		2.04			
<i>trans</i> -stilbene	4.08		-2.08	1.43	DMF		2.00		-2.65	
toluene	4.60	3.59		2.28	CH <sub>3</sub> CN				-2.32	-1.31
triphenylene	3.62	2.88		1.55	CH <sub>3</sub> CN				-2.07	-1.33
<i>o</i> -xylene	4.55	3.56		1.88	CH <sub>3</sub> CN				-2.67	-1.68
<i>m</i> -xylene	4.55	3.48		1.91	CH <sub>3</sub> CN				-2.64	-1.57
<i>p</i> -xylene	4.51	3.49		1.77					-2.74	-1.72

<sup>a</sup> From ref 323. <sup>b</sup> From Meites, L.; Zuman, P. "CRC Handbook Series in Organic Electrochemistry"; CRC Press: Cleveland, Ohio, Vol. 1, 1976. <sup>c</sup> Calculated from eq 1 and 2 in section I. <sup>d</sup> For further examples, see ref 325a (fluorescein in its dianionic form) and ref 276 (review on photosensitization).

TABLE VII. Spectroscopic and Redox Properties of Some Inorganic Photoexcited Sensitizers

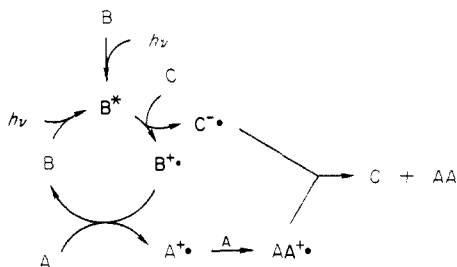
complex <sup>a</sup>	$E_{O-O}$ (M-M*), eV	$E_{1/2}$ <sup>b</sup> (M/M*), <sup>b</sup> V	$E_{1/2}$ <sup>b</sup> (M <sup>+</sup> /M), <sup>b</sup> V	$E$ (M*/M <sup>-</sup> ), <sup>c</sup> V	$E$ (M <sup>+</sup> /M*), <sup>c</sup> V
Cr(bpy) <sub>3</sub> <sup>3+</sup>	1.71	-0.25 <sup>d</sup>	>1.6	1.46	>-0.1
Cr(phen) <sub>3</sub> <sup>3+</sup>	1.71	-0.25 <sup>d</sup>		1.46	
Ir(bpy) <sub>3</sub> <sup>3+</sup>	2.81	-0.76 <sup>e</sup>	2.17 <sup>e</sup>	2.05	-0.64
Ir(bpy) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	2.62	-1.03 <sup>e</sup>	2.11 <sup>e</sup>	1.59	-0.51
Ir(phen) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	2.67	-1.12 <sup>f</sup>		1.55	
Os(bpy) <sub>3</sub> <sup>2+</sup>	1.85	-1.18	0.83	0.67	-1.02
Os(4,4'-Me <sub>2</sub> bpy) <sub>3</sub> <sup>2+</sup>	1.78	-1.31	0.72	0.50	-1.06
Os(phen) <sub>3</sub> <sup>2+</sup>	1.78	-1.21	0.82	0.57	-0.96
Os(5-Clphen) <sub>3</sub> <sup>2+</sup>	1.78	-1.09	0.93	0.69	-0.85
Os(5-Mephen) <sub>3</sub> <sup>2+</sup>	1.78	-1.24	0.79	0.54	-0.99
Ru(bpy) <sub>3</sub> <sup>2+</sup>	2.12	-1.28 <sup>e</sup>	1.26	0.84	-0.86
Ru(4,4'-Me <sub>2</sub> bpy) <sub>3</sub> <sup>2+</sup>	2.04	-1.37	1.10	0.67	-0.94
Ru(4,4'-Ph <sub>2</sub> bpy) <sub>3</sub> <sup>2+</sup>	2.02		1.17		-0.85
Ru(bpy) <sub>2</sub> (CN) <sub>2</sub>	2.15	-1.30 <sup>g</sup>	1.09 <sup>g</sup>	0.61	-1.30
Ru(phen) <sub>3</sub> <sup>2+</sup>	2.18	-1.36 <sup>e</sup>	1.26	0.82	-0.92
Ru(phen) <sub>2</sub> (CN) <sub>2</sub>	2.19	1.79 <sup>d</sup>	1.12 <sup>d</sup>	1.09	-1.07
Rh <sub>2</sub> (br) <sub>4</sub> <sup>2+</sup> <sup>h</sup>	1.7				-0.56
br = 1,3-diisocyanopropane					(experimental)
(Re <sub>2</sub> Cl <sub>8</sub> ) <sup>2-</sup> <sup>i</sup>	1.75		<1.97	1.14	<-0.22
Fe(bipy) <sub>3</sub> <sup>3+</sup> <sup>j</sup>	0.9	-1.26	1.05	-0.4	≈0.1
Rh(phen) <sub>3</sub> <sup>3+</sup> <sup>j</sup>	2.8	-0.7	>1.5	2.1	>-1.3

<sup>a</sup> Room temperature, aqueous solution, unless otherwise noted. <sup>b</sup>  $E_{1/2}$  vs. NHE. <sup>c</sup> Calculated from eq 1 and 2 in section I. <sup>d</sup> The value vs. SCE was corrected to NHE by adding 0.24 V. <sup>e</sup> The value in CH<sub>3</sub>CN vs. SCE was corrected to H<sub>2</sub>O vs. NHE by adding 0.07 V. <sup>f</sup> In DMF vs. SCE. <sup>g</sup> In DMF vs. NHE. <sup>h</sup> From Milder, S. J.; Goldbeck, R. A.; Klinger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* 1980, 102, 6761. <sup>i</sup> From Nocera, D. G.; Gray, H. B. *Ibid.* 1981, 103, 7349. <sup>j</sup> From ref 22b.

crystal violet (tris(*p*-(diethylamino)phenyl)methane)<sup>320</sup> in the presence of CCl<sub>4</sub> will not be dealt with in this

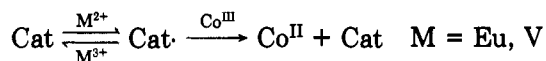
review. Tables VI and VII gather some typical redox sensitizers and their redox potentials; they could help

Scheme VIII



in searching for the right sensitizer but are not at all exhaustive because of the lack of data on the redox potentials. Many practical examples may be found in ref 76, 321, and 322a, and Albini recently published a review<sup>276</sup> on organic photosensitization. The simplest foregoing systems (D + A + photosensitizer) may become more elaborated as shown by Scheme VIII. *N*-vinylcarbazole (A) dimerizes when irradiated in acetone in the presence of perylene (B) and dicyanobenzene (C).<sup>283b</sup> This reaction may be explained by the scheme.

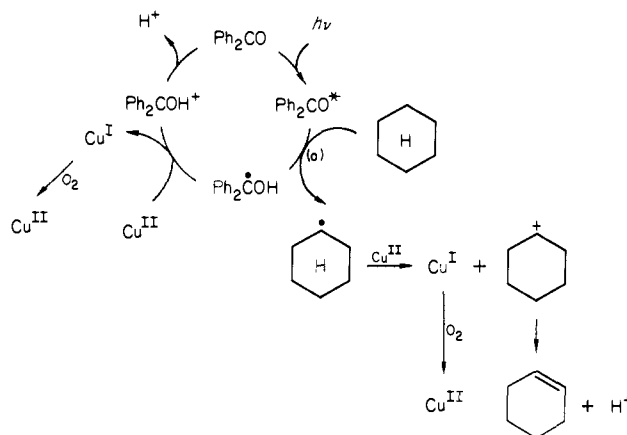
This third class of photoelectron-transfer catalysis could be connected with electrocatalysis.<sup>322b-d,325b-329,483,963</sup> In this process, a product (called mediator) is used to accept an electron from a cathode and transport it to a substrate which cannot be directly reduced on the cathode because of its high overpotential. Albini's review<sup>276</sup> clearly stresses, however, the relations between the photochemical and electrochemical experiments. The differences originate from the fact that electrochemistry takes place at a concentrated long-lived surface (electrode); therefore, the presence of excess electrons or holes is often the rule, whereas photochemistry may be viewed as a chemistry taking place on a highly diluted and short-lived microelectrode. This third class of photoelectron-transfer catalysis presents some analogies with the thermally catalyzed outer-sphere reduction of Co<sup>III</sup> thoroughly studied by Gould's group:<sup>324</sup>



This case of photochemical catalysis may coexist with the preceding one.<sup>63</sup> in Scheme II, if the channel christened "minor pathway" had been strengthened by any means, the cycle would have needed less photon to continue its work. It would be worthwhile to check if some of the metal-sensitized photoreactions<sup>331a</sup> involve electron-transfer processes.

Some authors, aiming to give a consistent interdisciplinary treatment of electron-transfer mechanisms (see section I5c) propose to class S<sub>H</sub>2 process as inner-sphere electron-transfer mechanisms. In this representation (Scheme IX), photosensitization by catalytic amounts of benzophenone<sup>330,331b</sup> becomes inner-sphere class III examples of photoelectron catalysis. When a very long chain follows the initiation act<sup>333,334</sup> there is even no need for regeneration of the sensitizer, and the border between class II and class III becomes rather fuzzy. It is sometimes difficult to distinguish between an inner-sphere (H transfer) and an outer-sphere electron transfer; this fundamental question has been dis-

Scheme IX



<sup>a</sup> For the *n* orbital initiated photochemistry of ketones, see ref 332.

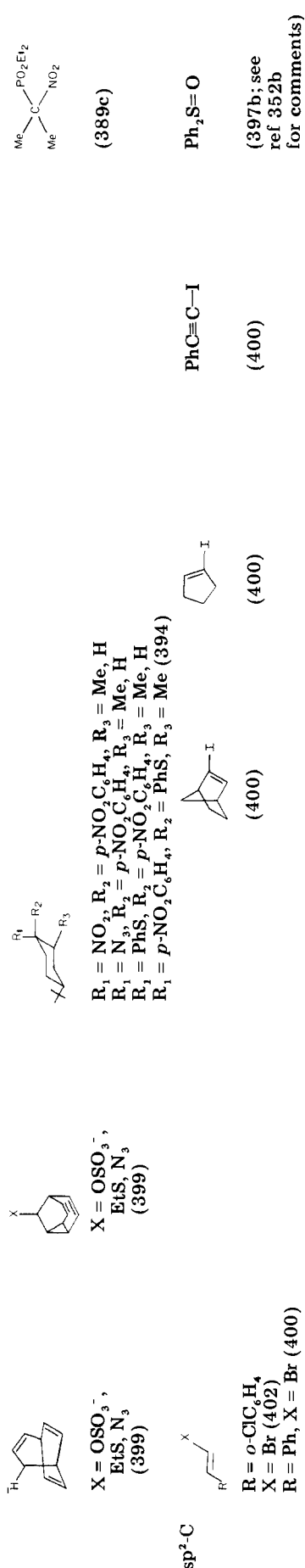
cussed in section I5c, and it is worthwhile mentioning the efforts by Roth<sup>144</sup> and Wong<sup>142</sup> to attack this problem through chemically induced dynamic electron polarization, flash photolysis electron spin resonance spectroscopy, and chemically induced nuclear polarization.

T. J. Meyer classified photoredox catalytic reactions according to an important operational principle: he distinguishes photochemically catalyzed exoergonic reactions where the photocatalyst catalyzes a spontaneous reaction ( $\Delta G_{\text{reaction}} < 0$ ) from photochemically catalyzed endoergonic reactions where light is used to drive the reaction into an "antithermodynamic" direction.<sup>335</sup> This distinction is of fundamental importance for the utilization of solar energy.<sup>336</sup> Class III photoelectron-transfer catalysis seems particularly adapted to this aim in contrast with most known class I examples where the catalyzed reactions are exoergonic. The foregoing considerations show that it would be easy to overclassify the facts. Along the same line, we do not develop here the subclassification<sup>43</sup> based on the mechanistic characteristics (inner-sphere, outer-sphere, etc.) of the main electron transfers involved in photoelectron-transfer catalysis (2 for class I and II, 1 for class III) because they are, for the moment, too elaborated for the stage of development of electron transfer in photochemistry.

One important point must be stressed before beginning the section dealing with specific examples of photostimulated and induced electron-transfer catalysis. In many cases the reaction actually studied is a thermal or an electrochemical one; the reader could therefore feel that many examples that we give are irrelevant to the photochemical focus indicated in the title of the present review. This feeling must be fought against; the main aim of this review is to convince that many more catalytic systems may be designed provided that the connections between thermal ETC without external catalysts, thermal ETC with added catalysts, photochemical ETC with and without sensitizers, electrochemical ETC with and without mediators and, in a more prospective sense, sonochemical ETC are clarified. A first step in this direction is obviously to gather in the same text the relevant widely dispersed information.

TABLE VIII. Variety of  $sp^3$ -C,  $sp^2$ -C (Nonaromatic) Structures Where the  $S_{RN}1$  (Radical Chain Substitution) Mechanism Has Been Studied<sup>a</sup>

$sp^3$ -C						
para X = Cl (345-347) X = $^+NMe_3$ , OTs, Br (306, 348)	para X = Cl (350, 351) X = $NO_2$ (353) X = $SO_2$ , Ph, CN (354a)	R = Me, <i>i</i> -Pr, <i>t</i> -Bu (356, 357)	para X = Y = Cl (359, 360) X = Br, Y = Br, Cl (361) X = Y = Br (362)	X = Cl, $NO_2$ (363, 364)	X = $NO_2$ , Cl (365)	(366)
ortho X = Cl (349)	meta X = Cl, $NO_2$ (358)		meta X = Y = Br (362)			
meta X = Cl, only $S_{N2}$ (347)	no $NO_2$ X = $NO_2$ (354b)					
no $NO_2$ (352a)						
				$R_3CNO_2$		
(367)	(365)	(369)	(370)	$R = Me$ (364, 371, 372)	X = Cl (373a, 375-378, 389) X = Br (379, 380, 389) X = $NO_2$ (382, 389) X = CN (383) X = I (384, 389b)	$R_1 = R_2 = Me$ , X = Cl $R_1 = Me$ , $R_2 = Et$ , X = Cl, <i>p</i> -Ts $R_1, R_2 = (CH_2)_4$ , X = Cl, <i>p</i> -Ts (381)
				several R (354c, 355)		
				$CCl_4$ and polyhaloalkanes		
X = Me (380, 381, 385) X = H (380)	(386, 387)	(388)	X = SR (389a,c) X = $N_3$ (389d)	see section III1c2 (390, 391, <sup>a</sup> 881c, 965)	X = Br (388) X = CO <sub>2</sub> Et (392b) X = COR, CN, $NO_2$ (392a) X = C(CH <sub>3</sub> ) <sub>2</sub> CN (363, 395)	X = Cl (396, 398) X = OAc (397a)



<sup>a</sup> Numbers in parentheses are references. <sup>b</sup> Nonchain electron-transfer substitutions have been reported,<sup>150, 309d, 393</sup> their borders with chain processes remain to be delineated.

### III. Examples of Photoelectron-Transfer Catalysis in Solution

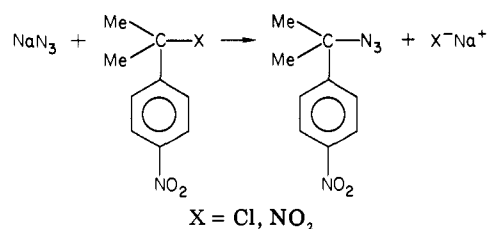
#### 1. Reductively Activated Nucleophilic Substitutions

##### a. Substitutions with a Central Carbon in the Electrophilic Substrate<sup>337</sup>

The first actually identified reaction submitted to photoelectron-transfer catalysis is the nucleophilic attack of *p*-nitrobenzyl bromide by a polarizable nucleophile. It has been used as an example to introduce the scheme of photoinduced electron-transfer catalysis (section II2a). Tables VIII–X give an idea of the types of acceptors concerned with this kind of substitution. These tables are not exhaustive; readers interested by the following specific aspects should consult the relevant papers: theoretical treatments on  $\text{sp}^3\text{-C}$ ,<sup>338</sup>  $\text{sp}^2\text{-C}$ ,<sup>339</sup> new synthetic possibilities for  $\text{sp}^3\text{-C}$  electrophilic centers,<sup>50</sup> mechanistic aspects of  $\text{sp}^2\text{-C}$  electrophilic centers,<sup>61,62,340</sup> synthetic aromatic applications,<sup>52</sup> synthetic heteroaromatic substitution,<sup>54,341a</sup> role of nitro group in relation with,<sup>342–344</sup> electrochemical<sup>63</sup> aspects of, stereochemistry of,<sup>341b</sup> regiochemistry of,<sup>352b,368</sup> steric effects,<sup>368</sup> fragmentation of intermediates.<sup>373b</sup> The purpose of the table is to illustrate the wide scope of this reaction. We must, however, stress the point that donors suitable for a given acceptor *do not necessarily* react with the other acceptors gathered in the tables via an  $\text{S}_{\text{RN}}1$  mechanism. A clear example is that of nitronate anions and anions of  $\beta$ -dicarbonyl compounds, which react via chain substitution mechanisms with many of the substrates included in Table VIII but do not react by  $\text{S}_{\text{RN}}1$  mechanism with substrates of Table IX.

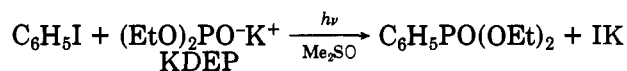
In view of the importance of this new mechanism, it is noteworthy that such a small amount of fundamental photochemical work has been performed on it. There are only two fundamental studies dealing with the measurements of quantum yields for  $\text{S}_{\text{RN}}1$  on  $\text{sp}^3\text{-C}$  and  $\text{sp}^2\text{-C}$ , respectively, and three excellent reports on pulse radiolysis,<sup>342–344</sup> but no flash photolysis or any other kind of studies allowing the determination of the active electronic excited states involved in the initiation step.

Wade and Kornblum<sup>228</sup> measured the quantum yields for the reaction:



and found values as high as 6000 for the leaving group Cl.

Hoz and Bunnett<sup>405d</sup> performed a detailed investigation of the reaction between iodobenzene and diethyl phosphite ion to form diethyl phenylphosphonate:



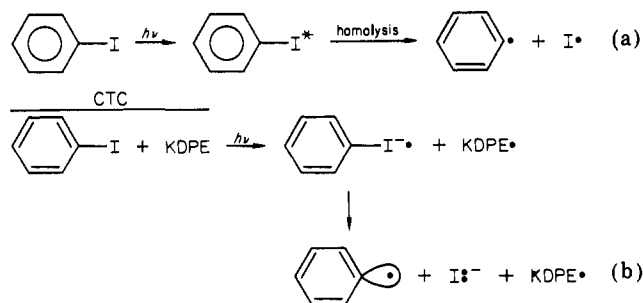
Because of its high methodological interest this work

TABLE IX. Variety of Aromatic Substrates Where the  $S_{RN}1$  Mechanism Has Been Studied<sup>c</sup>

X = (401, 403, 404, 405a-h, 406, 411a, 413-417, 421-424, 426, 461) X = Br (401, 404a, 405e-h, 411a, 413-416, 422-424, 451) X = F (401, 405e,g,h, 414, 416, 422, 429c,d) X = Cl (401, 404a,b, 411a, 413-416, 422, 428, 429c,d) X = SPh (405e, g,h, 422) X = OPO(OEt) <sub>2</sub> (405c,e, 414) X = SePH (401, 422) X = N <sup>+</sup> Me (401, 405g,h, 414, 422) X = N <sup>+</sup> =N (427, 410) X = OPh (401) X = CH <sub>2</sub> CN (416)	ortho-ortho' sterically hindered (429a-c)	X = Cl, Y = NRCOCH <sub>2</sub> R X = Cl, Y = NH <sub>2</sub> (430-432) X = OMe, Y = CH = NPh (433) X = I, Y = NH <sub>2</sub> (407, 409) X = Y = Br (408) X = I, Y = OMe (421, 436a) X = I, Y = Cl, Br (437)	X = Br, Y = I (405a, 417, 441-443) X = Br, Y = CH = CHAr <sup>b</sup> (444) X = Cl, Y = I (405a, 421, 441) X = N <sub>2</sub> <sup>+</sup> , Y = NO <sub>2</sub> (445) X = I, Y = MeO (411, 421) X = I, Y = F (405a, 421) X = I, Y = CF <sub>3</sub> (405a, 421) X = I, Y = I (405a)	X = Cl, Y = I (441) X = Br, Y = OMe (405e, 411a) X = N <sup>+</sup> Me <sub>3</sub> , Y = OMe (405e) X = Br, Y = Cl (404b) X = I, Y = MeO (405f, 411a, 419, 421) X = I, Y = PhO (421) X = I, Y = I (405a, 421) X = Br, Cl, Y = CH <sub>3</sub> CO (411a, 438-440) X = I, Br, Y = CN (439) X = Cl, Br, I, Y = CN (440, 446) X = I, Y = F (405f) X = Y = Cl X = Y = Br X = Br, Y = I (434)	X = Cl, I (447, 448) X = Br, dihalo (406, 449, 450) X = Cl (1- or 2-) (418, 428, 439, 446, 451) X = 1-Br (406, 418, 446) X = 1-I (405a, 421, 438) X = 4-Br (406, 439, 446)	X = Cl (428, 451, 452)
X = Br (428, 449, 456) X = Cl, Br, I (446)	(421a)	(400)	(436b)	(421b)		

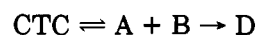
<sup>a</sup> When the other substituents are inactive (alkyl, etc) they are not counted as substituents. <sup>b</sup> Ar = *m*-HOC<sub>6</sub>H<sub>4</sub>. <sup>c</sup> Numbers in parentheses are references. Aromatic substrates may be involved in non-chain electron-transfer mechanisms (see, for example, the oxidative addition of aryl halides to Ni<sup>0</sup> complexes.<sup>258</sup>

should be consulted by people interested in the mechanistic uses of quantum yields. There is a restriction, however, to this statement because it seems that some termination steps evidenced by electrochemistry<sup>478</sup> were not identified by this photochemical study. One point deserves further mention: this quantitative study of quantum yields did not allow an unambiguous choice between the equations a and b:

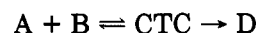


Electrochemical results on the  $\bar{E}CE$  scheme<sup>479-482</sup> reported by J. M. Saveant's group<sup>83</sup> prove that equation

b is a very reasonable one. They do not, however, sweep away equation a. Examples gathered in Table XI show that reductive dissociative activation covers a broad range of values. On the other hand, the question "Are CTC evidenced in a reaction medium innocent bystanders:



or efficient actors:



in the chemical transformation?" has not yet received a definite answer (ref 39a, 152, 501-508, 709, 710, 967). Table XII summarizes some of the leading references treating this problem. Recent discussions of this topic may be found in ref 509. The widespread occurrence of photochemical homolysis and the recent report<sup>525</sup> that low energy electrons are 10<sup>4</sup> times more effective for fragmentation of chlorofluoromethanes than are photons should lead to more experimental work on this important question. Even when this fundamental question has been answered, it will still remain to be

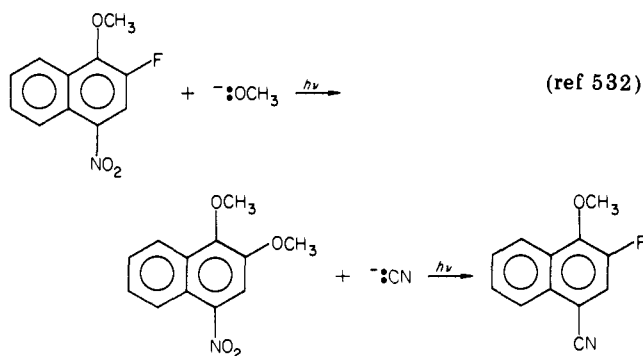
TABLE X. Variety of Heteroaromatic Structures Where the  $S_{RN}1$  Mechanism Has Been Studied<sup>a</sup>

X = Cl (406, 451) X = Br (410, 455)	(455, 457)	(458)	X = Cl (439, 440, 453, 454, 459a-c, 465) X = I (425, 440) X = Br (440)	(463)	(457, 464)	(467)
R = Ph, <i>t</i> -Bu, X = Cl, Br (469)	X = I (468) X = Br (471) X = CH <sub>2</sub> COCH <sub>3</sub> (412a)	(470-472)	(473-475)	X = F, Cl, Br, I (476)		
X = Cl, R = R' = H X = OMe, R = OMe, R' = Cl (412b, 466)	(466)	X = I (420) X = Cl (406, 420)	(435a)	(435a)		

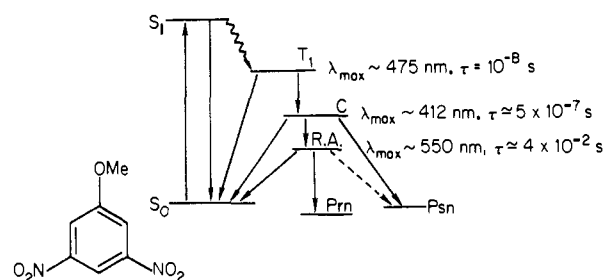
<sup>a</sup> The  $S_{RN}1$  mechanism also plays a role in heterocyclizations,<sup>788</sup> yielding indoles and derivatives,<sup>407,409</sup> isoquinolones,<sup>460</sup> and, possibly, thiadiazoles (mechanism being investigated).<sup>435b</sup> Numbers in parentheses are references. Non-chain electron-transfer mechanism is described for pyridinium salts.<sup>150</sup>

found whether the dissociation of the bond following the electron transfer occurs in the excited state or in the ground state (Peyerhimmhoff<sup>6526</sup> has indeed performed calculations that suggest that for some C-X bonds the radical anion is more dissociative in the ground state than in the excited state).

Other types of aromatic substitutions have been shown to be photostimulated. Many examples may be found in the reviews on photosubstitutions in aromatic compounds:<sup>284,527-531</sup>



This kind of photosubstitution seems to better develop with aromatic compounds where a NO<sub>2</sub> substituent is present. The leaving group ability obeys the following pattern of decreasing reactivity: F = Cl > Br > I. These substitutions have been found to work on heteroaromatics such as bromopyridine.<sup>533</sup> It is therefore natural to wonder if any overlapping exists between some of these substitutions and the photostimulated  $S_{RN}1$  processes. Many of them indeed involve the attack of a nucleophile on a photoexcited substrate, and Cornelisse-Havinga's group has performed remarkable flash photolysis experiments that are lacking the  $S_{RN}1$

Scheme X<sup>a</sup>

<sup>a</sup> C = complex between T<sub>1</sub> and the nucleophile (Meisenheimer? Exciplex?). RA = radical anion (ESR evidence), Prn = reduction products (reaction between the radical anion, and any surrounding H<sup>+</sup> donor), Psn = substitution product (of the OMe group), (---) channel not evidenced on this substrate, would correspond to an  $S_{RN}1$  (see text).

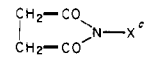
processes. Let us select two of their most relevant contributions related to the problem of overlapping between  $S_{RN}1$  and these kinds of processes.

Based on kinetic and flash photolytic evidences (nanosecond pulses), Scheme X was proposed for photohydrolysis of 3,5-dinitroanisole in alkaline medium.<sup>534</sup>

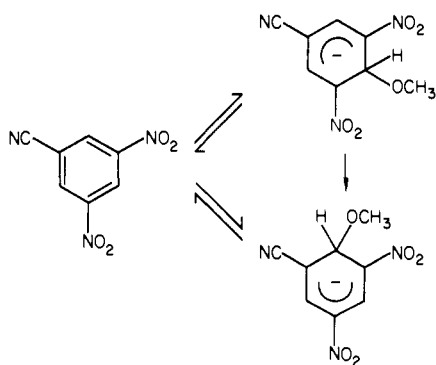
So, provided that intersystem crossing occurs, one can reach photoexcited states of considerable lifetime (RA  $\approx 4 \times 10^{-2}$  s). The long lifetime of the radical anion may be understood in light of Todres' results.<sup>535-537</sup> This author has indeed shown that when the NO<sub>2</sub> group accepts one electron it is transformed into a new kind of substituent whose Hammett  $\sigma$  values could challenge that of good electron-releasing groups (MeO, NH<sub>2</sub>). Therefore, the substrate becomes "inert" toward substitution (this inertness disappearing when no NO<sub>2</sub> substituent is present). This does not tell us if fast



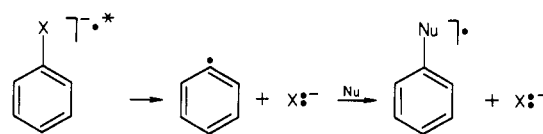
TABLE XI. Some Data Related to the Stability of C-X<sup>-</sup> Species

radical anion	technique	data	solvent	ref
<i>p</i> -nitrobenzyl chloride	pulse radiolysis	$4 \times 10^3$ <sup>a</sup>	<i>t</i> -BuOH	342 <sup>f</sup>
<i>o</i> -nitrobenzyl chloride	pulse radiolysis	$10^4$ <sup>a</sup>	<i>t</i> -BuOH	342 <sup>f</sup>
<i>m</i> -nitrobenzyl chloride	pulse radiolysis	$< 5$ <sup>a</sup>	<i>t</i> -BuOH	342 <sup>f</sup>
<i>p</i> -cyanobenzyl bromide	pulse radiolysis	$6 \times 10^7$ <sup>a</sup>	H <sub>2</sub> O	344
2-chloroquinoline	electrochemistry	$6 \times 10^5$ <sup>a</sup>	DMF	484
9-chloroanthracene	electrochemistry	$1.5 \times 10^{12}$ <sup>a</sup>	Me <sub>2</sub> SO	484, 500
9,10-dichloroanthracene	electrochemistry	$15.8$ <sup>a</sup>	N,N-dimethylformamide	500
		$3 \times 10^5$ <sup>a</sup>	Me <sub>2</sub> SO	484
9-bromoanthracene	electrochemistry	$2.6 \times 10^5$ <sup>a</sup>	CH <sub>3</sub> CN	446
		$2.5 \times 10^5$ <sup>a</sup>	DMF	500
9-iodoanthracene	deuterium incorporation experiments	$1.5 \times 10^5$ <sup>a</sup>	CH <sub>3</sub> CN	446
		$7 \times 10^5$ <sup>a</sup>	Me <sub>2</sub> SO	446
1-chloronaphthalene	electrochemistry	$5 \times 10^7$ <sup>a</sup>	Me <sub>2</sub> SO	484
1-bromonaphthalene	electrochemistry	$3 \times 10^8$ <sup>a</sup>	Me <sub>2</sub> SO	484
1-iodonaphthalene	deuterium incorporation experiments	$6 \times 10^8$ <sup>a</sup>	Me <sub>2</sub> SO	446
4-chlorobenzonitrile	electrochemistry	$5 \times 10^8$ <sup>a</sup>	CH <sub>3</sub> CN	484, 495
4-bromobenzonitrile	deuterium incorporation experiments	$7 \times 10^{10}$ <sup>a</sup>	CH <sub>3</sub> CN	446, 495
4-iodobenzonitrile	deuterium incorporation experiments	$5 \times 10^{10}$	CH <sub>3</sub> CN	446
4-(4-chlorostyryl)pyridine	electrochemistry	half-life 5 s, 252 K	DMF	485, 486
4-(3-chlorostyryl)pyridine	electrochemistry	half-life 10 s, 296 K	DMF	485, 486
RX <sup>b</sup>	ESR in matrix $\approx 77$ K	not observed; possibly charge-transfer adduct R·IX <sup>-</sup>	H <sub>2</sub> O glass	268
			CH <sub>3</sub> OH glass	268
			MeTHF glass	268
	ESR in matrix - 77 K	observed as a $\sigma^*$ anion radical	single crystal or powder samples	488
BrCN		observed as a $\sigma^*$ anion radical	single crystal or powder samples	489
PhC≡CI		observed as a $\sigma^*$ anion radical	CH <sub>3</sub> OH glass	490
CF <sub>3</sub> X (X = Cl, Br, I)	ESR in matrix	observed as a $\sigma^*$ radical anion	matrix of tetramethyl silane	491
	molecular beam studies	transient radical ion	gas phase	492
RSSR <sup>d</sup>	ESR in matrix	observed as a $\sigma^*$ radical anion	matrix	268
(CO) <sub>5</sub> MnMn(CO) <sub>5</sub>	ESR in matrix	observed as a $\sigma^*$ radical anion	2-MeTHF	493a
(MeO) <sub>2</sub> P(S)Br	ESR in matrix	observed as a $\sigma^*$ radical anion	matrix	493b
PhI	ESR in matrix			268
PhCl		not observed		268
<i>p</i> -PhCOC <sub>6</sub> H <sub>4</sub> Br		not observed		
CH <sub>3</sub> Br	ESR in matrix	radical anion not observed; charge transfer between Br <sup>-</sup> and CH <sub>3</sub> ·	matrix of CH <sub>3</sub> CN	499
<i>o</i> - and <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> X <sup>e</sup>	cryoelectrochemistry	relative rates of decomposition for radical anion path: <i>o</i> -I > <i>o</i> -Br >> <i>p</i> -I > <i>m</i> -I (500:122:1:0.34)	DMF	496-498

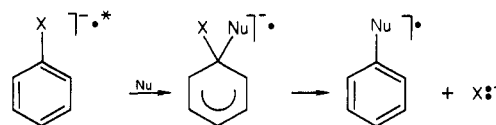
<sup>a</sup> K, s<sup>-1</sup> at 25 °C. <sup>b</sup> Any kind of alkyl group, X = F, Cl, Br, I. <sup>c</sup> X = Cl, Br, I. <sup>d</sup> Reversible dissociation to RS<sup>·</sup> + RS<sup>-</sup>. <sup>e</sup> Reversible dissociation to NO<sub>2</sub>Ph<sup>·</sup> + I<sup>-</sup> except for *o*-bromonitrobenzene. <sup>f</sup> The most thorough studies in solution originate from this group (see also ref 343).



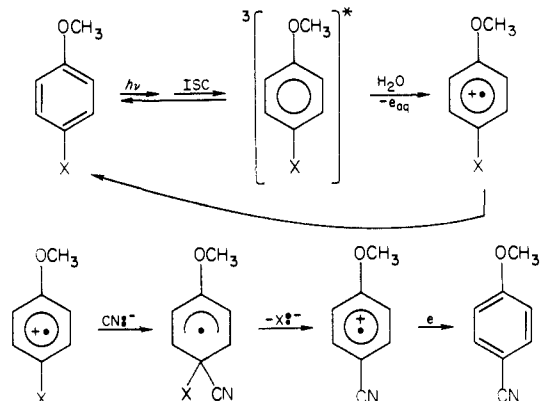
equilibration comparable to that found in thermal<sup>1538</sup> reactions has time to settle, but it suggests that with appropriate substrates<sup>53</sup> it could be possible to check if in the initiation step the S<sub>RN</sub>1 is actually monomolecular (i.e., → in the Scheme X):



or if it possesses an S<sub>RN</sub>2 character:

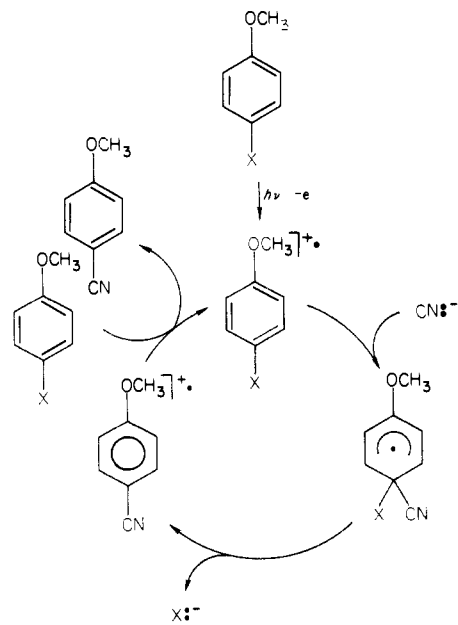


The second contribution more directly connects "normal" photosubstitution and S<sub>RN</sub>1 processes. It originates from the nucleophilic photosubstitution at electron-rich aromatic systems in solvents such as water. Cornelisse<sup>539</sup> proposed the following:



In a typical run, 1.45 mmol of substrate and 50 mmol of cyanide ion were irradiated 3 h in an aqueous solution, and 63% of the starting material was converted into products. Noteworthy is the fact that no oxidant is present in this medium; the normal solution would even be considered as a mildly reducing one. Nevertheless, electronic excitation transforms local parts of this macroscopically reducing solution into a highly oxidizing medium. This illustrates again the very remarkable incidence of electronic absorption on the redox properties of a substrate. The careful study of quantum yield evolution vs. the concentration of chloroanisole brings crucial information for the understanding of the partial overlap that could link "normal" photosubstitution and photostimulation  $S_{RN}1$  processes. At higher concentrations in aromatic substrate, the quantum yield becomes greater than 1. The authors explain this observation by Scheme XI. This is clearly an ETC process,<sup>42</sup> and we reach a conclusion that we already proposed in a paper dealing with DAISSET applied to organometallic substrates: *there is a continuum<sup>43</sup> of situations between the so-called photostimulated  $S_{RN}1$  process and the "normal" photosubstitution reactions.* The quantitative study of borderline cases would be instructive in that it could teach us the successive patterns of reactivity associated with the development of a chain process. Other information that

Scheme XI<sup>a</sup>

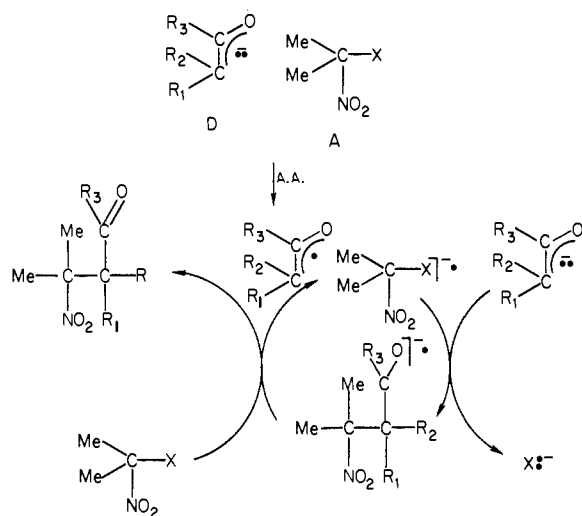


<sup>a</sup> X = Cl.

TABLE XII. "Direct" Photochemical Homolysis vs. "Indirect" (e.g., via CTC Complex<sup>510,511</sup> or Photochemically Induced Electron Transfer)

reaction	mechanism proposed	value of $K^a$ in the CTC DA interaction	$\phi$ homolysis for RX	ref
$\text{Ph} \xrightarrow{h\nu} \text{Ph}^1\text{I} + \text{I}_2$	lowest excited singlet of $\text{PhI}^*$ → $\text{Ph} \cdot + \text{I} \cdot$	not determined (overlap with benzene bands)	0.39 (254 nm)	512-514
$\text{Ph} + {}^{131}\text{I} \rightarrow \text{Ph}^{\cdot 131}\text{I} + {}^{131}\text{I}$			0.30 (334 nm)	
$\text{CTC not active in the radioiodine exchange}$			0.22 (365 nm)	
$\text{I}_2 \xrightarrow{h\nu} 2 \text{I} \cdot$			0.04 in deaerated solutions <sup>e</sup>	
$\text{R}_4\text{Sn} + \text{I} \cdot \rightarrow \text{CTC}$		R = Me, 0.06 M <sup>-1</sup> , CCl <sub>4</sub> R = Et, 3.6 M <sup>-1</sup> , CCl <sub>4</sub>	1 <sup>f</sup>	516, 517
$\text{R}_4\text{SnI} \rightarrow \text{products}$		R = <i>i</i> -Pr, 4.9 M <sup>-1</sup> , CCl <sub>4</sub>		
$\text{CTC not active in the overall reaction}$				
$\text{Naphth-Cl} \xrightarrow{h\nu} \text{Naphth-Cl}^*$		exciplex	$2 \times 10^{-3}$	519
$\text{Naphth-Cl}^* \xrightarrow{\text{D}} \text{exciplex}$		$\lambda_{\text{max}} = 435 \text{ nm}$		
$\text{exciplex} \rightarrow \text{Naphth} \cdot + \text{Cl} \cdot$				
$\text{active exciplex}$		no value given in the original report		520
$\text{PhBr} + \text{Cl}_2 \rightleftharpoons \text{CTC}$				
$\text{PhBr}^{\cdot+} + \text{Cl}_2^{\cdot-} \rightarrow \text{PhCl} + \text{BrCl}$				
$\text{active charge-transfer complex (521, 522)}$				
$\text{A} = \text{Naphth-Cl}$				
$\text{D} = \text{triethylamine}$				
$\text{A} + \text{D} \rightleftharpoons \text{A} \cdot \text{D}^{\cdot+} + 0.5 \text{Cl}_2 \xrightarrow{\text{ca}_4} \text{A} \cdot \text{D}^{\cdot+} + 0.5 \text{Br}_2$				

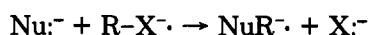
<sup>a</sup>  $K$  equilibrium constant of formation for CTC. <sup>b</sup> Examples are known where the CTC is less reactive toward homolysis than the uncomplexed species.<sup>519</sup> <sup>c</sup> Some CTC are A·D<sup>+</sup> in the ground state and AD in the excited state.<sup>524</sup> <sup>d</sup> For reviews on the reactivity of CTC, see ref 37-41, 152 (mixed valence compounds), 187, and 967. <sup>e</sup> Reference 515. <sup>f</sup> Reference 518.

Scheme XII<sup>a</sup>

<sup>a</sup> AA = associative activation of the substrate (or activation toward electron transfer).<sup>60b</sup> Cf. this scheme with ref 53 and 1436.

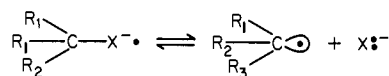
transpires from the study of "normal" photosubstitution reactions is that the mechanistic features of photostimulated  $S_{RN}1$  connected with all the studied substrates (Tables VIII–X) probably cannot be rationalized by a unique type of photoinitiation mechanism. This proposal is strengthened by the fact that still other mechanisms have been proposed for Havinga's photosubstitution of substrates involved in  $S_{RN}1$  processes.<sup>540–542</sup> Most of them can accommodate the building up of a chain at an appropriate step of their development. This point clearly deserves further experimental studies.

Until now we have concentrated mainly on monomolecular substitution mechanism; in these mechanisms the addition of an electron is supposed to activate the substrate strongly enough toward dissociation so that it can react without further external assistance of the nucleophile. The leaving-group effects (compare, however, with Saveant's recent paper which provides another interpretation for leaving group effects in  $S_{RN}1$  type reactions<sup>546</sup>) obtained on  $sp^3$ -C substrates by Russell's group point out, however, the possibility for an  $S_{RN}2$  type mechanism in the reaction between monoenoate anions and  $XCMe_2NO_2$  ( $X = Cl, NO_2, p$ -MePhSO<sub>2</sub>) (Scheme XII).<sup>60b,543,544a</sup> In this mechanism, the initiating electron transfer activates the substrate toward association with another molecule of the surrounding anion. Some important consequences of this new scheme merit a comment. The first one is that it calls for a thorough reexamination of other so-called  $S_{RN}1$  reactions where structural factors, unusual observations<sup>477,544b</sup> (cf. with ref 546), or long-lived anion radical lifetimes (Table XI) suggest such a mechanism. Secondly, if this mechanism proved to be general, theoretical chemists<sup>338</sup> would have to rationalize the transition state of:

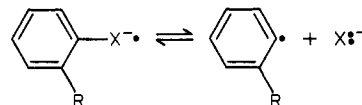


Thirdly, as this mechanism does not involve free-radical species, some reactions of this kind could develop even in good hydrogen-donor solvents without risks of ruining the chain participation. This proposition is clearly of such mechanistic importance that it calls for con-

firmations based on pulse radiolysis,<sup>344</sup> free-radical clocks,<sup>545a</sup> stereochemical labeling,<sup>392b</sup> verification that the related radical anions display an enhanced stability (see Table XI for the relevant techniques). Data gathered in Table XI evidence in any case that the stability of  $C-X^{\cdot-}$  bond changes considerably with the structural environment. From the never evidenced  $CH_3Br^{\cdot-}$  radical anion to the rather stable 9-chloroanthracene radical anion, more than 9 orders of magnitude of rate constant are displayed for the reaction:



We write it under its equilibrated form<sup>411b,545b</sup> to recall that for some substrates this equilibrium may play an important role in reactivity. Furthermore, Parker was able to measure its position in *p*-iodo- and *p*-chloronitrobenzene.<sup>494</sup> For extreme cases it is totally displaced, but for the very wide range where this type of interaction has been evidenced there must be a continuum of situations. In *homogeneous series* of  $sp^3$ -C-centered radical anions, naive considerations would suggest that it is displaced toward the left for highly electroattractive R groups (it is indeed known that the half-wave potentials of reduction of  $\alpha$ -halonitroalkanes<sup>547</sup> are more positive than their haloalkane counterparts, and display an increased stability of the associated radical anion in the former)<sup>374</sup> or for weak steric interactions between  $R_1, R_2, R_3$ . For aromatic species one can expect the steric effects to play an opposite role (ortho substitution destabilizes the radical anions), but electronic effects should play in the same direction; e.g., substituents that render the radical more



electrophilic should shift the equilibrium toward the right. The generality of this interaction should justify quantum chemical treatment; so work begins to appear (see note 17 in ref 548) in this direction. This need is further enhanced by the fact that the naive way of reasoning that we adopted in this section is very probably wrong if compared with the captodative approach,<sup>281</sup> in this approach, it is not the less electrophilic radical that displays the higher tendency to remain "free" but the most stabilized by captodative stabilization. The unidimensional representation of radical reactivity (i.e., electrophilic vs. nucleophilic)<sup>549</sup> seems insufficient if factors such as captodative stabilization are to be considered. Solvent effects play a major role in both the position of the equilibrium and the rate at which it is attained.<sup>343,523a</sup>

#### b. Substitutions with a Central Metal in the Electrophilic Substrate

(1) *Inorganic Complexes.* As early as 1954, H. Taube<sup>552</sup> was able to evidence the chain character of the radiochlorine exchange reaction of  $Pt^{IV}$  complexes:

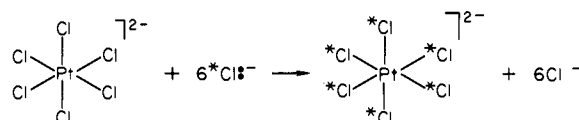


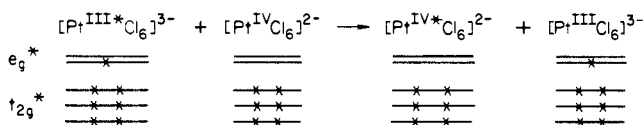
TABLE XIII. Possible Examples of Electron-Transfer-Catalyzed Substitution Reactions Occurring with Platinum(IV) Complexes<sup>a</sup>

reaction	solvent	ref
$\text{PtCl}_6^{2-} + 6^* \text{Cl}^- \rightleftharpoons \text{Pt}^* \text{Cl}_6^{2-} + 6 \text{Cl}^-$	$\text{H}_2\text{O}$	552-555
$\text{Pt}^{\text{IV}} \text{Br}_6^{2-} + 6^* \text{Br}^- \rightleftharpoons \text{Pt}^{\text{IV}} \text{Br}_6^{2-} + 6 \text{Br}^-$	$\text{H}_2\text{O}$	234, 556, 557
$\text{Pt}^{\text{IV}} \text{I}_6^{2-} + 6^* \text{I}^- \rightleftharpoons \text{Pt}^{\text{IV}} \text{I}_6^{2-} + 6 \text{I}^-$	$\text{H}_2\text{O}$	558
$\text{Pt}^{\text{IV}} \text{Cl}_6^{2-} + 6 \text{Br}^- \rightleftharpoons \text{Pt}^{\text{IV}} \text{Br}_6^{2-} + 6 \text{Cl}^-$	$\text{H}_2\text{O}$	559, 560
$\text{Pt}^{\text{IV}} \text{Cl}_6^{2-} + 6 \text{I}^- \rightleftharpoons \text{Pt}^{\text{IV}} \text{I}_6^{2-} + 6 \text{Cl}^-$	$\text{H}_2\text{O}$	562
$\text{Pt}^{\text{IV}} \text{Br}_6^{2-} + 6 \text{Cl}^- \rightleftharpoons \text{Pt}^{\text{IV}} \text{Cl}_6^{2-} + 6 \text{Br}^-$	$\text{H}_2\text{O}$	561
$\text{OsCl}_6^{2-} + 6^* \text{Cl}^- \rightleftharpoons \text{Os}^* \text{Cl}_6^{2-} + 6 \text{Cl}^-$ <sup>b</sup>	$\text{H}_2\text{O}$	563, 564
$\text{PtBr}_6^{2-} + 6 \text{I}^- \rightleftharpoons [\text{PtI}_6] + 6 \text{Br}^-$	$\text{H}_2\text{O}$	565
$\text{Pt}^{\text{IV}} \text{Cl}_6^{2-} \xrightarrow{\text{H}_2\text{O}} \text{Pt}^{\text{IV}} \text{Cl}_5 \text{H}_2\text{O}^- + \text{Cl}^-$	$\text{H}_2\text{O}$	566
$\text{Pt}^{\text{IV}} \text{I}_6^{2-} \xrightarrow{\text{H}_2\text{O}} \text{Pt}^{\text{IV}} \text{I}_5 \text{H}_2\text{O}^- + \text{I}^-$	$\text{H}_2\text{O}$	550, 567

<sup>a</sup> We have kept out of this table the case of  $\text{Pt}^{\text{II}}$ -catalyzed substitutions of  $\text{Pt}^{\text{IV}}$  complexes.<sup>551</sup> These cases have been discussed elsewhere.<sup>42</sup> <sup>b</sup> Negative experiment.

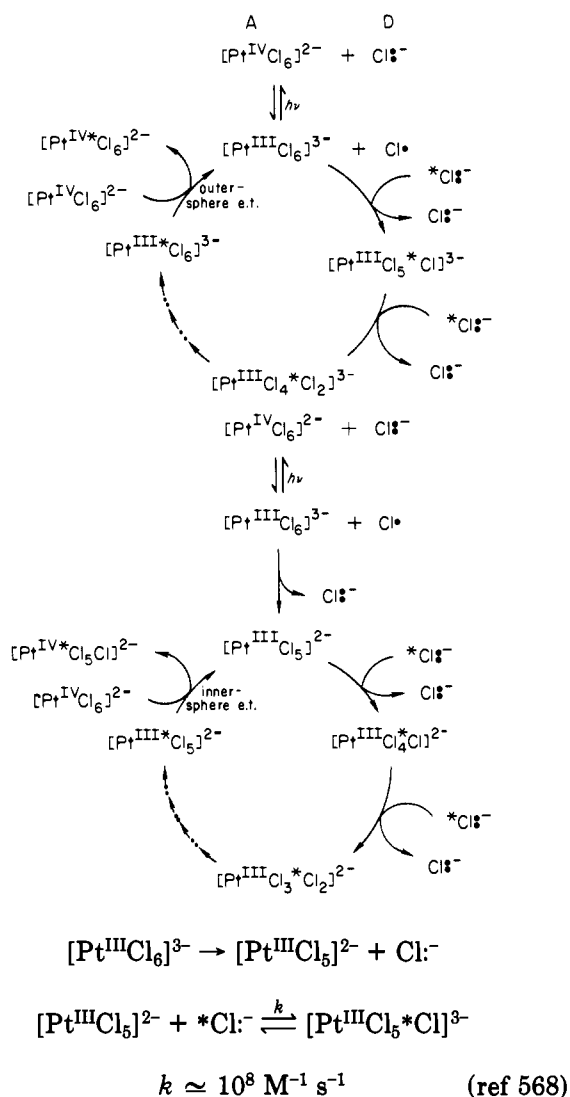
We have shown elsewhere that this reaction possesses all the experimental earmarks of an  $\text{S}_{\text{RN}}1$  type reaction, and other examples of such kind of reaction are collected in Table XIII. It was originally viewed as initiated by direct homolysis of  $\text{Pt}^{\text{IV}}\text{-Cl}$  bond, but Fleischer's flash photolysis experiments<sup>550</sup> suggest that the initiation step is, at least for some cases of electron transfer, the induced type. When solutions of  $\text{Pt}^{\text{IV}}(\text{SCN})_2(\text{NH}_3)_4^{2+}$  are flash photolyzed in the absence of the appropriate anion, the apparition of  $\text{Pt}^{\text{III}}$  transients is delayed in comparison with what is observed when this anion is present. There exists no such kind of flash photolytic data for each of the examples gathered in Table XIII, but Poe<sup>562</sup> has shown that addition of very small amounts ( $10^{-7}$  M) of reducing agents significantly changes the rate of thermal exchange. More work is needed to clearly delineate direct homolytic vs. indirect in these series. The available experimental data do not allow a clear choice between the two following catalytic cycles (Scheme XIII); both, however, correspond to ETC process submitted to photostimulation.

In the first one, the electron-transfer step which closes the chain is outer-sphere. Consideration of molecular orbital diagrams suggests, however, that such a step should be energetically unfavored because it involves an electron transfer of the  $\sigma^* \rightarrow \sigma^*$  type which are known to be slow.<sup>84b</sup>

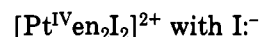
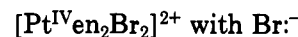


A way to circumvent this difficulty would be to suppose that a CTC exists between the two interacting molecular species, but no experimental evidence has backed such an hypothesis until now. In the second scheme, the difficulty is overcome by supposing that this propagation step involves an inner-sphere mechanism. This second scheme, however, yields a product where five out of six chlorines have been exchanged. To obtain a complete exchange the complex must therefore enter another catalytic cycle.  $\text{Pt}^{\text{III}}$  complexes are well known to be highly labile; therefore, the foregoing catalytic cycles could probably be better represented by substeps such as:

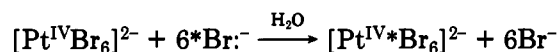
Scheme XIII



This reaction has been submitted to thorough photochemical experiments. Poe<sup>565</sup> found that the photostimulated exchange had its rate enhanced by the addition of appropriate reducing agents. He also evidenced charge-transfer complexes in the following examples:<sup>569</sup>



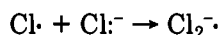
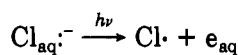
Adamson<sup>234</sup> measured the quantum yields for the following reaction:



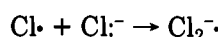
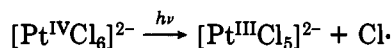
and his results were discussed in section I9 because of their methodological importance. Despite the high amount of experimental work performed on this type of reaction, the ETC photocatalytic scheme was never discussed (see ref 42). Shagisultanova<sup>570</sup> reported, however, that photolysis of  $[\text{Pt}^{\text{IV}}(\text{Gly-H})_3]\text{X}$  (with  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ; Gly-H = glycinate) resulted in the photooxidation of outer-sphere anions with reduction of the central atom to give  $\text{Pt}^{\text{III}}$ .

Other flash photolysis experiments were performed by Adamson and Laurence. Adamson<sup>571</sup> found that  $[\text{Pt}^{\text{IV}} \text{I}_6]^{2-}$  + iodide solutions display a long-lived tran-

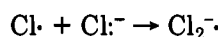
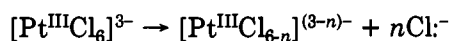
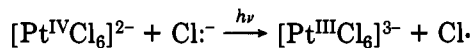
sient (410  $\mu\text{m}$ ) with a half-life of about 0.1 s. Laurence<sup>572a</sup> precised these observations on the  $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}/\text{Cl}^-$  system and confronted their results with independent pulse radiolysis<sup>573</sup> experiments. Fifty milliseconds after flashing an aqueous  $5 \times 10^{-5}$  M solution of  $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$  in the presence of  $\text{Cl}^-$  ( $10^{-3}$  to  $10^{-1}$  M) and  $\text{H}^+$  ( $10^{-5}$  to  $10^{-1}$  M), he observed a transient in the same wavelength range (350–450 nm) as the one produced by pulse radiolysis.<sup>573</sup> This transient decays by a second-order process (lifetime 0.1 s). In concentrated solutions of chloride ion ( $>10^{-3}$  M), flash photolysis of the complex also produced  $\text{Cl}_2^-$  radical anions. These do not originate from the reactions:<sup>574</sup>



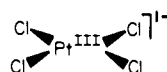
Laurence explained their apparition by:



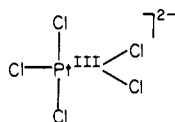
Another possibility is obviously a photoinduced electron transfer from  $\text{Cl}^-$  to excited  $\text{Pt}^{\text{IV}}$  complexes.



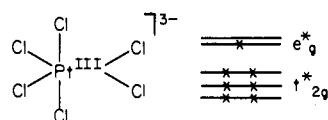
$[\text{Pt}^{\text{III}}\text{Cl}_{6-n}]^{(3-n)-}$  intermediates react rapidly with  $\text{Fe}^{2+}$  ( $k_2 \simeq 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ) and, from the slope of the plot  $\log k_2$  vs. the square root of ionic strength, Laurence deduced that the reactive transient formed in the solution should be charged 1-. Therefore, he proposed the structure:



On the other hand, from pulse radiolysis studies Adams<sup>573</sup> concludes that the corresponding transient is probably:

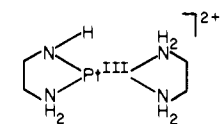
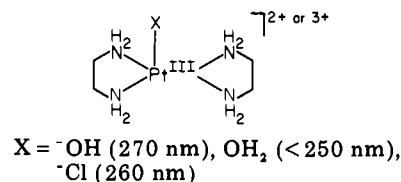


In terms of the photoinduced electron-transfer catalysis approach, the choice between the two structures comes to attributing a more or less predominant role to the Jan Teller effects in the complex:



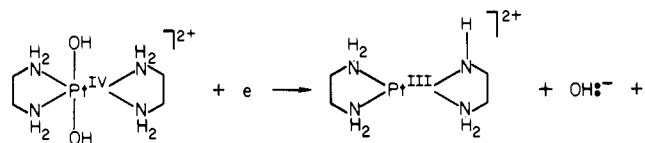
Because of the hyperfine coupling constant between the unpaired electron and the chlorine ligands,<sup>575,576</sup> ESR would appear to be a method of choice to solve this problem. Storer and Waltz<sup>577</sup> did not meet with success when trying to study the products of the reaction of  $\text{trans-Pt}(\text{en})_2\text{Cl}_2^{2+}$  with isopropanol radical in aqueous

media at room temperature. These searchers performed the most extensive study of transients playing a role in the reactivity of  $\text{Pt}^{\text{IV}}$  and  $\text{Pt}^{\text{II}}$  complexes.<sup>568</sup> Their more recent work allows a distinction between penta- and tetracoordinated  $\text{Pt}^{\text{III}}$  transients based on their UV spectra:



340 nm and 480 nm

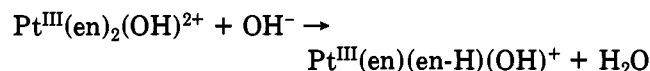
The tetracoordinate complex is the major product of the reaction of the hydrated electron and *trans*-dihydroxobis(ethylenediamine)platinum(IV) perchlorate which could lend some credence to the tetracoordinate  $\text{Pt}^{\text{III}}$  structure proposed by Laurence<sup>572a</sup> for the transient (350–450 nm) generated by flash photolysis of  $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ :



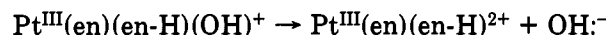
H<sub>2</sub>O

The detailed mechanism of formation, however, depends on the pH of the solution:

$$5 < \text{pH} < 10$$

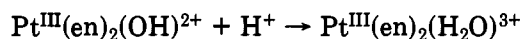


$$k = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$



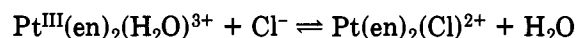
$$\text{pH} < 4.5$$

$$k = 3 \times 10^{-5} \text{ s}^{-1}$$



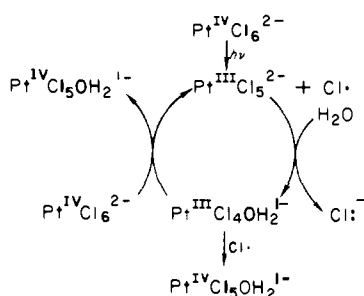
$$k \simeq 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

And when chloride ion is present in acidic medium it rapidly and reversibly substitutes the  $\text{OH}_2$  ligand:



$$k = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Therefore, the nature of observed transients depends both on the presence (absence) of excess halide anion and on the pH. According to the concentration of  $\text{Cl}^-$  in the medium and pH of the solution, equilibrium between different intermediates can be "frozen," the final composition of products reflecting both the position of the equilibrium and the relative rates of oxi-

Scheme XIV<sup>a</sup>

<sup>a</sup> All steps proposed by the authors are reversible.

dation of these intermediates. We detailed this example to illustrate how tricky the determination of a photochemical mechanism may become because of subsequent dark reactions, and also to show all the work that remains to be done on inorganic substrates to clearly delineate the generalized  $S_{RN}1$  mechanism.

For a possible photoelectron-transfer catalysis aquation reaction, the basic reference is provided by the work of D. G. Peters and co-workers.<sup>566</sup> These searchers evidenced that the photoaquation of hexachloroplatinate(IV) to pentachloroplatinate(IV) in perchloric acid medium has an overall quantum yield which varies from 0.8 to values as high as 33; however, if traces of  $Cl_2$  (oxidizing agent) are present, this yield falls to values  $<0.1$ . This pattern is specified for hexachloroplatinate and was not evidenced for hexabromoplatinate(IV).<sup>567,578</sup> Peters proposed the mechanism in Scheme XIV.<sup>566</sup>

The initiation steps involve a direct homolysis of the  $Pt^{IV}-Cl$  bond. This seems a natural possibility in the absence of any anion present in the solution (but in many cases  $Cl^-$  was deliberately added by the authors to prevent the photoaquation of  $PtCl_6^{2-}$  from proceeding beyond formation of  $PtCl_5OH_2^-$ ); when some  $Cl^-$  has been formed in the solution, there may be competition between "direct homolysis" and electron-transfer-induced cleavage of the bond. These authors have indeed evidenced that, under irradiation,  $[Pt^{IV}Cl_6]^{2-}$  becomes an oxidizing agent strong enough to transform barium diphenylsulfamate into diphenylbenzidine violet.

At this point it is important to remark that if these substitutions are not exactly parallel to the  $S_{RN}1$  process the underlying mechanics remain exactly the same, which led us to group all these processes under the heading "Double Activation Induced by Single Electron Transfer."<sup>42</sup> Indeed, the first transfer of electron activates the inorganic complex toward dissociation (but associative substitution similar to  $S_{RN}2$  is also conceivable for other cases) and, from the created reactive intermediate, a catalytic cycle is initiated. From the substrates that we have already identified as undergoing single electron-transfer-catalytic (ETC) processes, we can tentatively extract which configurations in hexacoordinated complexes seem compatible with reductive ETC:  $d^3$  and  $d^6$  are the best candidates. From the rate values of water exchange for the first row dipositive transition-metal ions given in Figure I of R. G. Linck's review,<sup>579a</sup>  $d^2$  and  $d^8$  configurations should also provide good candidates. This does not mean that photoelectron-transfer-catalytic reactions will be observed with all the complexes having this configuration.

We know indeed that, besides appropriate redox potentials, favorable lifetimes and symmetries of photoexcited states are demanded to allow the occurrence of the first electron transfer. Furthermore, even if the first activation takes place, the catalytic cycle has still to build up. Keeping these cautions in mind, one can use Table XIV to search possible photoinduced electron-transfer catalysis in other inorganic complexes. This table gives some examples of thermal or electrochemical ETC substitution processes that have already been identified. Starting from it, we searched the photochemical counterparts in the literature (photoaquation and photosubstitution of appropriate complexes; an excellent overview of these inorganic photo-reactions may be found in ref 81). The results are gathered in Table XV. Comparison of Tables XIV and XV calls for some comments.

With these inorganic examples we indeed meet something not recognized for organic systems: many complexes which could be expected to display a DAISSET behavior from their chemical properties apparently do not evidence a photochemically induced ETC pattern. At this point it is difficult to give a unique explanation for this observation. Several can be offered between which further experiments should allow an unambiguous choice. The first one is that the lifetime of the excited state is not long enough to allow an electron transfer from the nucleophile to the complex despite its improvement in oxidizing properties. This situation could possibly be improved by an appropriate change of solvent, but thorough studies on  $Cr^{III}$  doublet state suggest that this modification can be smaller<sup>653</sup> than generally thought.<sup>654</sup>

A second explanation could be that the most appropriate solvent has not been examined for the photochemical experiment: the  $Cr^{III}$  example (Table XV) is especially illustrative with regard to this possibility. As long as photosubstitutions were performed in water no clear-cut ETC pattern was evidenced, but when Porter did the experiments in  $Me_2SO$  he demonstrated it beyond any doubt. A third possibility is that too short a chain develops yielding small overall quantum yields (see section Ig). Slight structural modifications are sufficient to change the situation from a chain to a normal reaction; e.g., photoaquation of  $PtCl_6^{2-}$ <sup>566</sup> and  $PtBr_6^{2-}$ .<sup>567</sup> A fourth one is that, for the thermal examples, the triggering of the chain is performed by an inner-sphere electron transfer with atom-transfer mechanism. There is not much evidence that this type of electron transfer can be directly photoinduced. The fifth explanation follows from the elegant kinetic analysis of  $S_{RN}1$  performed by Amatore:<sup>546</sup> this author indeed showed that the ratio of nucleophile to substrate concentration has a particularly strong influence on the reaction time for the systems associated with a chain process of low efficiency. This analysis suggests that for many systems described in Table XIV the suitable conditions of concentration were not fulfilled (see a photochemical example illustrating this proposition in ref 539). Besides these general explanations, every system warrants its own specific examination; for example, with iron(III) some problems may arise because of the variety of  $Fe^{III}$  species<sup>654</sup> present in the aqueous solution, e.g.,  $[Fe^{III}(OH_2)_6]^{3+}$ ,  $[Fe^{III}(H_2O)_5OH]^{2+}$ ,  $[Fe^{III}(H_2O)_4(OH)_2Fe^{III}(OH_2)_4]^{4+}$ . In fact, much remains to be done with the photochemistry of these inorganic



TABLE XIV. Examples of Substitutions of Ligands in Inorganic Complexes Induced by Single Electron Transfer

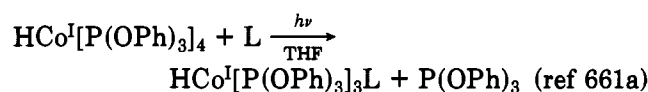
electron transfer	technique	ref
$\text{Cr}^{\text{III}}(\text{bipy})_3^{3+} \xrightarrow[\text{Cr}^{\text{II}}]{\text{cat}} \text{Cr}^{\text{III}}(\text{bipy})_2(\text{H}_2\text{O})_2^{3+}$	chemistry	580-582
$\text{Cr}^{\text{III}}(\text{CN})_6^{3-} \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{H}_2\text{O}, \text{OH}^-} \text{Cr}^{\text{III}}(\text{OH})(\text{OH}_2)_5^{2-}$	electrochemistry, chemistry	583, 584
$\text{trans-Pt}^{\text{IV}}(\text{H}_2\text{O})_4\text{Cl}_2 \xrightarrow{\text{HCl}} \text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$	chemistry	585
$\text{Cr}^{\text{III}}(\text{OH}_2)_6^{3+} + 3\text{en} \xrightarrow[\text{Cr}^{\text{II}}]{\text{cat}} \text{Cr}(\text{en})_3^{3+ a}$	chemistry	586, 587
$\text{Rh}^{\text{III}}(\text{OH}_2)\text{Cl}_5^{2-} + \text{py} \xrightarrow{\text{EtOH}} \text{Rh}^{\text{III}}(\text{py})_4\text{Cl}_2 + b$	chemistry	588-590
$5\text{H}^+ + \text{Cr}^{\text{II}}(\text{H}_2\text{O})_6^{2+} + \text{Cr}^{\text{III}}(\text{NH}_3)_5\text{Cl}^{2+} \rightarrow$ $\text{Cr}^{\text{II}}(\text{H}_2\text{O})_6^{2+} + \text{Cr}^{\text{III}}\text{Cl}(\text{H}_2\text{O})_5^{2+} + 5\text{NH}_4^+$	chemistry	591
$5\text{H}^+ + \text{Cr}^{\text{II}}(\text{EDTA})^{2-} + \text{Cr}^{\text{III}}(\text{NH}_3)_5\text{Cl}^{2+} \rightarrow$ $\text{Cr}^{\text{II}}(\text{H}_2\text{O})_6^{2+} + \text{Cr}^{\text{III}}(\text{EDTA})^{1-} + 5\text{NH}_4^+ + \text{Cl}^-$	chemistry	592
$5\text{H}^+ + \text{Cr}^{\text{II}}(\text{Ac})_3^- + \text{Cr}^{\text{III}}(\text{NH}_3)_5\text{Cl}^{2+} \rightarrow$ $\text{Cr}^{\text{II}}(\text{H}_2\text{O})_6^{2+} + \text{Cr}^{\text{III}}(\text{Ac})_3^{3+} + 5\text{NH}_4^+ + \text{Cl}^-$	chemistry	593
$\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6^{3+} + 6\text{L} \xrightarrow[\text{Cr}^{\text{II}}]{\text{cat}} \text{Cr}^{\text{III}}\text{L}_6 + 6\text{H}_2\text{O}$	chemistry	594a, 595
$\text{Co}^{\text{III}}\text{Br}_2\text{en}_2^+ + 6\text{H}_2\text{O} + e \rightarrow \text{Co}^{\text{II}}(\text{H}_2\text{O})_6^{2+} + 2\text{Br}^- + 2\text{en}$	electrochemistry	480
$\text{Cr}^{\text{III}}(\text{OH}_2)_5\text{Cl}^{2+} \xrightarrow[\text{cat V}^{2+}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^-$		596
$\text{Cr}^{\text{III}}(\text{H}_2\text{O})_4\text{Cl}_2^+ \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}(\text{H}_2\text{O})_6^{3+} + 2\text{Cl}^-$		597
$\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6^{3+} + 6\text{L} \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}\text{L}_6^{3+} + 6\text{H}_2\text{O}$		595, 598
$\text{Cr}^{\text{III}}\text{Cl}(\text{H}_2\text{O})_5^{2+} + * \text{Cl}^- \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}*\text{Cl}(\text{H}_2\text{O})_5^{2+} + \text{Cl}^-$		599, 601, 602
$\text{Cr}^{\text{III}}\text{I}(\text{H}_2\text{O})_5^{2+} + \text{X}^- \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}\text{X}(\text{H}_2\text{O})_5^{2+} + \text{I}^-$ $\text{X}^- = \text{Cl}^-, \text{Br}^-$		600, 601
$\text{H}^+ + \text{Cr}^{\text{III}}\text{F}_2(\text{H}_2\text{O})_4^+ + \text{H}_2\text{O} \xrightarrow[\text{cat Cr}^{\text{II}}]{\text{cat Cr}^{\text{II}}} \text{Cr}^{\text{III}}\text{F}(\text{H}_2\text{O})_5^{2+} + \text{HF}$		603
$\text{Fe}^{\text{III}}\text{Cl}(\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O} \xrightarrow[\text{cat Fe}^{\text{II}}]{\text{cat Fe}^{\text{II}}} \text{Fe}^{\text{III}}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^-$		604-606
$\text{Co}^{\text{III}}(\text{CN})_5\text{X}^{3-} + \text{CN}^- \xrightarrow[\text{cat CoCN}_5^{3-}]{\text{cat CoCN}_5^{3-}} \text{Co}^{\text{III}}(\text{CN})_6^{3-} + \text{X}^-$		607
$\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Br}^{2+} + \text{CN}^- \xrightarrow[\text{cat CoCN}_5^{3-}]{\text{cat CoCN}_5^{3-}} \text{Co}^{\text{III}}(\text{CN})_5\text{Br}^{3-}$		608, 609
$\text{V}^{\text{III}}\text{X}^{2+} + \text{H}_2\text{O} \xrightarrow[\text{cat V}^{\text{II}}]{\text{cat V}^{\text{II}}} \text{V}^{\text{III}}\text{H}_2\text{O}^{3+} + \text{X}^- e$		610, 611
$\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{Cl}^{2+} + \text{H}_2\text{O} \xrightarrow[\text{cat Ru}^{\text{II}}(\text{NH}_3)_5\text{OH}_2^{2+}]{\text{cat Ru}^{\text{II}}(\text{NH}_3)_5\text{OH}_2^{2+}} \text{Ru}^{\text{III}}(\text{H}_2\text{O})_5\text{Cl}^{2+}$		612-615
$\text{Au}^{\text{III}}\text{Cl}_4^- + * \text{Cl}_4^- \xrightarrow[\text{cat Fe}^{\text{II}}]{\text{cat Fe}^{\text{II}}} \text{Au}^{\text{III}}*\text{Cl}_4^- + 4\text{Cl}^-$		616-618a <sup>f</sup>

<sup>a</sup> en = ethylenediamine. <sup>b</sup> py = pyridine. <sup>c</sup> EDTA = ethylenediaminetetraacetate. <sup>d</sup> Ac = CH<sub>3</sub>COO<sup>-</sup>. <sup>e</sup> X = N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>-COO<sup>-</sup>. <sup>f</sup> This table is not exhaustive; for further examples, see R. G. Linck<sup>579</sup> and A. Yamada.<sup>480</sup>

complexes simply because the photoinduced electron-transfer catalysis has not been searched for in most of the systems. When it is realized that ETC photocatalysis has many applications (see section VII) the field seems worth further exploration. In any case, information of the utmost importance for organic systems may be extracted from the foregoing section: some electron-transfer-catalytic systems do not display photostimulation.

(2) *Organometallics*. The situation that we have met with inorganic complexes in the preceding section is found again with organometallics. In some respects, it is even worse because photochemical electron-transfer catalysis was eventually born in the inorganic field,<sup>42,552</sup> whereas in organometallic chemistry<sup>43</sup> the importance of this topic was totally neglected until very recently.<sup>231</sup> Therefore, we can only give tentative examples of possible photoinduced electron-transfer-catalyzed substitutions in this field. For every initiation step we will

then be faced with the pervasive dilemma, "direct homolysis or photoelectron-transfer-stimulated homolysis?". None of the reviews denoted to photostimulated substitutions of organometallic compounds<sup>64,655-659</sup> deals with this question. It would therefore seem that the "direct homolytic" pathway is the only one acceptable for this class of compounds. The recent Smith contribution<sup>660</sup> shows, however, that some organometallic bonds are stronger than usually thought: Fe-C in Fe(CO)<sub>5</sub> has a bond energy of 48 kcal/mol. In the first paper<sup>42</sup> of this series we suggested that some organometallic compounds could in fact undergo ETC photostimulation, representative examples to be tested being:



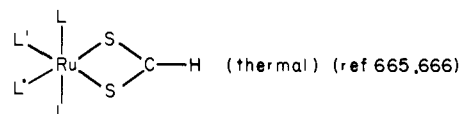
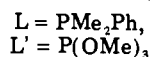
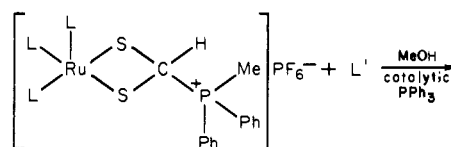
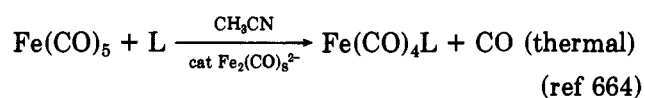
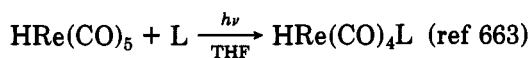
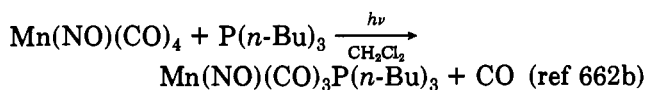
L = CO

Table XV. Photochemical Counterparts of the Thermal and Electrochemical Reactions Described in Table XIV<sup>a,b</sup>

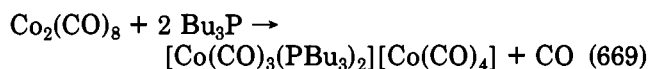
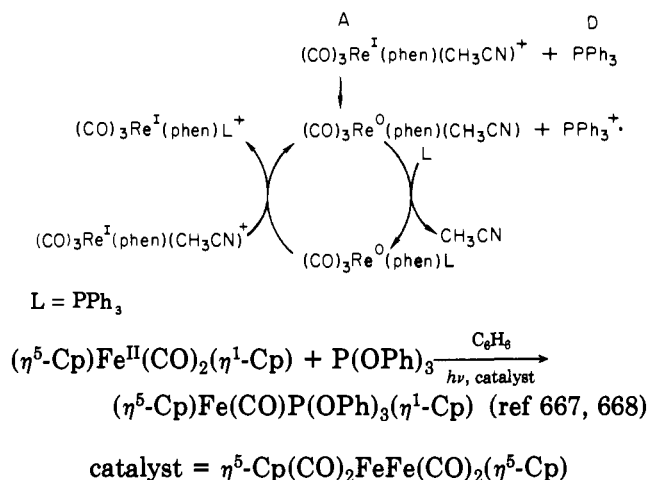
complex	reaction	$\Phi$	data of av lifetimes <sup>622</sup>	ref
<b>Cr<sup>III</sup></b> $[\text{Cr}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$	aquation	>0.5	doublet state, <sup>2</sup> E <sub>g</sub> radiat lifetime $\tau_0 \approx 10^{-2}-10^{-3}$ s	572b, 619
$[\text{Cr}(\text{bipy})_3]^{3+}$	partial aquation (2 H <sub>2</sub> O replace 1 bipy) in Me <sub>2</sub> SO as solvent	not measured but chain reaction evidenced in water $\Phi^{624} = 0.001$ (pH = 4), 0.1 (pH = 9)	actual lifetime $\tau \approx 10^{-3}-10^{-5}$ s, quartet <sup>4</sup> T <sub>2g</sub> , $\tau_0 \approx 10^{-6}$ s, $\tau_0 \approx 10^{-8}$ s (but see ref 620-623)	622 624
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	anation by Cl <sup>-</sup> (in H <sub>2</sub> O)	$\approx 1 \times 10^{-3}$		625
$[\text{Cr}(\text{DMSO})_6]^{3+}$	anation by N <sub>3</sub> <sup>-</sup> (in Me <sub>2</sub> SO)	$1 \times 10^{-2}$		626
<b>Fe<sup>III</sup></b> $[\text{Fe}(\text{CN})_6]^{3-}$	exchange <sup>c</sup> with radiocyanide (alkaline solution)	not determined		630, 631
	substitution N <sub>3</sub> <sup>-</sup> or SCN <sup>-</sup>	see original		632
$[\text{Fe}(\text{CN})_6]^{3-}$	aquation	0.009 (pH = 4)		633
<b>Co<sup>III</sup></b> $\text{Co}^{\text{III}}(\text{CN})_6^{3-} + \text{I}^- \rightarrow$ $\text{Co}(\text{CN})_5\text{I}^{3-} + \text{CN}^-$ $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}^{2+} + \text{H}_2\text{O} \rightarrow$ $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^-$ $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{N}_3^{2+} + \text{NH}_3$	photoaquation	not determined water 0.01 (370 nm) $1.5 \times 10^{-3}$ (550 nm) 0.2		634, 635 636a,b, 637, 640a 639 <sup>f</sup>
$\text{Co}^{\text{IV}}(\text{en})_3^{3+} + 3\text{L} \xrightarrow{\text{H}_2\text{O}}$ $\text{Co}^{\text{III}}\text{L}_3 + 3\text{en}$ L = bis(2-hydroxyethyl) dithiocarbamate		0.3-0.8 (460 nm)		641b, 644
<b>Ru<sup>III</sup></b> $\text{Ru}(\text{NH}_3)_4\text{Br}^+$	photoaquation	$5.6 \times 10^{-3}$ (330 nm) $2.7 \times 10^{-3}$ (382 nm) $1.4 \times 10^{-3}$ (434 nm)		645 979
$[\text{Ru}(\text{bipy})_3]^{2+}\text{Cl}^- \rightarrow$ $\text{Ru}(\text{bipy})_2\text{Cl}_2 + \text{bipy}^e$				
<b>Rh<sup>III</sup></b> $\text{Rh}(\text{NH}_3)_5\text{I}^+$	photoaquation	0.9 (470 nm)		643
$\text{Rh}(\text{py})_2\text{Cl}_4^- \xrightarrow{\text{H}_2\text{O}}$ $\text{Rh}(\text{py})_2\text{Cl}_3(\text{H}_2\text{O})$			Rh(NH <sub>3</sub> ) <sub>6</sub> 79 μs at 77 K <sup>i</sup>	646, 648
$\text{Rh}(\text{py})_3\text{Cl}_3 \xrightarrow{\text{HCCl}_3}$ $\text{Rh}(\text{py})_2\text{Cl}_3(\text{H}_2\text{O})$			RhX <sub>2</sub> Y <sub>2</sub> <sup>+</sup> , X = Cl, Br, I; Y = 2,2'-bipyridyl <sup>g</sup>	648
$\text{Rh}(\text{NH}_3)_5\text{L}$	photoaquation	for a tabulation of $\Phi$ in Rh <sup>III</sup> photoaquation, see ref 91 and 647	10 to 500 μs ethanol-methanol glass at 77 K	649
<b>Au</b> Au <sup>III</sup> salts components of photographic emulsion because of their high photosensitivity	chain reaction			652

<sup>a</sup> To obtain more complete views on the photochemistry of the complexes gathered here, see ref 81, 82, 90, and 91.

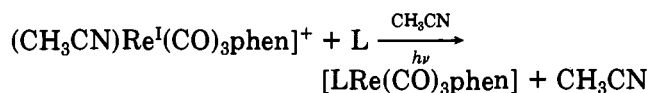
<sup>b</sup> For Pt<sup>IV</sup> see text. <sup>c</sup> For inorganic complexes photoexchange reactions are often the result of a photoaquation followed by anation.<sup>84</sup> <sup>d</sup> A recent reference<sup>91</sup> discusses in detail the photosubstitutions of hexacoordinated complexes: no section, however, deals with the possibilities of ETC photosubstitution. <sup>e</sup> Excess halide in the medium accelerates this reaction which suggests the intervention of a photoelectron-transfer mechanism for this reaction. <sup>f</sup> For additional values of Co<sup>III</sup>  $\Phi$  see ref 647. <sup>g</sup> Reference 650 and 651. <sup>h</sup> For more data on Cr<sup>III</sup> photochemistry see ref 627-629. <sup>i</sup> Reference 643.



Scheme XV



(thermal reactions could possibly be photostimulated).  
 More recently, M. S. Wrighton<sup>231</sup> independently proposed a new mechanism for photosubstitution of organometallic complexes:



$L = \text{pyridine}$  or  $\text{PPh}_3$ , phen = phenanthrolyl

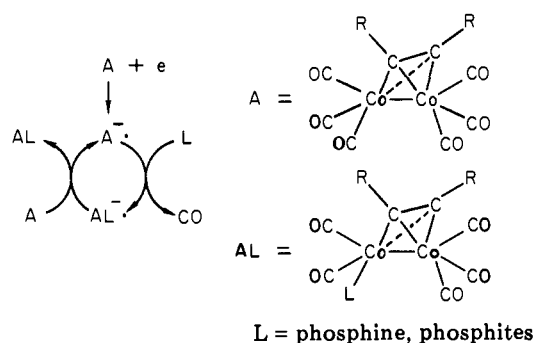
The proposed mechanism was carefully established by quantum yields measurements, Stern-Volmer quenching, and electrochemical measurements of coulomb efficiency. It exactly corresponds to the photoelectron-transfer-catalytic Scheme XV.

A fundamental point is that when  $L = \text{PPh}_3$  both quantum yields ( $8 < \Phi < 24$ ) and coulomb efficiency ( $16 < \text{CE} < 45$ ) agree with the chain character of the reaction, whereas when  $L = \text{pyridine}$  quantum yields do not directly prove the chain character ( $0.2 < \Phi < 0.74$ ), however it is proved by the value of coulomb efficiency ( $6 < \text{CE} < 23$ ). It is remarkable also that organometallic compounds are usually thought to be good electron donors in D.A. interaction; here the light induces a drastic umpolung: the organometallic compound becomes a good oxidizing agent, and the relative values of excited lifetime and rate of electron transfer<sup>670</sup> allow the production of a 19-valence-electron complex. Such complexes are generally labile,<sup>269,671-674</sup> although long-lived negative ions of this kind have been observed in the gas phase.<sup>675</sup> Polar donor solvents ( $\text{CH}_3\text{CN}$ , THF, pyridine) that favor the photoinduced formation of metal carbonyl anions should be used when this type of process is desired. Pico- and nanosecond flash photolytic studies in the presence of appropriate donors or acceptors will help precisizing the actual importance of these indirect homolytic schemes.

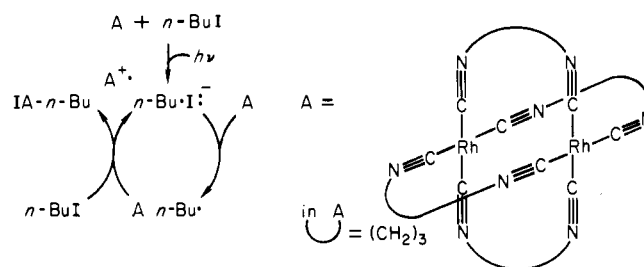
A recent electrochemical<sup>676</sup> report shows that photoinduced electron-transfer-catalytic substitution indeed merits some attention. Scheme XVI is indeed evidenced by Bezems. The electrochemically generated  $\text{A}^-$  displays a rather long lifetime (10 ms). No photochemical experiments are described for this system.

S. Fukuzumi<sup>594b</sup> recently extended the field of photoelectron catalysis to the reactivity of multiple-bonded

Scheme XVI



Scheme XVII



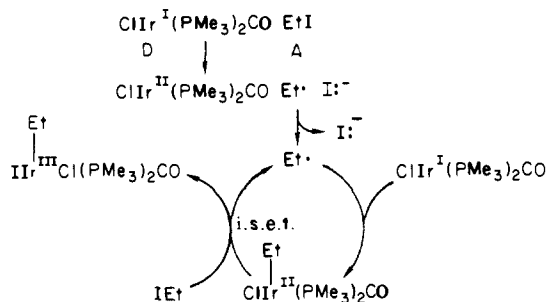
transition metals.<sup>618b</sup> Irradiating an acetonitrile solution of  $[\text{Rh}_2(\text{dicp})_4]^{2+}$  (dicp = 1,3-diisocyanopropane) in the presence of butyl iodide by the visible light (553 nm), he observed a reaction of oxidative addition leading with high quantum yields ( $\Phi \approx 25.2$ ) to the adduct  $[\text{Rh}_2(\text{dicp})_4(n\text{-Bu})\text{I}]^{2+}$ . The scavenging effect of electron acceptors (*p*-dinitrobenzene, *p*-benzoquinone, chloranil) and radical scavengers (oxygen and isopentyl nitrite) led to the formulation of the catalytic cycle (Scheme XVII).

### c. Substitutions Where the Attack Is Supposed To Occur on a Halogen Atom

(1) *Oxidative Addition of Organometallics.* We have considered elsewhere<sup>43</sup> the bipolarity of any C-X bond toward generalized donors. It is difficult to prove unambiguously at which end of a C-X or M-X bond an outer-sphere (or inner-sphere without atom transfer) electron transfer occurs. It has indeed been evidenced by beam scattering studies that in the interaction between K and  $\text{CH}_3\text{I}$ , electron transfer occurs at both ends.<sup>677</sup> Therefore, it should be clear that, presently, the title of this section has a character of organizational convenience rather than actual links with reality. This remark will also hold true for the titles of sections III1d and III1e.

The radical path in the oxidative addition of organometallics to alkyl halides was first evidenced by Osborn and Labinger<sup>678</sup> in 1972. A typical example is provided<sup>679</sup> by the reaction between ethyl iodide and  $\text{ClIr}^{\text{I}}(\text{CO})(\text{PMe}_3)_2$ . This reaction is photostimulated with quantum yields greater than 1 (estimation from the authors), and the most efficient wavelength of photostimulation (436 nm) corresponds neither to an absorption of EtI nor to an absorption of  $\text{IrClCO}(\text{PMe}_3)_2$ ; if we discard a tail-band effect, an attractive explanation is the involvement of a CTC. The mechanism proposed by the authors corresponds to the ETC cycle (Scheme XVIII).

## Scheme XVIII

Table XVI. Examples of Radical Oxidative Additions Involving Organometallics as Donors<sup>a</sup>

reaction	ref
$\text{cis-Me}_2\text{Pt}^{\text{II}}\text{L}_2 + \text{ArSO}_2\text{Cl} \rightarrow \text{ArSO}_2\text{Pt}^{\text{IV}}\text{ClMe}_2\text{L}_2$ L = $\text{PMe}_2\text{Ph}$ ; Ar = <i>p</i> - $\text{MeC}_6\text{H}_4$	680a
$\text{Sn}^{\text{II}}[\text{CH}(\text{SiMe}_3)_2]_2 + \text{PhBr} \rightarrow \text{PhSn}^{\text{IV}}[\text{CH}(\text{SiMe}_3)_2]_2\text{Br}$	681
$\text{Pt}^0(\text{PEt}_3)_3 + \text{MeCHBrCO}_2\text{Et} \rightarrow \text{BrPt}^{\text{II}}(\text{PEt}_3)_3\text{CHMeCO}_2\text{Et}$	682
$\text{ClIr}^{\text{I}}(\text{PMe}_3)_2\text{CO} + n\text{-C}_4\text{H}_9\text{Br} \rightarrow \text{ClBrIr}^{\text{III}}\text{C}_4\text{H}_9(\text{PMe}_3)_2\text{CO}$	683
$\text{Pd}^0(\text{PEt}_3)_3 + n\text{-C}_4\text{H}_9\text{Br} \rightarrow \text{BrPd}^{\text{II}}(\text{PEt}_3)_3\text{C}_4\text{H}_9$	682
$(\text{Co}^{\text{I}})^{\text{I-b}} + \text{RBr} \rightarrow \text{RCo}^{\text{III}} + \text{Br}^-$	638
$(\text{CH}_3)_2\text{Zn} + t\text{-BuCl} \rightarrow 2\text{C}(\text{CH}_3)_4 + \text{ZnCl}_2$	640b
$\text{Mg} + \text{RX} \xrightarrow{\text{MgIX}} \text{RMgX}$	523b
$(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4) + \text{CH}_2\text{Cl}_2 \rightarrow$	641a
$(\text{Ph}_3\text{P})_2\text{PtClCH}_2\text{Cl} + \text{Cl}_2\text{Pt}(\text{PPh}_3)_2$ (9-anthryl)arylmethyl chlorides + Grignard reagents	661b

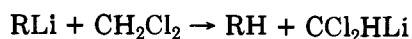
<sup>a</sup> For further examples and discussion, see in ref 43, section IB1. <sup>b</sup>  $(\text{Co}^{\text{I}})^{\text{I-b}}$  = cobaloxime.

It differs from the classical  $\text{S}_{\text{RN}}1$  mechanism in that the propagation step involves an inner-sphere electron transfer (i.s.e.t.) whereas this step is outer-sphere for the  $\text{S}_{\text{RN}}1$  case. The initiation step may, as in the  $\text{S}_{\text{RN}}1$  mechanism, be either outer-sphere or inner-sphere electron transfer. We have discussed this mechanism in another paper.<sup>43</sup>

Table XVI gathers some well identified examples of ETC oxidative additions involving organometallics as donors. This table includes nonphotochemical examples where the photochemical excitation could possibly increase the rates of reaction.

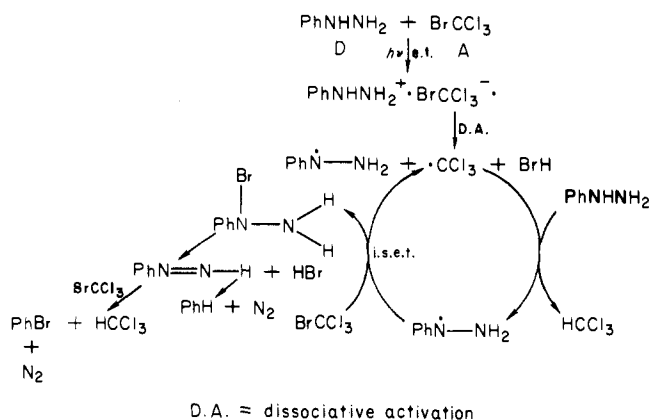
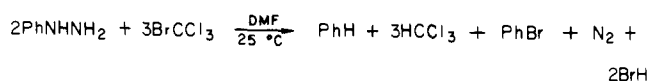
The distinction between reduction and substitution reactions is often a matter of convention: the reduction of C-X bonds by Sn-H are treated with the other reductions (section III8); it is clear, however, that they are included in the group of reactions where electron transfer "takes place" on the halogen end.

(2) *Substitution Reactions of Polyhalomethanes.* The electron affinity of  $\text{CX}_n\text{Y}_{4-n}$  is rather high; therefore, they accept electrons from a great variety of donors.<sup>684-688</sup> Their reactivity in D.A. interactions may, however, be much more complicated than the simple electron-transfer-catalytic scheme operating for the other alkyl halides, because the  $(\text{CX}_n\text{Y}_{3-n})\cdot$  radicals created by the first activation are electrophilic enough to evolve toward a carbene<sup>689</sup> via the capture of another electron.



This carbenic reactivity has led some authors to propose

## Scheme XIX



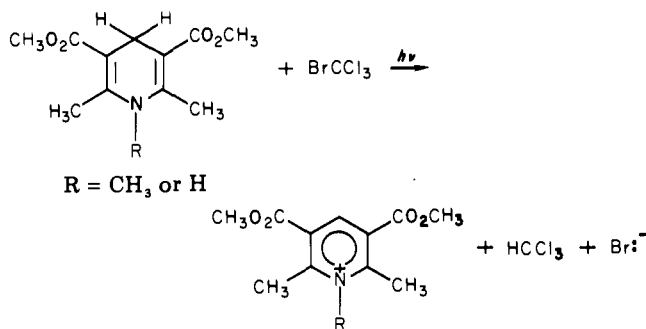
D.A. = dissociative activation

an ionic<sup>680b,690,691</sup> chain mechanism to rationalize certain aspects of this reactivity; further experiments are needed to delineate the frontier between this ionic mechanism and the radical one.<sup>692-695a</sup> I. Rico indeed showed their coexistence in the same reaction with appropriate substrates.<sup>695b,c</sup> This is especially true because the scope of radical anion radical pair (RARP) model proposed by Meyers<sup>693</sup> could be far wider than the thermal examples for which it has been discovered and deserves, therefore, careful photochemical experimentation.

The chemistry of polyhalomethanes was reviewed<sup>696</sup> and we focus here only on electron transfer catalytic aspects of this reactivity. These were already clearly pointed out in the Harmony review<sup>697</sup> devoted to molecular-assisted homolysis. A typical example<sup>698</sup> is the reaction between bromotrichloromethane and phenylhydrazine that occurs spontaneously in the dark at room temperature but can be accelerated by light or by addition of a few mole percent of diacetyl peroxide (Scheme XIX). The reaction involves the formation of phenyldiimide which then may react following two competitive paths<sup>699a</sup> yielding different products; none of them involves the phenyl radical.

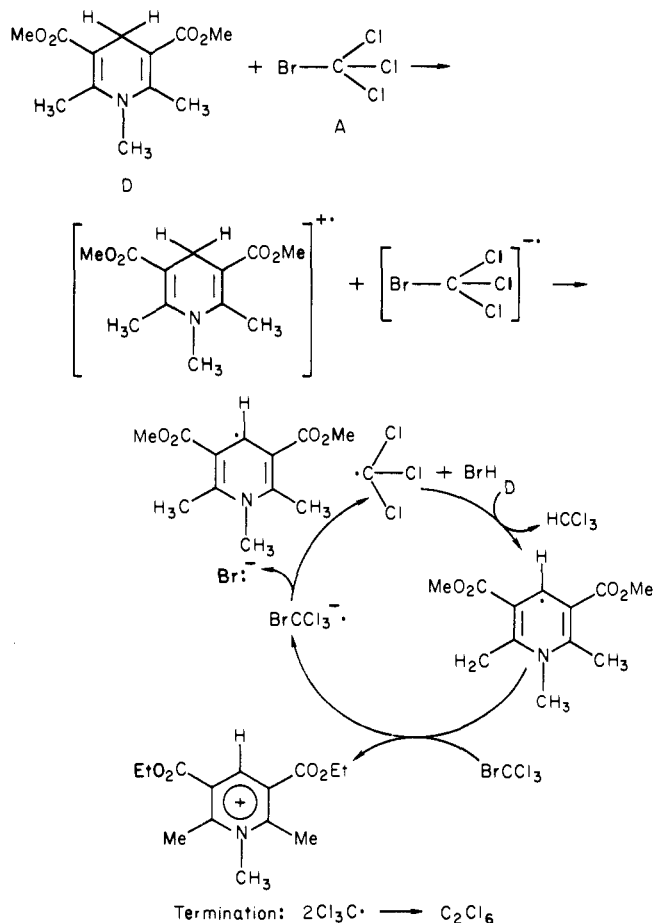
Huyser<sup>698</sup> proposed that the dark reaction was initiated in a bimolecular process in which two chain-carrying radicals are formed along with hydrogen halide. For the photochemical stimulation he suggested a unimolecular homolytic cleavage of the C-X bond. It should be interesting to check if the CTC frequently reported between amines and carbon tetrachloride<sup>692a,700b,701</sup> bears any connection with this reaction. T. Latowski<sup>701</sup> indeed suggests that the photostimulated (3130 Å) reaction of  $\text{CCl}_4$  with *N,N*-dimethylaniline involves the initial formation of an exciplex. The measured quantum yield for the formation of HCl in this reaction is 12.7 (in  $\text{CCl}_4$  as solvent) and depends on the concentration of  $\text{CCl}_4$  when the solvents are MeOH or dioxane. The photoreaction of diphenylamine and halogenated compounds to yield triphenylmethane dyes is also chain reaction.<sup>702</sup>

As early as 1961, F. Westheimer provided a very clear-cut example of electron-transfer catalysis involving bromotrichloromethane as acceptor:<sup>703</sup>



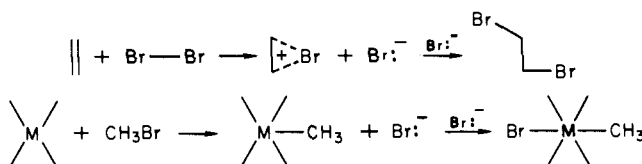
The quantum yield of the photostimulated (366 nm) reaction increases approximately with the square root of the concentration in the donor over a range from  $3.5 \times 10^{-3}$  to  $60 \times 10^{-3}$  M. It is independent of the concentration of bromotrichloromethane when this concentration exceeds 1.7 M but decreases by a factor of 2 at 0.17 M. The photochemical rate varies with the square root of light intensity. The highest quantum yield observed (79) suggests a rather long kinetic chain length. Interestingly, the same measurements performed with CCl<sub>4</sub> as acceptor gave the far lower 0.2 value for the quantum yield. These experimental data agree with an electron-transfer-catalyzed process developing according to Scheme XX. It is worthwhile to note that at this time Westheimer already discussed the possible involvement of CTC in this reaction.<sup>704</sup> The low reactivity of CCl<sub>4</sub> compared with BrCCl<sub>3</sub> follows from the higher electron affinity of the latter. This factor then intervenes in both the initiation and prop-

Scheme XX



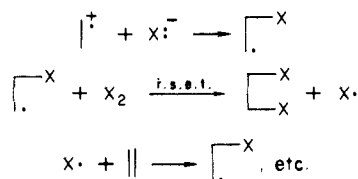
agation steps. The overwhelming importance of solvent in these reactions is illustrated by Harmony's results when the reaction is performed in acetonitrile.<sup>705</sup> In this solvent, the reaction is first-order in dihydropyridine, whereas the studies performed in methanol as solvent give a kinetic order in dihydropyridine that ranges from 1.2 to 1.4. J. A. K. Harmony explains this observation by a difference in the nature of the main termination step: in methanol, this would involve the coupling of trichloromethyl radicals, whereas in acetonitrile a cross coupling (pyridinyl + trichloromethyl) would be preferred. Whatever the reason, these results draw the attention to some difficulties to expect when a precise kinetic treatment of these reactions is attempted and to the importance of solvent choice in the study of photoelectron-transfer catalysis. Other donors (carbanions,<sup>778a,1154</sup> enamines<sup>695a</sup>) can enter into chain reactions when opposed to appropriate CX<sub>n</sub>Y<sub>4-n</sub> acceptors, but the factors affecting the border between chain and nonchain mechanism are not yet totally clarified (see, however, ref 693 for a successful attempt in this direction for thermal reactions). Another unanswered problem is that of the frontier between ionic<sup>680b,690</sup> and radical chains<sup>692</sup> in these reactions.<sup>695c</sup>

(3) *Radical Halogenation of Olefins.* Although addition to olefins is usually not considered as an oxidative addition, it falls in line with the oxidative addition that we treated in the preceding section. This does not come as a surprise if one considers both reactions in terms of generalized donor-acceptor interactions. Both olefins and organometallics create a "free valency" in their own structure when they react with an electrophilic center; then, if a leaving group is released in the medium, one would have good chances to react with this "free valency":



As such, these generalized donors differ from the other ones (RO<sup>-</sup>, RS<sup>-</sup>, C=S, CNR<sub>3</sub>) for which the first act of electron donation does not create an obvious activation in the donor toward the released group. The coexistence of both radical and ionic pathways in the halogenation of olefins is a well recognized phenomenon,<sup>706,707</sup> as it is also known that photochemical and thermal radical halogenations can display experimental features corresponding to very long chains. Furthermore, charge-transfer complexes between olefins and halogens have been repeatedly reported<sup>39b,708-710</sup> and E. A. Shilov<sup>708</sup> proposed some years ago that they can play an active role in the very act of halogenation. On the other hand, the question of CTC as active intermediates vs. inactive bystanders in the reaction has long been debated, and a lucid discussion of this point is given for electrophilic substitutions in ref 172b and 509. To make easier the discussion of photoelectron-transfer catalysis applied to the halogenation of olefins (Scheme XXI), we first give a putative photoelectron-transfer mechanism and will then discuss its limitations.

A more probable variation involves the following steps after the escape from the cage:

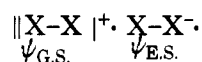


We take for granted that the participation of CTC in halogenation has been "demonstrated" by Dubois,<sup>709</sup> Sergeev,<sup>710</sup> and, more recently, Kochi.<sup>509</sup> Among the most compelling evidences, one can cite the measurement of negative temperature coefficients and the IR evidence for CTC between propene and Cl<sub>2</sub> at 70 K before their reaction at 80 K.<sup>716,717</sup> We therefore address the only question: Can the scheme of electron-transfer catalysis rationalize the competition between polar and radical paths?

Experimental results which agree with this scheme are the following:

In the competition between ionic and radical mechanisms<sup>718,719</sup> the radical mechanism is favored by high concentrations of olefins.<sup>720a</sup> This can be understood if one admits that a bromine radical escaping from the cage has several possible fates<sup>712,721</sup> (reaction with Br<sub>2</sub>, reaction with SH, reaction with the olefin); only the latter goes to products by a chain mechanism. Obviously, increasing the concentration of olefin increases the probability of trapping the escaped Br<sub>2</sub> radical.

X-ray diffraction has established that the formation of complexes involving halogens is associated with an increase in their internuclear distances.<sup>722,723</sup> This falls in line with a representation of the ground-state charge-transfer complex bearing some contribution of the excited state:



In the excited state, part of the electronic population of the  $\pi$  cloud is transferred to the antibonding  $\sigma^*$  orbital of X<sub>2</sub> leading to a weakening of this bond.<sup>724,725</sup> It is important to realize that the thermal and photochemical patterns of reactivity are correlated. Hush<sup>168</sup> explains the basis for this correlation in a paper dealing with inorganic mixed-valence compounds (see section I5).

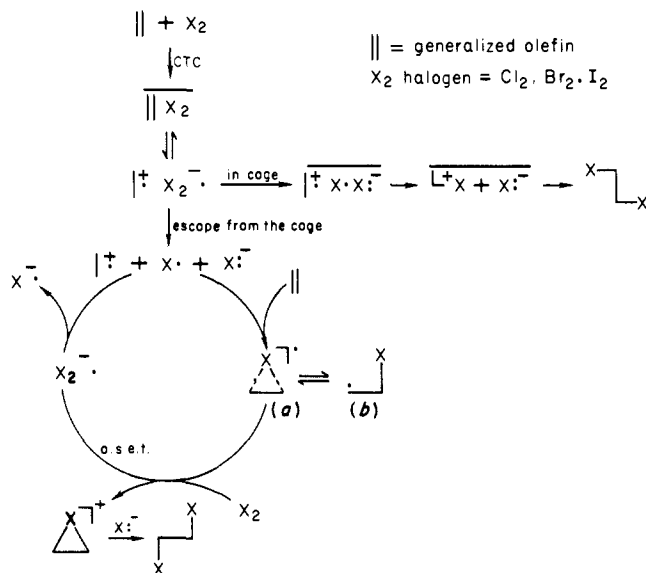
Halogenation is sensitive to steric effects.<sup>726,727</sup> This fits with an i.s.e.t. for which Kochi recently demonstrated the importance of steric effects in contrast with what is observed for outer-sphere electron-transfer mechanisms.

In the photochemical bromination of olefins, quantum yields decrease from 10<sup>3</sup>-10<sup>4</sup> to 10 when dissolved O<sub>2</sub> is present.<sup>728</sup>

Toluene, which is stable towards short-term action of bromine, reacts with the latter in the presence of an unsaturated compound.<sup>729</sup> This is a clear example of molecular assisted homolysis<sup>711,730</sup> whose connection with electron transfer has been emphasized several times.<sup>42,697,731</sup>

The phenomenon of entrainment, which was clearly evidenced with S<sub>RN</sub>1 type mechanisms,<sup>314,315</sup> is described in the chlorination of various substrates. Akopyan<sup>732</sup> observed that the radical chlorination of alkynes induces benzene or tetrachloroethylene to enter into chlorination. T. D. Stewart<sup>729,733,734</sup> demonstrated a long time ago that the chlorination of aromatic and saturated

Scheme XXI



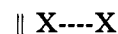
|| = generalized olefin  
X<sub>2</sub> halogen = Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>

<sup>a</sup> This form for trans stereospecific addition.<sup>713-715</sup>

<sup>b</sup> This form for weak stereoselectivity.<sup>711,712</sup>

hydrocarbons may be induced by addition of alkenes (see also ref 720).

When radical and ionic paths compete in a homogeneous series of alkenes, the participation of the radical path increases in the order<sup>735</sup> Cl<sub>2</sub> < Br<sub>2</sub> < I<sub>2</sub>. Three explanations may be offered to this pattern; all three possibly participate. The first one is that the transition state of electron transfer is looser with I<sub>2</sub>; by looser we mean when the average distances between nucleus in the system



are farther away from equilibrium values (e.g., X-X or C-X) for the weakest bond<sup>724</sup> (dissociation energies at 298 K in kcal mol<sup>-1</sup>: Cl<sub>2</sub> = 57.9, Br<sub>2</sub> = 46.1, I<sub>2</sub> = 36.1). Therefore, the probability of escaping from the cage of solvent is greater. The second explanation is more speculative and rests on the retro-CIDNP hypothesis that we formulated elsewhere.<sup>42</sup> It supposes that because of the increasing values of L-S coupling constants in the series, Cl, Br, I, the probability of singlet → triplet transition in the radical pair is increased. As triplet states usually display a greater tendency toward escape from the cage, the radical pathway should be favored for higher L-S values. The third explanation rests on the lifetime<sup>736</sup> of the X<sub>2</sub>· formed after the first electron transfer: the longer their lifetime, the greater their chance of escaping from the primary cage and, therefore, to react according to the radical pathway. Unfortunately, their relative overall stability results from the combination of thermodynamic factors and kinetic (reactivity toward R-CH-CH<sub>2</sub><sup>+</sup>) considerations not easy to disentangle at the present time. It may be noticed that there is apparently no participation of external olefins in the "extraction"<sup>737</sup> of the radical from the original cage. It is indeed recognized that halogen atoms form complexes with organic donors,<sup>738,739</sup> the stronger ones being observed with the atoms of higher electron affinity (i.e., Cl > Br > I). It follows that if olefins were to participate in the "extraction" of the radical from the cage the increasing order of radical

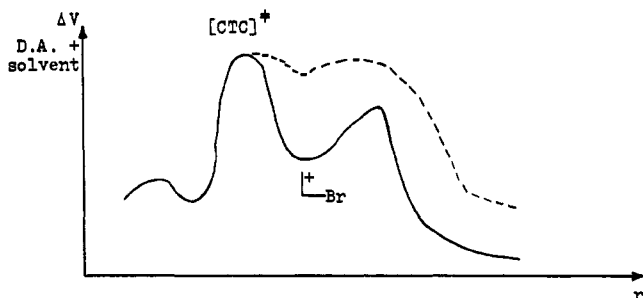


Figure 15. [CTC]\* means a representation of the D.A. interaction rather close<sup>745</sup> to D<sup>+</sup>·A<sup>-</sup>.

participation would be just the opposite of the one actually observed.

Photochemical stimulation favors the radical channel when present. For example, V. L. Heasley<sup>712</sup> observed that the bromination of butadiene at  $-15^{\circ}\text{C}$  leads to higher radical participation with illumination than with safe light. The effect is not totally unambiguous, but the production of *cis*-1,4-dibromo-2-butene and the quantities of formation of ( $\alpha$ -bromoethyl)benzene (ethylbenzene being the solvent of reaction) both converge to suggest an increasing participation of the radical path. Two explanations can be offered to rationalize this observation. The first one is simply that photochemical excitation trains a direct homolysis of some Br<sub>2</sub> molecules which then initiate a chain reaction. The second is that in the electron-transfer-catalyzed scheme the photochemical excitation either leads to higher S-T mixing or generates excited radical pairs whose return to the ground state is accompanied by an excess of translational energy favoring the escape from the cage. Much work is required to clarify this point. In any case, there is no need to overemphasize the importance of electron-transfer catalysis in photochemical processes, and we must remember that some cases of apparently molecular-assisted homolysis were in fact "inadvertently effected homolysis".<sup>740</sup> This could be the case for many photochemically induced halogenations, particularly when they are realized with olefinic substrates not especially prone to enter into CTC<sup>706</sup> or under conditions that favor the homolytic dissociation of X<sub>2</sub> bonds.<sup>741</sup> The quantum yields of I<sub>2</sub> homolysis<sup>744</sup> are very close to 1, the rate of dissociation is very high, and the subsequent fate of radical rather elaborated.<sup>743</sup>

The last experimental point relevant to the problem of ionic vs. electron-transfer-catalytic paths of halogenations is provided by the effect of olefin structure on this dichotomic pattern. For alkylated olefins undergoing spontaneous initiation, Poutsma<sup>719,742a</sup> has demonstrated that the radical path is preferred for linear olefins (terminal and 1,2-disubstituted) but that the polar process largely dominates the reaction for olefins with branching at the double bond. 1,1-Dialkyl olefins can still partially be induced to react through the radical channel by external illumination. Tetraalkyl olefins, however, exclusively react by the polar mechanism even under illumination. A possible rationalization of these observations within the ionic electron-transfer-catalytic pathway can be provided using the Sergeev scheme of potential energy along reaction path (Scheme I in ref 39b) and extending it to a two-dimensional representation as shown in Figure 15. At the col on the potential energy surface of the system

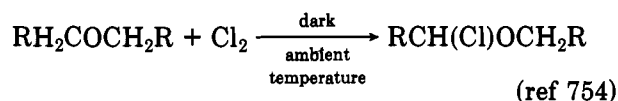
D.A. + solvent the [D<sup>+</sup>·A<sup>-</sup>] couple has the choice between two valleys, one going to <sup>1+</sup>X and the other going to escape from the original cage. If the path descending to the valley <sup>1+</sup>X is the steepest (stabilized cation), the system has a natural propensity to follow this way.<sup>746,747</sup>

Among the other oxidative additions to olefins which at least partially display characteristics of electron-transfer-catalyzed processes we can cite: The addition of (SCN)<sub>2</sub> to alkenes and alkynes.<sup>748,749</sup> The reaction of bromo azides with olefins.<sup>750,751</sup> The reaction of 2,3-pentadiene<sup>752</sup> or 2-butyne<sup>753</sup> with *tert*-butyl hypochlorite.

Caution should be exercised, however, before any hasty choice between direct<sup>740</sup> and indirect homolysis,<sup>42</sup> we give these examples with the main purpose of providing the physical chemists with a set of examples large enough to include appropriate systems allowing the performance of the crucial pulse radiolysis and flash photolysis experiments needed to positively identify the actual intermediates in these reactions (for example, X<sub>2</sub><sup>-</sup>). This identification would not even give the last word, as such, because the chemistry of these radical anions is rather complex.<sup>736</sup> Activation toward electron transfer by Lewis acid complexation of the halogen (section VII) may still increase this complexity.

(4) *Halogenation of C-H Bonds*. In the range of donor ability the C-H bond ranks still lower than olefins. Contact charge-transfer complexes have nevertheless been recognized between alkanes and iodine.<sup>684</sup>

These could possibly explain within an electron-transfer-catalytic approach reactions such as:

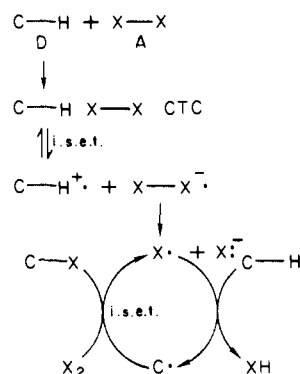


(ref 754)

We must, however, stress the point of the high uncertainty associated with an electron-transfer mechanism if only redox properties of the donor and the acceptor are considered. If such a mechanism was to be adopted, it would heavily rely upon a positive role of the charge-transfer complex and possibly also on the formation of highly stabilized radicals.<sup>281,282</sup> The electron catalytic scheme for these cases would be that shown in Scheme XXII.

Here again, more short time scale spectroscopic works are clearly needed to delineate what, respectively, pertains to chains induced by direct homolysis<sup>740</sup> and to chains induced by single electron transfer.<sup>42</sup> It seems that in this field of molecular assisted homolysis<sup>730</sup> the use of fast spectroscopic methods<sup>766</sup> (flash photolysis, pulse radiolysis) is a compulsory stage to pass through to reach a deeper state of understanding. On the other hand, if we accept the proposition of K. U. Ingold,<sup>740</sup> "when 'spontaneous' radical formation has been reported to occur in the dark, it is improbable the light was rigorously excluded at all stages of sample preparation", the problem becomes manageable only at the highest experimental prices, because it is difficult to imagine any halogenation where reagents have never seen the light or to prove that a solution of halogenating agent does not contain any trace ( $<10^{-8}$ ) of initiating radical. Some organotin and organomercury compounds are reported to react in a radical chain reaction superimposed on the principal electrophilic substitution reaction.<sup>755</sup>

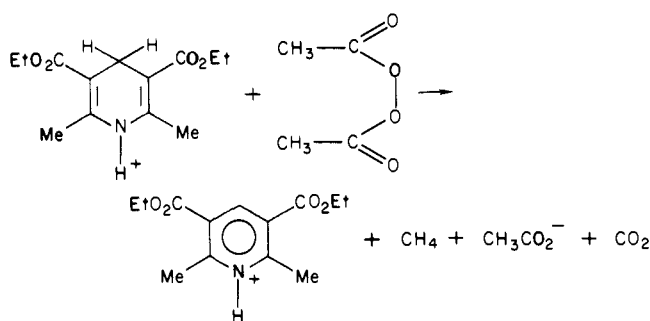
Scheme XXII



#### d. Substitutions on O Center

The reactivity of organic peroxides with some reagents capable of serving as one- or as two-electron donors displays some of the earmarks of electron-transfer-catalyzed reactions: coexistence<sup>756</sup> of both ionic and radical pathways in the same reaction, photostimulation, entrainment.<sup>757</sup> It can be further obscured by entanglement of electron-transfer catalysis with proton-transfer catalysis. We shall therefore retain only the cases where proton-transfer catalysis cannot intervene. More extensive reviews can be consulted for the other cases.<sup>697,758</sup>

For the reaction of 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine with acetyl or benzoyl peroxide at room temperature



E. Huyser<sup>759</sup> proposed the mechanism in Scheme XXIII.

The experimental evidences brought by the authors to support this scheme were:

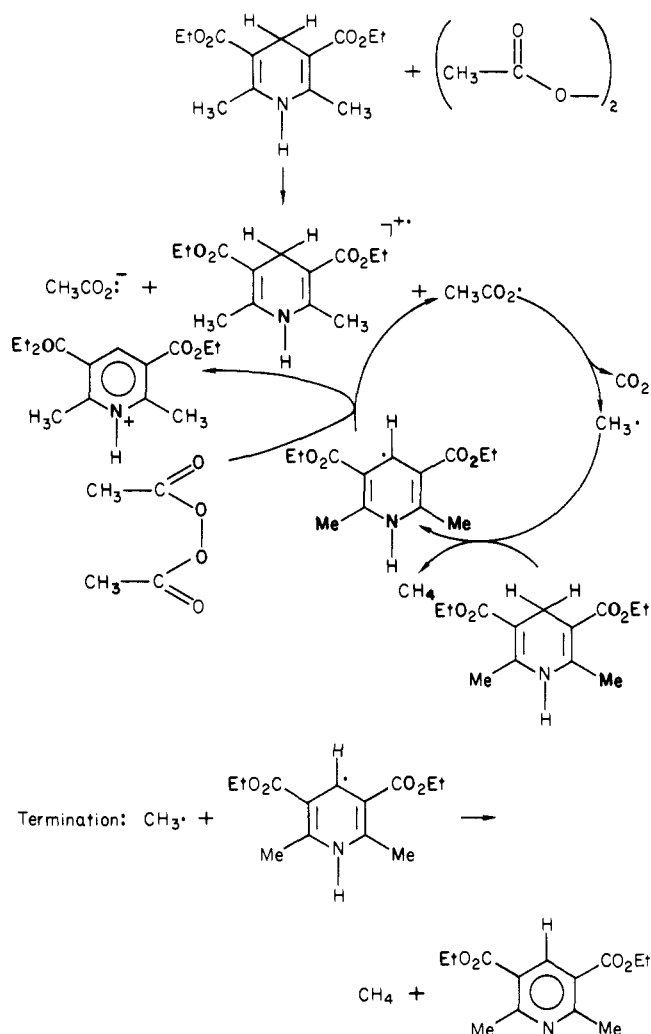
That acetyl peroxide and benzoyl peroxide oxidize the starting dihydropyridine spontaneously at temperatures below those required for unimolecular decomposition of peroxides. This contrasts with the temperature (>50 °C) needed for the same reaction performed with *tert*-butyl peroxide.

The formation of methane and carbon dioxide cannot be explained by a direct hydride transfer from the dihydropyridine.

The kinetic analysis at temperatures ranging from 10 to 40 °C and concentration ratios of  $\text{Ac}_2\text{O}_2$ /dihydropyridine ranging from 200 to 500 showed that the reaction was first-order in each of the reactants.

In agreement with the greater stability of the benzoyloxy radical ( $\text{PhCO}_2^{\cdot}$ ) compared with that of the acetoxy radical ( $\text{CH}_3\text{CO}_2^{\cdot}$ ), the reaction with benzoyl peroxide produced only trace amounts of  $\text{CO}_2$ . In this case, although the observed products could have been explained in terms of a hydride transfer, the kinetic

Scheme XXIII



analysis supported again a free radical chain mechanism.

The chain reaction proposed for the benzoyl peroxide case is given in Scheme XXIV.

At the time of publication the authors did not propose an electron transfer from the initiation of the chain, but later one student from the same group, J. A. K. Harmony, thoroughly discussed this possibility in a review.<sup>697</sup> The data relevant to such a hypothesis are:

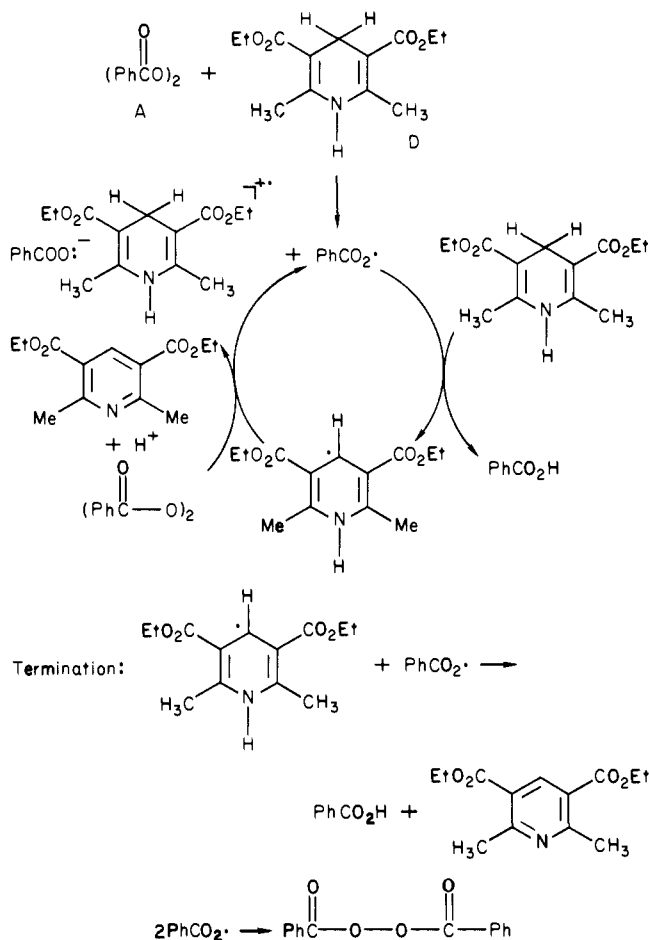
The rates of radical-forming reactions between *para*-substituted *N,N*-diethylanilines and benzoyl peroxide correlate well with Hammett  $\sigma$  values<sup>760</sup> ( $\rho = -2.7$ ). This negative  $\rho$  value fits well with a D-A interaction preceding electron transfer. Remarkably, when the effect of structure on the rate of spontaneous thermal decomposition of  $\text{Bz}_2\text{O}_2$  was investigated,<sup>761,762a</sup> it was found that the data fit closely with the Hammett equation, with the exception of the data on the  $\text{NO}_2$  group.<sup>763</sup>

If the  $\text{H}_2\text{O}_2$  case is discarded, spontaneous initiation seems to occur mainly with peroxides having good electron-acceptor properties: changing  $\text{CH}_3\text{CO}$  to *t*-Bu suppresses this kind of thermal initiation.<sup>697</sup>

Walling and Indictor<sup>764</sup> demonstrated that the *N,N*-dimethylaniline/benzoyl peroxide system is more efficient in initiating styrene polymerization at 0 °C than at 80 °C. According to G. B. Sergeev's criteria,<sup>716</sup> this suggests the participation of CTC in the initiation reaction. Such complexes have indeed been observed in



Scheme XXIV



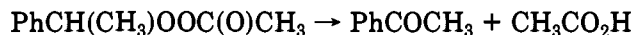
the reaction between *N,N*-diethylaniline and benzoyl peroxide in chloroform<sup>765</sup> and benzene.<sup>763</sup> They are, however, not necessarily involved in *all* reactive D.A. interaction peroxides. Schuster<sup>766</sup> recently discarded them in the reaction between olefins and phthaloyl peroxides.

Pobedimskii and co-workers<sup>767</sup> detected ESR signals attributed to the radical cations ( $R_3N^+$ )<sup>•</sup> when they mixed primary, secondary, or tertiary aromatic amines with benzoyl peroxide or dicyclohexyl peroxydicarbonate at room temperature in various solvents (toluene, DMF, acetone, acetonitrile, THF, dioxane, acetic acid, and perchloric acid). Protic solvents such as acetic acid seem to be more appropriate for observing these radical cations. Flash photolysis was also used to evidence these intermediates.<sup>766,768</sup>

It should be clear that, although for obvious reasons of relevancy we concentrate on the radical aspect of this reaction, the  $S_N2$  type mechanism coexists probably:<sup>764,769</sup> depending on the structure of the donor and the acceptor and on the medium, the general scheme could evolve from a typical  $S_N2$  type of mechanism to a typical radical chain mechanism with a continuum<sup>43</sup> of possibilities. This is indeed a characteristic of electron-transfer-catalyzed reactions, and the actual problem is now to evaluate the participation of each contribution.

More recently, G. Schuster and co-workers investigated thoroughly the reaction of phthaloyl peroxide with a variety of compounds capable of reacting as one- or two-electron donors.<sup>766</sup> They established that the rate-limiting step is the transfer of one electron from

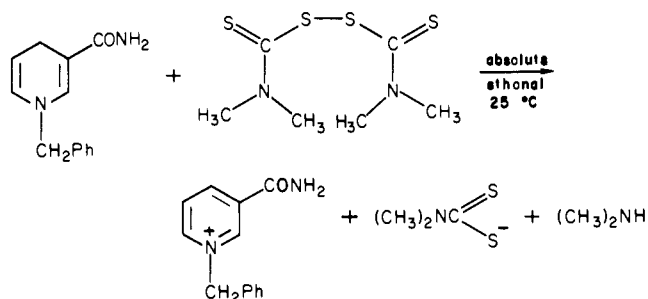
the reactant to the peroxide. The most interesting information brought by this work originated from nanosecond pulsed laser spectroscopy results. After a flash excitation ( $\approx 10$  ns) of a mixture of pyrene (Py) and phthaloyl peroxide in an acetonitrile solution, they observed the absorption spectrum of  $Py^+$ . The rate of the electron transfer between the singlet  $Py^*$  and the peroxide was found to be diffusion limited ( $k_2 = 1.67 \times 10^{10} M^{-1} s^{-1}$ ); as a consequence, a considerable quantity of transient may be recorded only 140 ns after the pulse. With anthracene singlet the reaction with the peroxide is essentially instantaneous ( $\approx 15$  ns). These data clearly point out that the photostimulation of electron-transfer-catalyzed reactions of peroxides can be expected to be very efficient. This result, however, does not tell us if a chain develops every time after the triggering acts of electron transfer and escape from the cage. Schuster<sup>766</sup> estimates that in acetonitrile the yield of cage escaped  $Py^+$  (relative to  $Py^{*1}$ ) is 50%, which could be sufficient to initiate a chain. Furthermore, another work by the same author<sup>770</sup> reports the catalytic effect of various donors (phenazines, perylene, rubrene, (diphenylamino)pyrene, 9,10-diphenylanthracene, etc.) on the thermal reaction:



It would therefore be very interesting to obtain quantum yields for the photostimulated reaction. Unfortunately, many published works do not even examine the possibility of a chain reaction and so the problem is only half-solved, because a radical escaping from the cage does not necessarily initiate a chain.<sup>43</sup> Presently, the situation is at this stage for many reactions of peroxides with donors where radicals have been suggested in the thermal reaction. Until now the focus has mainly been about the radical vs. ionic character of the reaction. At this point, we cannot do more than gather (Table XVII) the reactions between peroxides and various donors where radical species intermediates have been proposed; their chain vs. nonchain character remains, however, still to be precised. Voltamperometric<sup>63</sup> and quantum yield studies should help.

#### e. Substitutions on Electrophilic S Center

Until recently there were not many examples of electron-transfer-catalytic reactions involving the electrophilic center S, although ETC activation of sulfur itself has been devised by Kornblum.<sup>364</sup> Disulfides, however, are good candidates to accept electrons in their low-lying orbitals.<sup>107</sup> A nonchain radical mechanism was proposed for the reaction:<sup>789</sup>



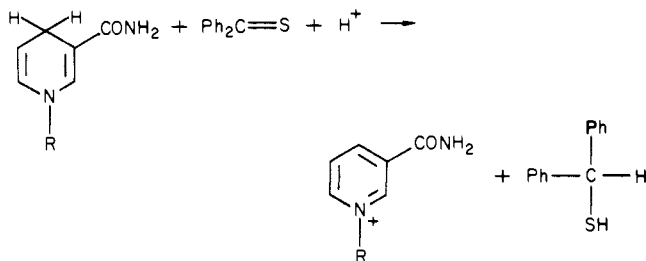
J. A. K. Harmony<sup>697</sup> wonders if a chain mechanism falling in line with the one described for peroxides

Table XVII. Some Examples of D-A Interaction Involving Peroxides as Acceptors and Where Radical Species Have Been Proposed<sup>a</sup>

donor	acceptor	technique	ref
styrene	cyclohexyl hydroperoxide	kinetics	771
	<i>tert</i> -butyl peroxide	kinetics	772, 773
	cumene peroxide	kinetics	773, 774
<i>trans</i> -4,4'-dimethoxystilbene	<i>m</i> -bromobenzoyl peroxide	kinetics, scavengers	775
<i>trans</i> -4,4'-dimethoxystilbene	<i>m,m'</i> -dibromobenzoyl peroxide	isotopic labeling stereochemistry	776
cyclohexene	acetyl peroxide	scavengers	777
9,14-dimethyl-9,14-dihydrodibenzo[ <i>a,c</i> ]phenazine	1-phenylethyl peroxyacetate	chemiluminescence, kinetics	770
acceptor itself	<i>tert</i> -butyl alicyclic percarboxylates	kinetics	779
dimethylaniline, tritolyamine	benzoyl peroxide	scavenging	780
I:·	persulfate	acceleration by Cu <sup>2+</sup> and Fe <sup>2+</sup>	781
I:·	benzoyl peroxide		782a
trialkyl phosphites	hydroperoxides	scavengers, chemiluminescence	758
ethylithium	di- <i>tert</i> -butyl peroxide	CIDNP	783
acceptor itself	peroxy esters of sulfonic acids	explodes	784
Et <sub>3</sub> SnH	benzoyl peroxide		785, 787
(PhS) <sub>2</sub> NH	benzoyl peroxide	kinetics, scavengers	786

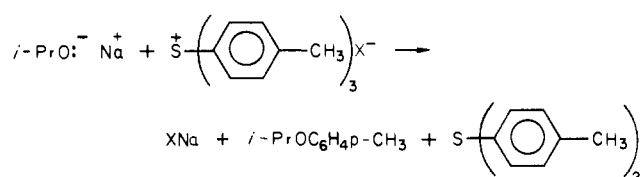
<sup>a</sup> This does not necessarily mean that ETC is involved; in most cases further studies are needed to settle this point, but in one case at least (given as a warning, ref 786) the proposed mechanism definitely differs from the ETC scheme. For other recent examples, see ref 699b, 700a, 720b, 742b and references cited therein.

(section IIIId) could apply to this reaction; the same question holds for the cleavage of diphenyl disulfide by *N,N*-dimethylaniline.<sup>790</sup> Both reactions occur spontaneously in the dark; measurement of quantum yields in the photostimulated reaction could help answer the question. The inherent difficulty<sup>791</sup> of separating the direct homolysis from the electron-transfer-induced one would, however, complicate the interpretation of experimental results. That the subject is important and deserves further study is attested by the high citation index still associated with the early work by Westheimer and Abeles<sup>792</sup> on the reduction of thiobenzophenone to benzhydryl mercaptan by 1-benzyl-1,4-dihydronicotinamide (see section III8).

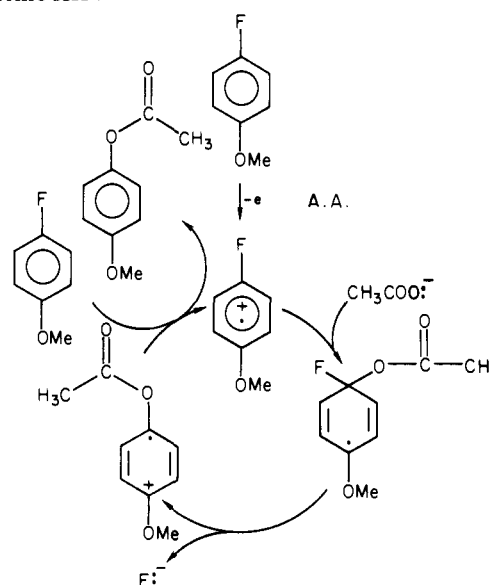


The most urgent task for this kind of reaction is to experimentally delineate the structural and medium factors which induce the reaction to follow a radical or anionic channel.

Besides these putative examples (see also ref 793-795), an actual example of electron-transfer substitution on S has recently been proposed for the reaction:



The preliminary form of the publication<sup>796</sup> precludes critical discussion of the results.

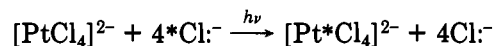
Scheme XXV<sup>a</sup>

<sup>a</sup> A.A. = associative activation.

## 2. Oxidatively Activated Nucleophilic Substitutions

### a. Inorganic and Organometallic Examples

In the first paper of this series,<sup>42</sup> we proposed that oxidative ETC substitution was indeed feasible as suggested by the early example provided by H. Taube:<sup>552</sup>



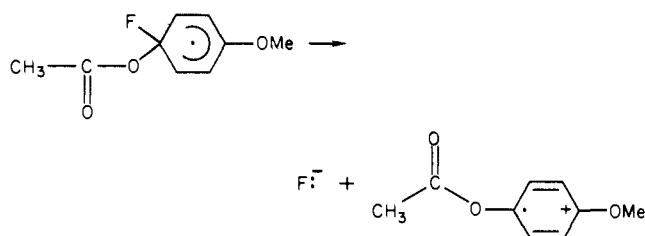
Not enough data are available to decide if the oxidation takes place directly on the square-planar complex or if it occurs on a five-coordinated Pt<sup>II</sup> complex formed by addition of Cl<sup>-</sup> on Pt<sup>II</sup>. In any case labile Pt<sup>III</sup> intermediates must play a crucial role. This class of reaction deserves further study because of its implications for the general class of photorearrangements and photo-substitutions of square-planar complexes.<sup>840a</sup> Kochi recently reported a case of anodic ETC ligand substi-

tution of metal carbonyl ( $M = W, Mo, Cr$ )<sup>877</sup> in line with previous observations by Nasielski.<sup>1108</sup>

### b. Organic Examples

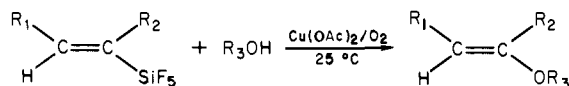
The first organic example was provided by Cornilisse,<sup>539</sup> but it was buried into a photochemical publication where the emphasis was elsewhere; its cycle was given in section III1a. The chain character of the process was proven by the values of quantum yields (up to 7).

More recently L. Ebersson and L. Jönsson<sup>249,762b</sup> specifically drew attention to such oxidative chain substitutions independently predicted by Alder<sup>797</sup> and one of us<sup>42</sup> and christened<sup>797</sup>  $S_{ON}2$  (Scheme XXV). The identified examples display rather short chain lengths. One interesting point covering organic, organometallic, and inorganic chemistry must be mentioned. In this cycle, the step:



corresponds to a very general property of paramagnetic compounds. It involves an intramolecular decomposition generating a paramagnetic compound and a generalized acid of bases. Examples of such intramolecular decompositions may be found in organic, inorganic, and organometallic chemistry (see Table V). A difference between inorganic and organic examples is that the inorganic example could possibly be shown to be  $S_{ON}1$  ( $Pt^{III}$  complexes are highly labile), whereas the organic example has been christened  $S_{ON}2$  (F is considered a very poor leaving group). More work is needed to precise this point.

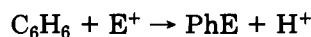
The solvolytic cleavage of alkenylpentafluorosilicates catalyzed by copper(II) acetate<sup>798</sup> in the presence of  $O_2$ :



advocates photochemical attempts in the same direction. Type III photoelectron-transfer catalysis should be tried to induce photosolvolytic.<sup>799</sup> Pac and Sakurai recently reported that unsubstituted aromatic hydrocarbons undergo photocyanation with NaCN in the presence of *p*-dicyanobenzene.<sup>782b,1126</sup>

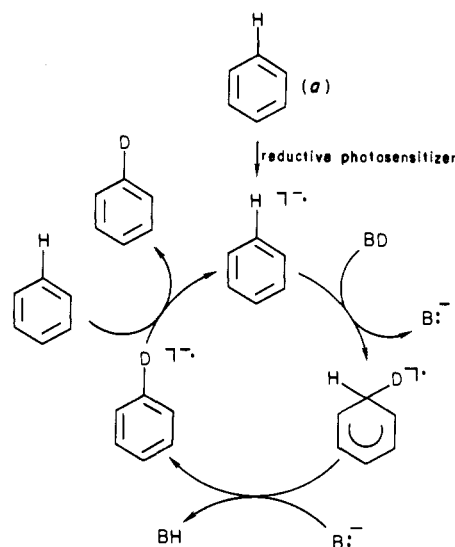
### 3. Reductively Activated Electrophilic Substitutions

Electrophilic substitution of aromatic substrates



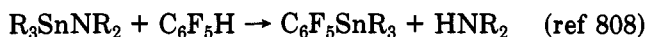
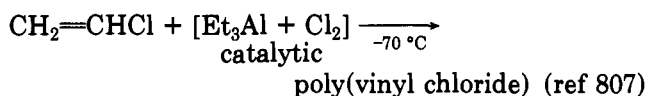
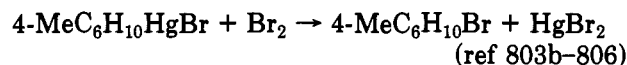
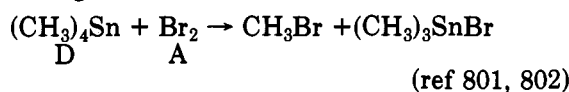
bears a close relationship to the addition of halogens to olefins if aromatics and olefins are considered to be generalized donors in the D-A interaction.<sup>239,240</sup> We have seen (section III1c3) that Shilov, Dubois, and Sergeev conferred an active role to EDA complexes in the very act of activation for these reactions. More recently, Fukuzumi and Kochi<sup>509</sup> (for the special case

Scheme XXVI

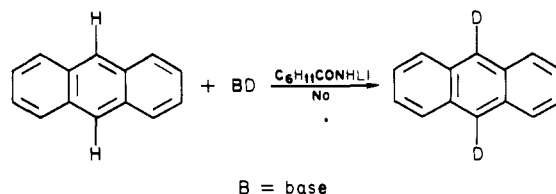


$a_{C_6H_6}$  stands for appropriate aromatic or heteroaromatic compound.

of nitrations, see also ref 800a,b, and for polyfluorinated aromatics, see ref 800c) extended this approach to electrophilic substitutions of aromatics after a thorough quantitative study of transient charge-transfer absorption band. For a series of benzene derivatives interacting with electrophilic substrates, they discovered a linear relation between their relative reactivities ( $\log k/k_0$ ;  $k_0$  rate for the benzene) and the relative CT transition energies  $\Delta h\nu_{CT}$ . This observation and correlation of data originating from previously unconnected fields (cyclic voltammetric peak potentials, gas-phase ionization potential, pulsed laser spectroscopy) led them to describe the activated complex for electrophilic aromatic substitution as an ion pair. These results strongly suggest that many reactions described as electrophilic substitution reactions and for which chain mechanisms have been proven could be viewed in a fresh light within the ETC scheme:



More recently Alder<sup>797</sup> suggested that some hydrogen-deuterium exchange reactions.<sup>809</sup>



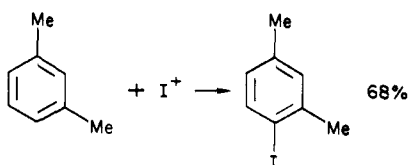
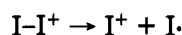
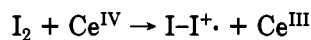
B = base

may involve electron-transfer catalysis. This points out an interesting possibility of electron-transfer photocatalysis (Scheme XXVI). Depending upon the effi-

ciency of the second electron-transfer step, either class III (one photon for every deuteration) or class II electron-transfer-photocatalyzed reaction could be designed.

#### 4. Oxidatively Activated Electrophillic Substitutions

T. Sugiyama<sup>810</sup> recently described the mild iodination of polymethyl- or polymethoxybenzenes by I<sub>2</sub> under the catalytic influence of hexanitratocerate (25 °C). Only aromatics bearing electron-donating substituents undergo this reaction; iodination shows an ortho-para orientation and occurs only on intracyclic carbons. This pattern of reactivity gives a hint of a catalytic cycle where the active agent would be a cationic halogen species:

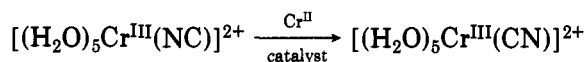


Such a reaction prompts attempts to realize electrophilic substitutions by class III electron-transfer catalysis as does the set of Kumada's reports on the oxidative cleavage of C-Si bonds in organo pentafluorosilicates.<sup>810b</sup>

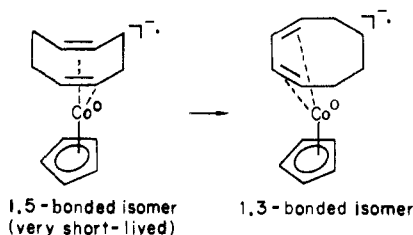
#### 5. Isomerizations

##### a. Regioisomerizations

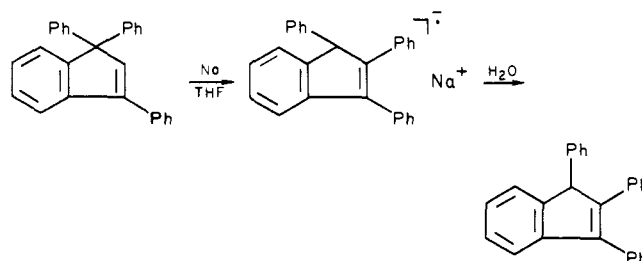
We did not find any examples of photochemical regioisomerizations occurring with high quantum yields. There is, however, no obvious reason why this kind of reaction should be rebellious to photochemical electron-transfer catalysis as attested by<sup>811</sup>



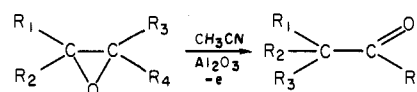
and also by the following reported observations: the isomerization reaction<sup>812</sup>



is many orders of magnitude faster for these radical anions than for the corresponding neutral species. The anion radicals of 1,1-disubstituted indenenes are especially prone to phenyl migration.<sup>813,814</sup> The foregoing reaction is of special interest as it shows that drastic accelerations in sigmatropic rearrangements could possibly arise by single electron-transfer activation. If generalizable,

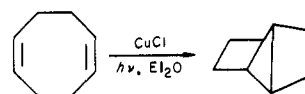


it could throw a new light on isomerization reactions of olefins catalyzed by alkali metals.<sup>815</sup> Simonet recently reported an anodically electron-transfer-catalyzed isomerization of epoxides into ketones:<sup>816</sup>

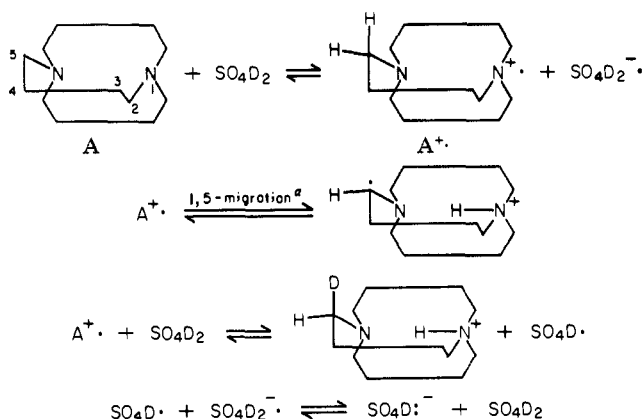


and Alder reported an unusual oxidatively induced H migration (Scheme XXVII).<sup>803a</sup> In this reaction SO<sub>4</sub>D<sub>2</sub> plays a double role: in the first step, it is the oxidant that triggers the reaction activating the substrate towards an internal S<sub>H</sub>2 reaction; in the other steps, it provides a D atom. The first role is catalytic and the second stoichiometric.

A. Commeyras<sup>819</sup> recently reported that the isomerization of *n*-butane into 2-methylpropane in superacidic medium may be catalyzed by anodic oxidation. All these results suggest that in photochemistry the methods for promoting isomerizations should be searched in the direction of redox photosensitizers. Photocatalyzed olefin isomerizations sensitized by catalytic amounts of W(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>,<sup>817,818</sup> or Cu<sup>I</sup><sup>820,821</sup> salts have been reported; they usually involve a preformed metal-olefin complex in the mechanism of sensitization. Srinivasan<sup>823,824</sup> reported, however, a photosensitized reaction of rearrangement where no appreciable formation of complex seems to precede the photochemical reaction and set forth carbenium type intermediates (compare with ref 822):

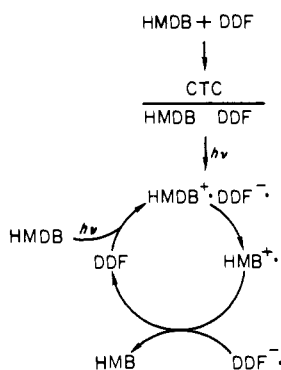


Kutal<sup>820</sup> proposed three classes of Cu(I) sensitization processes: class 2 and 3 in his classification could in fact be considered as potential photosensitized electron-transfer Scheme XXVII



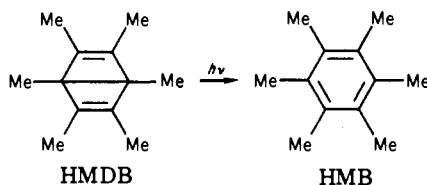
<sup>a</sup> 1,2-migration is also proposed by the authors.

Scheme XXVIII

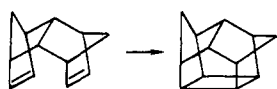


transfer-catalytic examples (section II2c) generating carbenium ions that are the actual intermediates undergoing the rearrangements or isomerizations.<sup>821</sup> Indeed, irradiation of methylenecyclopropane in the presence of catalytic Cu(I)<sup>825</sup> results in a plethora of skeletal reorganization products.

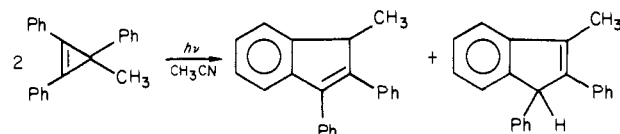
Another fascinating example of sensitized regioisomerization is provided by the reaction:<sup>827a</sup>



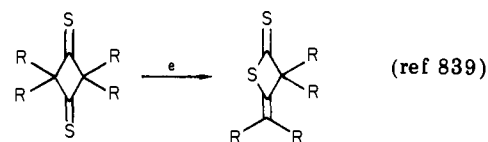
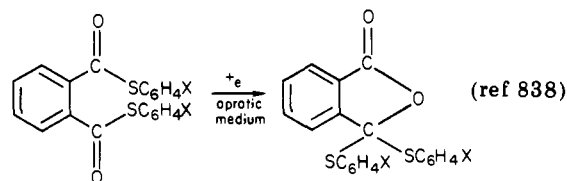
G. Jones and W. G. Becker showed that the highest quantum efficiencies (17) were observed for an excitation wavelength of 366 nm in acetonitrile as solvent of reaction and with diethyl 1,2-dicyanofumarate (DDF) present in the medium as an acceptor (1.5 M per mol of aromatic substrate). The proposed reaction mechanism confirms the earlier Evans idea<sup>828</sup> that provided the first example of such a photosensitized (naphthalene) chain reaction (Scheme XXVIII). Another mechanism of photosensitization (triplet adiabatic) has been proposed by Turro for other sensitizers.<sup>829</sup> This reaction may also be evidenced through exciplexes<sup>830</sup> and displays several interesting features. Contingent upon the solvent, a continuum of situations between chain and nonchain processes are observed;<sup>831</sup> addition of sodium or lithium perchlorates increases the quantum yields, whereas that of sodium acetate or formate decreases it;<sup>828</sup> photoisomerization quantum yields depend on excitation wavelength.<sup>827</sup> The continuum of situations between chain and nonchain processes well explained by G. Jones prompts a careful reexamination of several photoisomerization reactions driven by irradiation of charge-transfer complexes<sup>831-834</sup> to check if under suitable conditions quantum efficiencies greater than 1 may be obtained. G. Jones<sup>827b</sup> recently reported the following 1-cyanonaphthalene-sensitized reaction ( $\phi = 8.4$ ):



The 9,10-dicyanoanthracene-sensitized rearrangement of 3-phenyl-substituted cyclopropenes to indenenes<sup>835,836</sup> also follows the radical cation route:

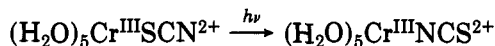


An attractive feature of this rearrangement is the different regioselectivity observed depending upon the presence or absence of redox photosensitizer. The chloranil-photosensitized isomerization of quadricyclane provides an example of the use of CIDNP to study these reactions.<sup>837</sup> The following electrochemical examples of electron-transfer catalysis:



drop a hint that the field of reductive photosensitized electron-transfer catalytic isomerization reactions deserves some exploration.

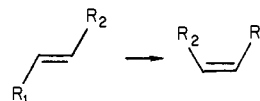
Linkage photoisomerization of metal complexes is illustrated by the following example:



and has been reviewed in detail by F. Scandola.<sup>840a</sup> Although several authors formulated a general radical pair mechanism<sup>841b-843</sup> whose crucial step is an intramolecular electron transfer from the ligand (e.g.,  $\text{SCN}^- \rightarrow \cdot\text{SCN}$ ) to the metal induced by the light (LMCT), it does not seem that redox intermolecular sensitization of this type of regioisomerization has been examined.

### b. Stereoisomerizations

The very simple reaction



or its reverse has given rise to a remarkable amount of experimental and theoretical work as indicated by the number of references treated (211) in the most recent review discussing this topic.<sup>844</sup> Unnoticed electron-transfer catalysis possibly played an early role<sup>845</sup> in the quantitative study of thermal isomerization leading to vastly (>35 kcal/mol) underestimated values of activation energies for these processes.<sup>846,847</sup> Bard clearly established the importance of this type of catalysis for cis-trans isomerization of several olefinic substrates electrochemically induced (Table XVIII). On the other hand, Ashby<sup>848</sup> used the electron-transfer-catalyzed isomerization

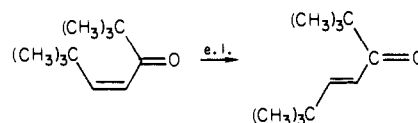
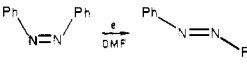
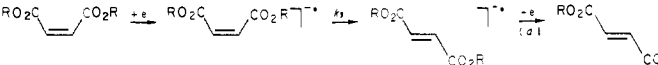
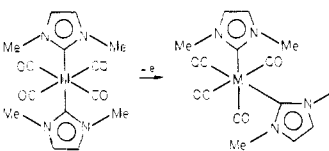
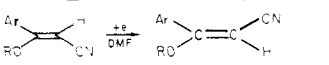
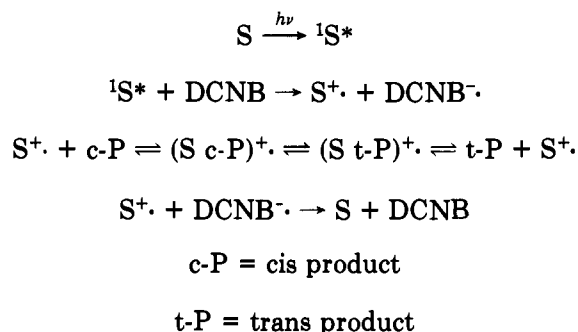


TABLE XVIII. Electrochemical Studies Related to Geometrical Isomerization<sup>b</sup>

reactions	solvent	ref
 	DMF THF	849, 850
<p>equilibrium <math>C^{\cdot-} \rightleftharpoons T^{\cdot-}</math> far faster  <math>(t_{1/2} \approx 5 \mu\text{s})</math> in THF than in DMF  <math>(t_{1/2} \approx 1 \text{ s})</math></p>		851 <sup>d</sup>
<p>R = Me, <math>k_1 = 2.2 \text{ s}^{-1}</math>; R = Et, <math>k_1 = 6 \text{ s}^{-1}</math>; R = <i>n</i>-Bu, <math>k_1 = 6.7 \text{ s}^{-1}</math></p>	DMF	853, 854
		855-857
<p>M = Mo, W<sup>c</sup></p>		
	DMF	857
<p>R = Me, <i>n</i>-Bu</p>		

<sup>a</sup> Step in competition with a rapid dimerization of the radical anion. <sup>b</sup> For a bibliography of conformational changes induced by electron transfer, see ref 840b and 841a. <sup>c</sup> For discussions concerning dissociative versus nondissociative contributions to this mechanism, see ref 860b and 877. <sup>d</sup> Compare with ref 852.

as a probe for detection of SET in Grignard reactions with ketones, and more recently Z. V. Todres<sup>279</sup> summarized some of the stereochemical changes induced by electron transfer in various substituted olefins. We can therefore suspect that class III photostereoisomerizations are feasible. This is indeed the case; Sakurai<sup>312</sup> recently reported an unambiguous example of redox photosensitized stereomutation of 1-phenoxypropene in acetonitrile.<sup>858,859</sup> The reaction does not occur in benzene or ethyl acetate used as solvents, and the coexistence of a sensitizer (S: phenanthrene, triphenylene;  $10^{-2}$  M) and *p*-dicyanobenzene (DCNB;  $10^{-1}$  M) in the medium is necessary for the transformation of the substrate ( $10^{-4}$  M). They proposed the following scheme to rationalize their experimental findings:



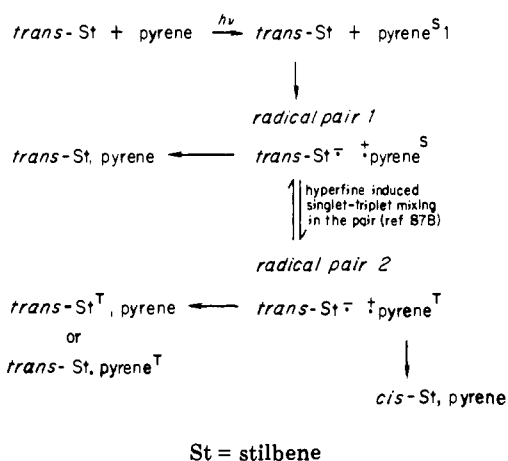
It should be noted that redox-photosensitized isomerization of *trans*- $\beta$ -methylstyrene and *trans*-anethole occurs in either the absence or the presence of isoprene<sup>312</sup> (sensitizer for the triplet mechanism<sup>844</sup>). Other examples of oxidative<sup>860</sup> activation toward stereoisomerization are provided by the chain *cis*-*trans* isomerization of 2-butene induced by irradiation with ionizing radiation in benzene solution at low doses.<sup>861</sup> *cis*-Stilbene<sup>862</sup> isomerizes to *trans*-stilbene under the same conditions in either benzene or cyclohexane solutions with *G* values ( $\approx 210$ ) clearly indicative of a chain mechanism (chain length  $\approx 2000$ ). These authors<sup>862</sup> propose a chain mechanism where the active species is the radical anion of stilbene in contrast with the scheme proposed by Harata.<sup>861</sup> Since both reductive<sup>850,863,864</sup> and oxidative<sup>279,865</sup> activation of double bond

toward stereoisomerization are feasible, the two schemes are formally possible. The fact that carbon tetrachloride and naphthalene (electron scavengers) increase the chain length whereas triethylamine practically quenches the reaction clearly favors the oxidative activation scheme.

At present, the generally accepted<sup>844</sup> mechanism of sensitized photostereoisomerization across a double bond consists of energy transfer<sup>866</sup> between the sensitizer molecules and the olefin; more experiments are needed to clearly delineate the scope of each type of mechanism. This is particularly important when sensitizers<sup>867</sup> such as quinones are used<sup>868-870</sup> and also from the point of view of this review when quantum chain processes<sup>871-874</sup> seem to be involved. The available kinetic data on stereoisomerization of radical anion in the ground state<sup>854</sup> show that the process may be relatively slow ( $10 \text{ s}^{-1}$ ); not much is known, however, about stereoisomerization of radical ions in the excited state. The richness of mechanistic schemes associated with this apparently very simple reaction of configurational isomerization is increased still more by the existence of nonredox photocatalytic reactions induced by transition-metal complexes.<sup>818</sup>

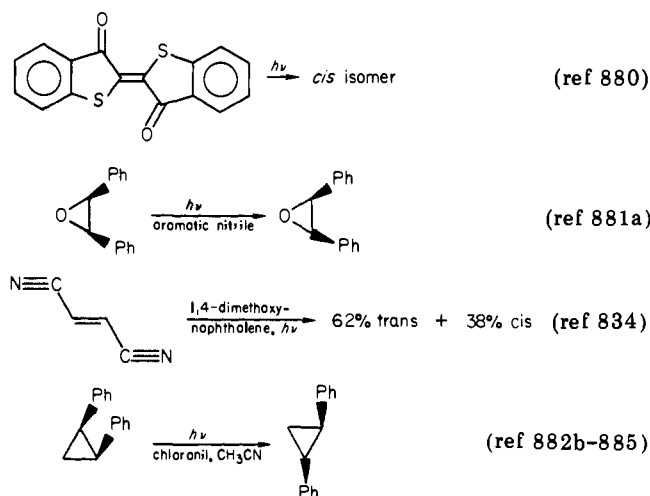
Recently, R. Z. Sagdeev and Y. N. Molin<sup>875</sup> observed CIDNP effects in the sensitized (pyrene, octafluoronaphthalene, benzophenone) photoisomerization of *trans*-stilbene and *trans*-1,2-bis(pentafluorophenyl)ethylene carried out in acetonitrile,  $\text{Me}_2\text{SO}$ , or hexafluorobenzene. They propose that the spin polarization occurs according to Scheme XXIX (see also ref 837 and 876). Dependence of the reaction rate on the intensity of magnetic field indicates that the radical ion path of the *trans*-*cis* isomerization is the main one. One other consequence of these results is to show that if photochemical excitation of a substituted olefin drastically changes the electronic population (intramolecular charge transfer) of the olefinic bond, a stereoisomerization may result. Particularly relevant to this point is Todres' elegant work. This author has shown that while *cis*-4,4'-dinitrostilbene stereoisomerizes in the presence of cyclooctatetraene anion, its isomer *cis*-2,4-dinitrostilbene does not undergo a change in its geom-

Scheme XXIX

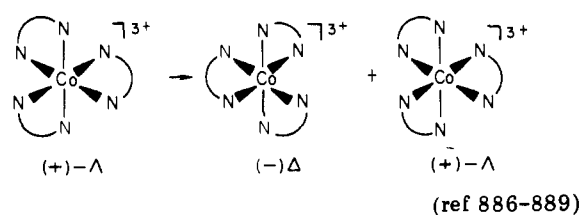


etry. Todres rationalizes this observation by the suggestion that in the second example, the unpaired electron is firmly fixed in one benzene ring and its localization in the double bond is only small.<sup>279</sup>

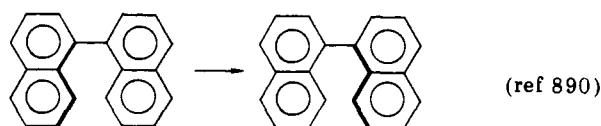
Chemical, electrochemical (Table XVIII), and photochemical results of electron-transfer-induced geometrical isomerization of the following substrates:



show that structural activations induced by single electron transfer are a quite general stereochemical concept. Racemizations such as:

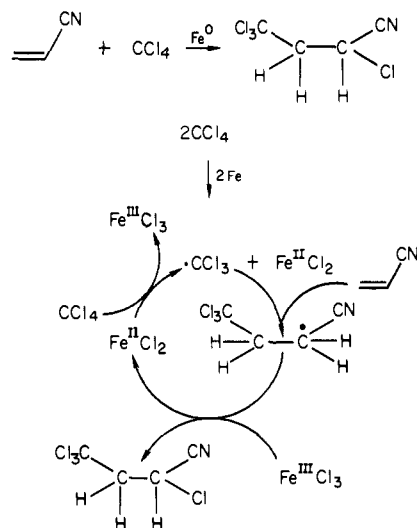


or



still emphasize this point and suggest that many more examples could be found in old references of stereo-isomerization (for inorganic examples, see ref 840). Exciting applications with chiral sensitizers could possibly be devised along this line<sup>888</sup> (section III7).

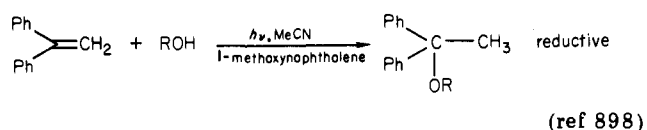
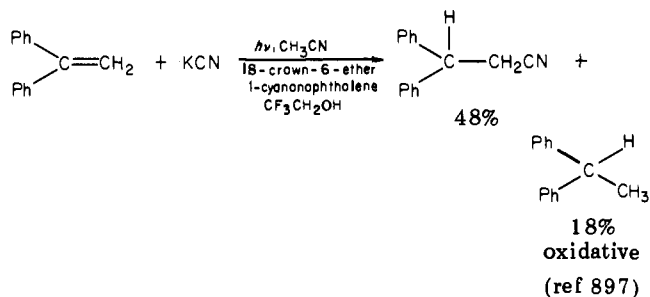
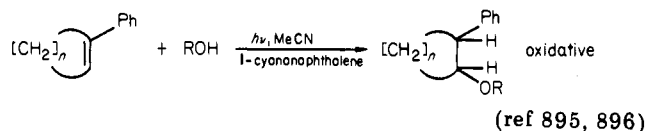
Scheme XXX



## 6. Additions and Polymerizations

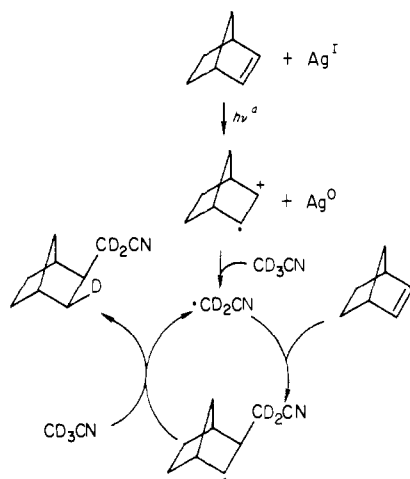
### a. Addition of Substrates Other than Olefins to Unsaturation

F. Minisci's review<sup>891</sup> on free-radical addition to olefins in the presence of redox systems provides various examples (see also ref 317a, 881b, 882a, 892, 902b, and 881c for alkynes) suggesting that photoelectron-transfer catalysis could be used for activating olefins (Scheme XXX). In the foregoing example the initiation step could tentatively be replaced by the photochemical irradiation of a CTC between  $\text{CCl}_4$  and the most appropriate donor<sup>893</sup> in the presence of  $\text{Fe}^{\text{II}}\text{Cl}_2$  and eventually suitably designed ligand.<sup>894</sup> Although this precise type of photoactivation does not seem to have been used yet, Arnold has created several new mild synthetic reactions by oxidative or reductive photosensitization:



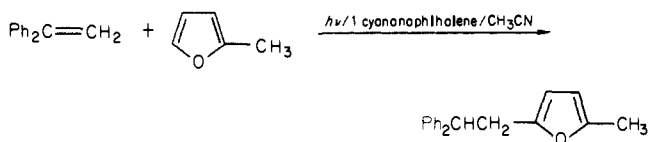
These photochemical reactions present an especially attractive characteristic: with oxidative sensitizer they activate the olefin in an anti-Markovnikov way, whereas the opposite orientation is obtained with reductive sensitizers.<sup>899</sup> Silver chloride photosensitized addition of acetonitrile to norbornene follows the same principle, although the mechanistic schemes proposed by Ar-

Scheme XXXI



<sup>a</sup> Via formation of a complex.

nold<sup>89b</sup> and Lewis<sup>900</sup> differ. This author recently reported<sup>123b</sup> on the photoinitiated addition of acetonitrile or methanol to norbornene and proposed Scheme XXXI. The remarkable 70-fold decrease in the yield of adduct A upon solvent deuteration agrees with the foregoing scheme: abstraction of H(D) from the solvent takes place in both the initiation and chain-transfer steps. An unusual example of addition reaction has been discovered by Mizuno.<sup>903a</sup>

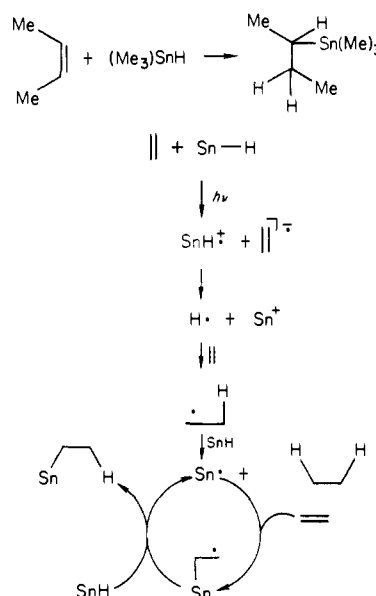


We discussed in another paper<sup>43</sup> the electron-transfer-catalyzed addition of tin hydrides to substituted olefins.<sup>244</sup> Photochemical activation through electron-transfer photocatalysis is needed for olefins nonactivated by electron-attracting substituents (Scheme XXXII).<sup>901</sup> Many more examples of this type may be found in Kupchik's review<sup>902a</sup> on organotin hydrides; they cover reactivity of polyenes, fluoroalkenes, allenes, and alkynes. Hydrostannation of ethynes containing exclusively electron-withdrawing substituents proceeds mainly by an ionic process, in contrast with ethynes containing electron-releasing substituents where the radical chain pathway predominates.<sup>903b</sup> Kochi and Klingler<sup>157a</sup> results drop a hint that much remains to be done in the mechanistic photochemistry of tin compounds,<sup>904</sup> whose synthetic aspects may still be improved by combination of pressure and photochemistry.<sup>927b</sup>

The chemistry induced by ionizing radiations is often of rather delicate mechanistic interpretation.<sup>905</sup> Keeping in mind this restriction, the reading of C. D. Wagner's review<sup>906</sup> about chemical synthesis by ionizing radiation is of rich heuristic value. It shows that a great variety of bonds are indeed possibly added to an unsaturation with interesting chain lengths and provides a challenge for the search of mild photoreactions induced by the appropriate redox sensitizers.

Although  $\alpha,\beta$ -unsaturated compounds may act as electron acceptors, it seems that they are not involved in electron-transfer-catalyzed processes: stoichiometric redox reactions are the main schemes proposed

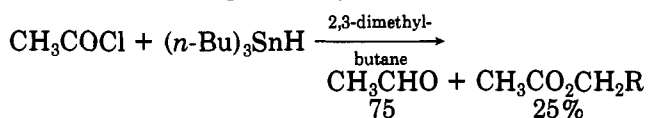
Scheme XXXII



there.<sup>907-909</sup> The photoaddition of alcohol  $\alpha,\beta$ -enones in the presence of  $\text{TiCl}_4$  is believed to involve a metal-assisted and photoassisted electron transfer from the alcohol to the carbonyl within the coordination sphere of the metal ion.<sup>931</sup>

We have seen in section III1c3 that radical chain addition of halogens to olefins could be viewed as class I type of electron-transfer catalysis. Another homopolar unsaturation is provided by the  $\text{N}=\text{N}$  bond. This bond has been shown to behave as a good electron acceptor toward Grignard reagents;<sup>910</sup> the photochemical aspects of this reaction were, however, not investigated, and much is left unexplored in the reaction of this structural block with tin compounds.

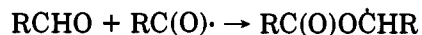
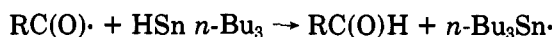
The heteropolar  $\text{C}=\text{O}$  link is well-known for its involvement in acid-base catalysis.<sup>911</sup> Less known are the data on its reactivity relevant to electron-transfer catalysis, most of the described electron-transfer reactions apparently being nonchain.<sup>908,909</sup> There are, however, many examples of electron-transfer chains known with donors such as Grignard reagents<sup>912</sup> and tin hydride.<sup>913</sup>



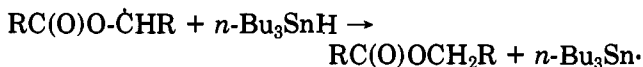
No light is needed, but electron-transfer photocatalysis is probably involved for the reaction of the less reactive esters.<sup>914</sup> Kuivila and Walsh<sup>913</sup> proposed the following propagation steps:



aldehyde formation



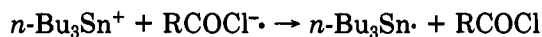
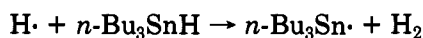
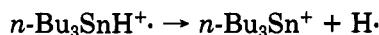
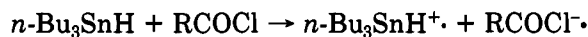
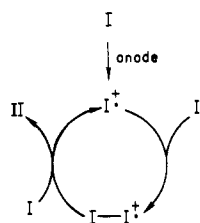
ester formation



Several initiation schemes are possible; among them are



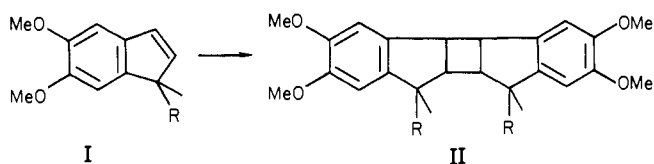
Scheme XXXIII



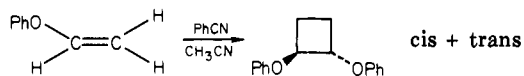
Grignard reagents differ as electron donors in this class of reactions, because it seems that complexation of the carbonyl group<sup>915</sup> is important in the overall reaction. Much photochemical and mechanistic work remains to be done aiming at the exploration of electron-transfer-catalytic schemes for the following heteropolar unsaturations:  $\text{C}=\text{N}^+$ ,<sup>916,917,928a</sup>  $\text{S}=\text{O}$ ,  $\text{N}=\text{O}$ , and  $\text{P}=\text{O}$ .

### b. Cycloadditions

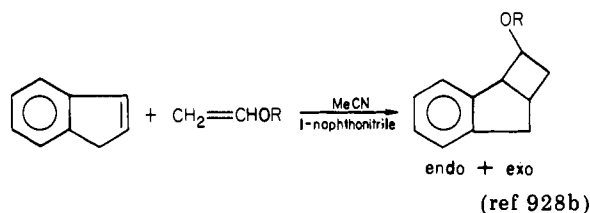
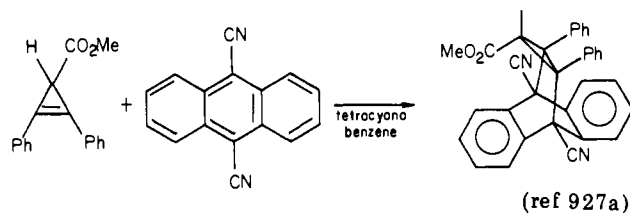
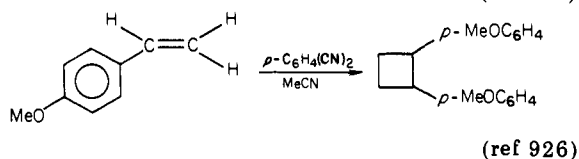
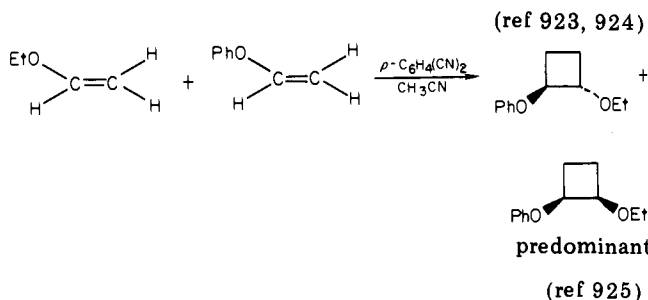
The anodic oxidation of 5,6-dimethoxyindene or 1-*tert*-butyl-5,6-dimethoxyindene in acetic acid leads to a mixture of  $2\pi + 2\pi$  cycloaddition and polymerization products with a low consumption of faradays:<sup>918</sup>



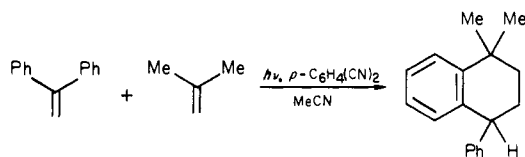
Ebersson proposes a mechanism (Scheme XXXIII) similar to that suggested for  $\text{Fe}^{\text{III}}$  salt catalyzed cycloadditions of *N*-vinylcarbazole.<sup>919-921</sup> These results suggest that appropriate photosensitizers could play the role of homogeneously dispersed anodes. This is indeed the case as shown by the following examples of photochemical cyclodimerization and cross cycloaddition:<sup>922</sup>



Fe and Mn complexes with 2,2'-bipyridyl also sensitize the reaction.<sup>924</sup>



(2e + 4e) cyclodimerizations<sup>926,929,930</sup> and cross cycloadditions are also feasible according to this activation:<sup>932-934</sup>



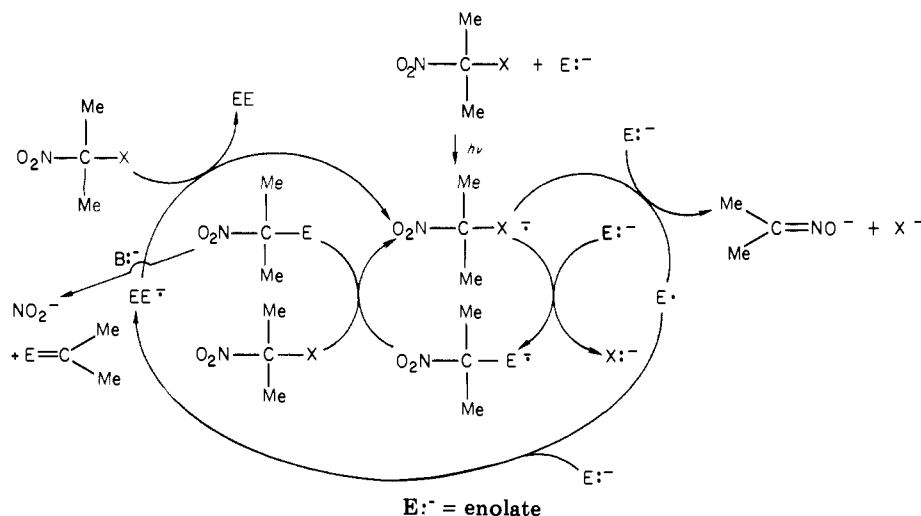
In the photocatalysis of cycloadditions by transition-metal complexes<sup>935-939</sup> it does not seem that the complex acts as an inorganic redox sensitizer. Mizuno's results<sup>924</sup> show, however, that this kind of catalysis is workable.

One can wonder if besides this well-documented class III type of photoelectron-transfer catalysis, the simple class I involving no additional reagent in the medium may occur. EDA complexes have indeed been observed between the reagents of [2 + 2] cycloadditions,<sup>940-942</sup> and the relation between exciplex or excimer formation and subsequent reactivity has been thoroughly discussed by Caldwell.<sup>185</sup> Positive evidence for a chain mechanism following an initial electron transfer are, however, still lacking for [2 + 2] cycloadditions. The relation between this possibility and the proposed hypothesis of exterplexes<sup>176,179,943-945</sup> formation is not yet clarified. This problem is of importance as terplexes seem to be involved in photosynthesis.<sup>946</sup>

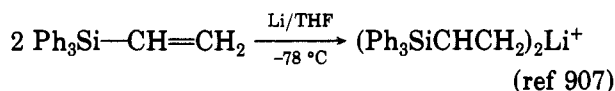
Charge-transfer complexes between reagents have been repeatedly<sup>947a,948</sup> reported in the medium where Diels-Alder reactions occur. Their quantitative study recently led Fukuzumi and Kochi to ascribe an active role to electron transfer in this class of reactions. From the more specific point of view of electron-transfer catalysis it is known that Diels-Alder type polymerizations are feasible<sup>949</sup> and that Bauld<sup>950,951</sup> reported cation radical catalysis in simple Diels-Alder reactions. Photochemical data related to class I photoelectron-transfer catalysis are, however, lacking. The same remark holds for class II photocatalysis despite the existence of the corresponding electrochemical examples discussed in section II2b. Besides the intellectual challenge, these reactions deserve more attention because of their economic importance.<sup>952</sup>

Mechanistic considerations related to the photogeneration of cycloaddition transition metal complex catalysts usually concentrate<sup>74</sup> on the "direct homolysis" scheme as primary photoprocess. The future will tell if in some cases an "electron-transfer-induced homolysis" can be involved.

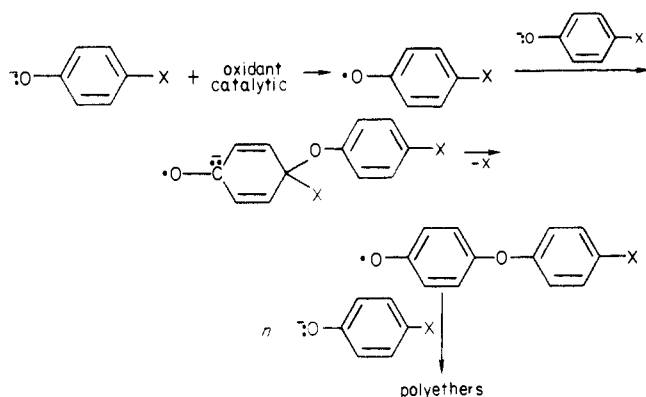
## Scheme XXXIV



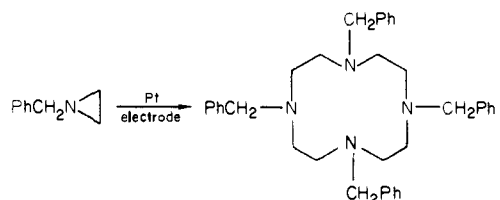
Although we have stressed the oxidative aspects of associative activation of olefins, the chemistry of alkali metal unsaturated hydrocarbons affords reductive illustrations of this activation not yet exploited in photochemistry:

c. Formation of  $\sigma$  Bonds

After the publication of the first paper<sup>42</sup> in this series, B. Saville called our attention to an interesting example of oxidative electron-transfer polymerization leading to the formation of polyethers.<sup>947b,953-955</sup>



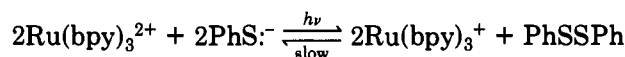
J. Simonet<sup>956</sup> recently described the anodically induced tetramerization of *N*-benzylaziridine:



This author demonstrated that the photochemical counterpart involved catalytic amounts of *p*-toluenesulfonic acid which suggests that, in some apparently acid-catalyzed photoreactions,<sup>957</sup> the acid could in fact act as an oxidant rather than as an acid (cf. ref 958).

Copper and silver salts initiate the photopolymerization of tetrahydrofuran.<sup>959</sup>

Recently G. Russell proposed a chain mechanism Scheme XXXIV for the oxidative dimerization of enolate anions in a reaction induced by a 275-W sunlamp.<sup>543,544a</sup> This scheme represents the overall process associated with the reaction described in section III1a,  $S_{RN}2$  reaction. A step toward class III photoelectron-transfer catalysis has recently been reported by Matsuda:<sup>960</sup> photoexcited tris(2,2'-bipyridine)ruthenium(II) oxidizes sodium benzenethiolate (in  $\text{CH}_3\text{CN}$ ) to its radical which then dimerizes; the formed disulfide is, however, reduced back by  $\text{Ru}^I$ , and the overall result is the equilibrium



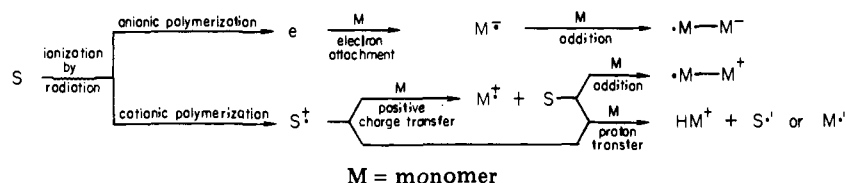
Class I electron-transfer-catalyzed formation of S-S bonds begins to appear in the literature.<sup>692,778b,965</sup>

The coupling of aryl groups catalyzed by copper(I) salts (Ullman synthesis of biaryls<sup>961</sup>) should be tried under photoelectron-transfer catalysis. A review by E. W. Stern<sup>962</sup> gives an excellent account of other oxidative coupling reactions (thiols, phenols, acetylenes...); it furnishes a wealth of examples where photochemical activation could bring improvements. In electrochemistry, the catalytic oxidative coupling of 1,1-diphenylethylene is followed by a second oxidation and reaction with  $\text{H}_2\text{O}$  leading to the overall formation of 1,2,4,4-tetraphenyl-3-buten-1-one.<sup>963</sup> Bowman<sup>389d</sup> recently described C-N bond formation induced by action of  $\text{Fe}^{\text{III}}$  on the mixture cyclohexyl nitronate and excess azide in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  solution.

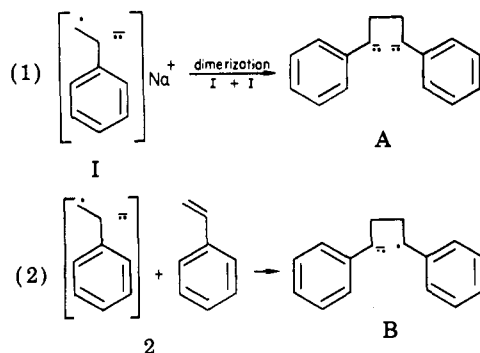
## d. Oligomerizations, Polymerizations, and Telomerizations

Electrolytic electron-transfer catalysis of polymerizations, either anodic or cathodic, is well documented.<sup>964-966b</sup> In many of the reactions described in section III6b the main byproducts are oligomers and/or polymers. Polymer science is of such a broad scope that we are unfit to give an objective account of the role played by photoelectron-transfer catalysis in this territory. (For example, in the *Spec. Period. Rep., Chem. Soc., London* (Vol. 10, 1978) the section on polymer photo-

Scheme XXXV



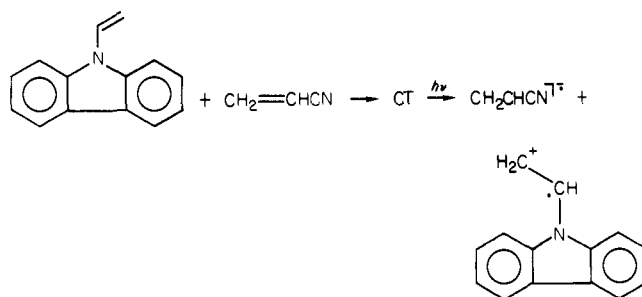
chemistry written by N. S. Allen and J. F. McKellar announces not less than 16 review articles on photoinitiated addition polymerization for the period 1976–1977. Good overviews of polymerization reactions may be found in the November 1981 issue of *J. Chem. Ed.* and in Odian's book "Principles of Polymerization" (2nd ed., Wiley, New York, 1981), and the most thorough review on charge-transfer polymerizations has been written by Shirota and Mikawa.<sup>967</sup> Rather, we shall try to orient the reader towards the most relevant reviews without any attempt at being exhaustive. H. Yoshida and K. Hayashi<sup>968a</sup> give a global scheme (Scheme XXXV) for the initiation process of radiation-induced ionic polymerization that can be taken as a good introduction to the field of electron transfer catalyzed polymerizations. This scheme suggests that radical cationic and radical anionic species can play an active role in polymerization, the field of which is more usually divided into the three main classes: cationic, anionic, and radical.<sup>968b</sup> From what we have learned in the preceding sections, we know that the distinction is not semantic from a mechanistic point of view. It is important to differentiate between the following two scenarios illustrated on the Szwarc method of polymerization<sup>969</sup> using the interaction of alkali metals in the presence of dry aprotic solvents like THF and polynuclear aromatic to produce a radical anion of the monomer:



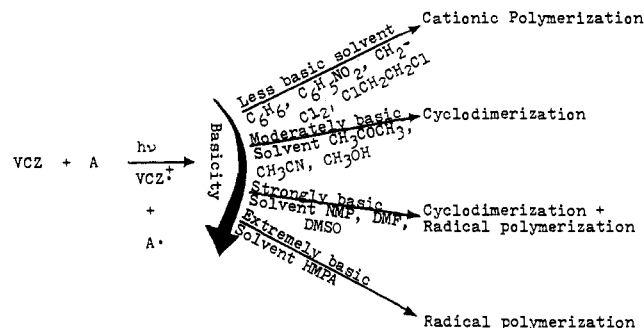
Scenario 1 is followed by anionic polymerization. Scenario 2 is followed by (a) radical polymerization at one end of the chain, anionic polymerization at the other, (b) overwhelming radical or anionic<sup>970</sup> polymerization because of rate preference, or (c) efficient transformation of the radical end into another carbanionic end by electron transfer. Scenario 1 is favored over scenario 2 on energetic ground terms (formation of a C–C bond), but unfavored because of the small concentration of radical anions in the medium compared with that of neutral monomers. Scenario 2c comes out to be equivalent to scenario 1. The radical anion B could be stabilized by the general intramolecular interaction radical-lone pair.<sup>241</sup> For anion radical polymerizations it does seem that either (1), (2c), or (2b) (anionic domination) usually explains most of the ob-

served results.<sup>971</sup> This simplified situation does not necessarily apply to cation radical photopolymerization where radical, ion pair, and free ion mechanisms may concurrently enter into the overall result<sup>972,973</sup> and for a given D.A. couple participate differently depending on the solvent of the reaction.<sup>967</sup>

In 1969, S. Tazuke<sup>974</sup> surveyed the reactions of polymerization photosensitized by charge transfer. The *N*-vinylcarbazole–acrylonitrile system was proposed to photopolymerize following simultaneous occurrence of cationic and radical polymerizations. The resulting polymer is a mixture of copolymer and homopolymer. Copolymer is thought to be formed by a radical mechanism (quenching by 2,2-diphenyl-1-picrylhydrazyl), whereas homopolymer would be formed by a cationic mechanism (quenching by ammonia). The initiation step is therefore supposed to be a photoinduced electron transfer:

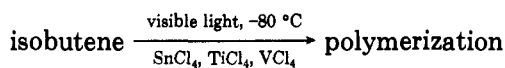


No homopolymer of acrylonitrile was isolated; this lends credence to an unimportant participation of the anionic polymerization under these conditions. This is reminiscent of the chain-substitution pattern of reactivity where the radical generated after oxidation of the nucleophile is often in such a small concentration that it cannot be observed (section III1a). Several independent works agree in proposing cationic propagation as the main mechanistic channel for polymerizations of *N*-vinylcarbazole in the presence of electron acceptors.<sup>975,976</sup> It should be stressed, however, that Shirota's contributions<sup>967,977</sup> have proven that photoinduced reactions of vinylcarbazole in the presence of the electron acceptor display multireaction courses involving (1) cationic homopolymerization of the substrate, (2) cyclodimerization, (3) radical homopolymerization (favored over (2) by an increase in the solvent basicity), and (4) radical copolymerization with the accepting monomer. The previous system may also react on simple heating, but the reaction is slower ( $\approx 3$  orders of magnitude) under these conditions; the thermal polymerization of EDA unsaturated couples has been treated by Stille.<sup>978</sup> A bunch of other organic EDA couples involved in photoelectron-transfer catalysis may be found in ref 967 and 981, and the photophysics of the primary processes have been elucidated in some detail.<sup>980</sup> These reactions may, however, be rather tricky, and Shirota's review<sup>967</sup> describes several exam-



**Figure 16.** Multiple reaction courses in the photoinduced reactions of vinylcarbazole in the presence of A, the electron acceptor (reprinted with permission from ref 967. Copyright 1978, Marcel Dekker.).

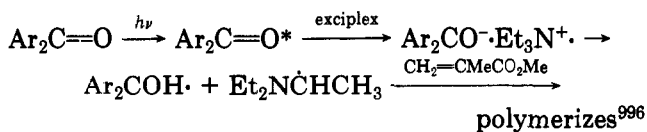
ples where the originally proposed ETC scheme was in fact wrong because unnoticed impurities had induced fast cationic or radical polymerization. Transition-metal complexes are also valuable candidates to sensitize by electron transfer the appropriate monomer. Some selected couples follow: acrylamide/uranyl ion (ref 981);  $\beta$ -propiolactone/uranyl ion (ref 982);  $\beta$ -propiolactone/ $\text{NaAuCl}_4$  (ref 983); methyl methacrylate/triethylaluminum (ref 984); 2-vinylnaphthalene/ $\text{ZnCl}_2$  (ref 985). In some interesting examples, metal salts usually viewed as Lewis acids behave possibly as redox couples<sup>986a,987b</sup> (cf., however, with ref 988 and 989). This



problem of Lewis acid initiation vs. oxidizing initiation has been carefully discussed in Shirota's review.<sup>967</sup> The mechanistic situation associated with photocatalysis induced by transition-metal complexes is manifold: beyond this redox role they can also be active because of homolytic dissociation of their ligands<sup>990-992</sup> or olefin complexation.<sup>993</sup>

The recent work by Turro's team<sup>994</sup> uses the flexibility of photoinduced emulsion polymerization combined with the action of magnetic field in the polymerization of styrene photoinitiated by dibenzyl ketones. That opens fascinating possibilities in the field of photopolymerizations following charge-transfer complexes or exciplexes.

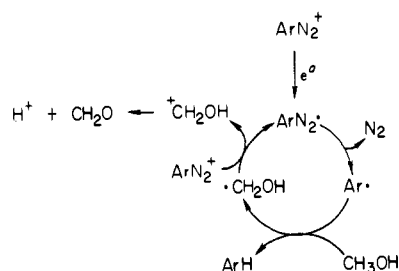
In all the previous cases the monomer was directly involved in the EDA or exciplexes initiating the polymerization. External charge-transfer complexes<sup>995</sup> may also play the role of photoinitiators after electron transfer



Other examples of such indirect involvement are known.<sup>41,997-999</sup>

Recently, G. Smets<sup>307</sup> stressed an interesting aspect of chain reactions viewed as methods of generation of initiator of polymerization with an intrinsic amplification of the quantum yield independent of the degree of polymerization of each growing polymer chain. Scheme XXXVI can be taken to illustrate the principle. Another entry into the catalytic cycle may be provided by the use of a triplet photosensitizer (methyl 2-

Scheme XXXVI



<sup>a</sup> Electron transferred from the counterion under the influence of  $h\nu$ .

naphthyl ketone) that abstracts hydrogen from methanol producing ketyl and hydroxymethyl radicals. In both cases, if a vinyl monomer is present in the medium it will start a free-radical chain rapidly transformed into a cationic chain after electron transfer from the radical end to the diazonium salt.

Related to this kind of two-stage fireworks is the case of molecular-assisted homolysis<sup>697,730</sup> where an additive (e.g., amine) is added to a precursor of radical (e.g., peroxide) to make the production of radicals possible under milder conditions. The mechanistic problems related to these kinds of processes are not all elucidated,<sup>740,766</sup> but some of the processes are clearly electron-transfer-induced chain reactions and as such may be tried in photosensitized polymerizations.

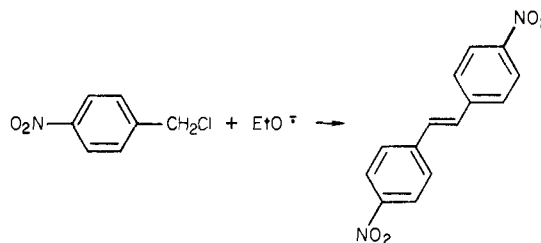
Photoelectron-transfer-catalyzed telomerizations have not been much studied until now; their thermal counterparts give good results<sup>1000-1004</sup> as does vinyl graft copolymerization.<sup>1005a</sup>

To close this section we must cite the historical example: in 1946 the first clear evidence for one-electron-transfer reaction was obtained when it was shown that free hydroxy radicals produced in the Fenton reaction could initiate polymerization of vinyl monomers.<sup>1006b,1007</sup> A photo-Fenton<sup>1008</sup> reaction would have done the same work.

## 7. Eliminations and Loss of Fragments

### a. Eliminations

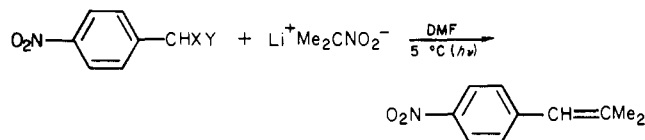
G. Russell<sup>1009</sup> recently proposed to reinterpret earlier results<sup>1010-1013</sup> on  $\alpha$ -eliminations ( $\alpha$ -E<sub>TC</sub>B) leading to carbenes on the basis of electron-transfer catalysis; among the evidences offered was the fact that irradiation with sunlamp accelerates the reaction



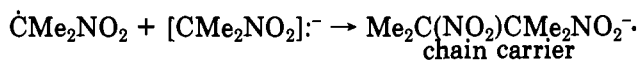
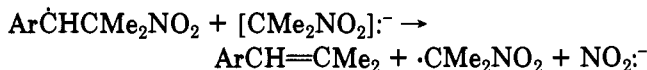
The proposed chain is given in Scheme XXXVII.

The various examples of electron-transfer-catalytic  $\beta$ -elimination are scattered in various parts of chemistry. The best known is the mild elimination discovered by N. Kornblum<sup>1014,1015</sup> and later confirmed (Scheme XXXVIII).<sup>1016</sup> More recent examples have been re-

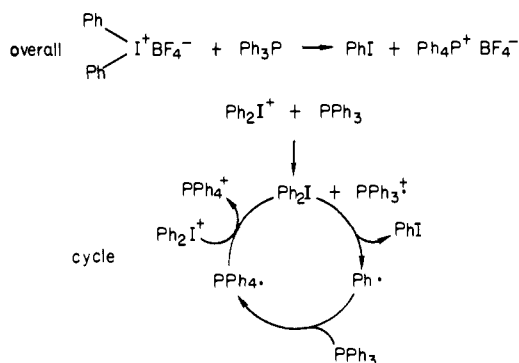
ported by R. K. Norris<sup>360-362</sup> in the reaction between *p*-dinitrobenzylidene dihalides and lithium 2-nitropropan-2-ide:



The catalytic effect of light is not strongly in evidence in this example, the overall result of which looks like a condensation reaction but where the critical steps correspond to an elimination:

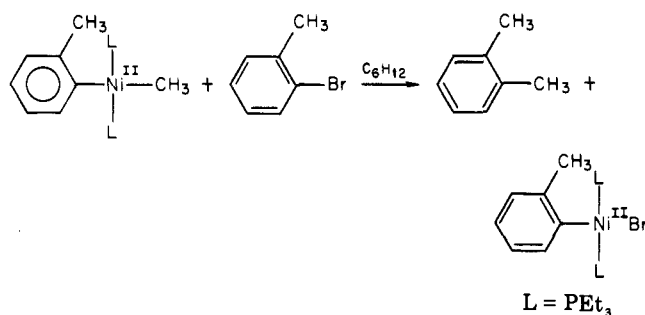


An early example was discovered by Reutov's group,<sup>1020,1021</sup> which identified it as a chain reaction but did not describe the influence of light on it:

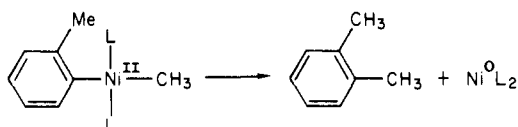


Hawley<sup>1022</sup> recently provided an elegant electrochemical example (Scheme XXXIX) that calls for class III photoelectron-transfer-catalytic experiments.

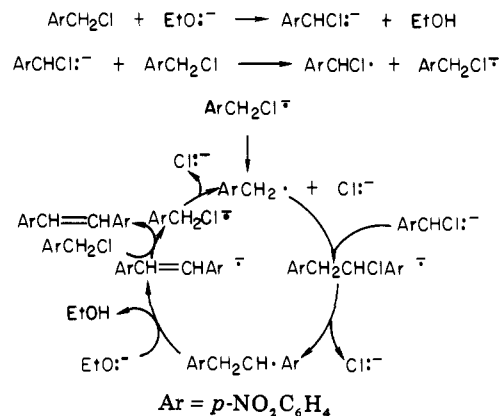
In the organometallic field, photoelectron-transfer-catalytic reductive elimination is involved in a "hidden" way:<sup>1023</sup>



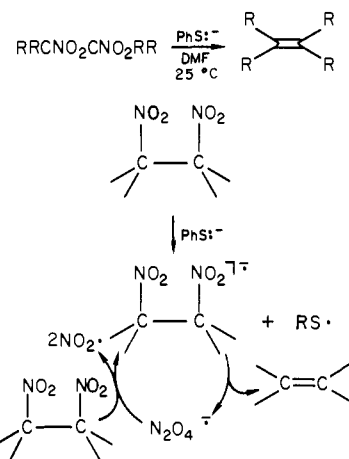
the overall induced decomposition involves the chain reductive elimination:



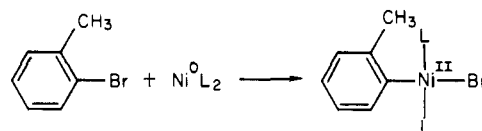
## Scheme XXXVII



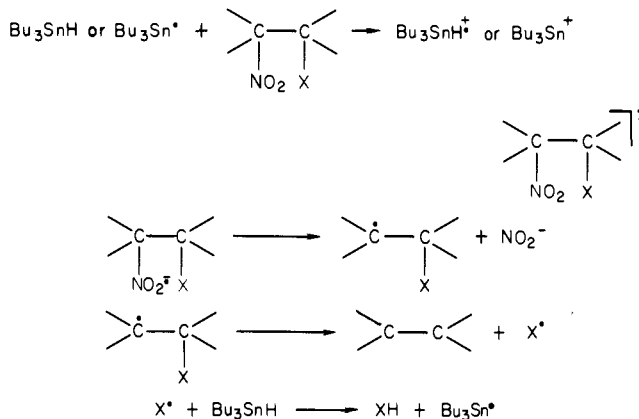
## Scheme XXXVIII



followed by an oxidative addition:



The very rich radical reactivity of tin compounds<sup>904</sup> associated with their good properties of electron donors<sup>687</sup> indicate that they are excellent substrates for photoelectron-transfer-catalytic studies. Recently, N. Ono and co-workers<sup>1024</sup> proposed the free-radical chain elimination of  $\beta$ -nitro sulfones and vicinal dinitro compounds leading to olefins:



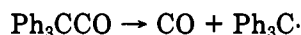
This mechanistic scheme is only one of several compatible with the chain behavior, and further experi-

ments will no doubt precise this point and answer the question concerning the existence and study (quantum yields, etc.) of the photochemical counterpart of this reaction.

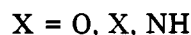
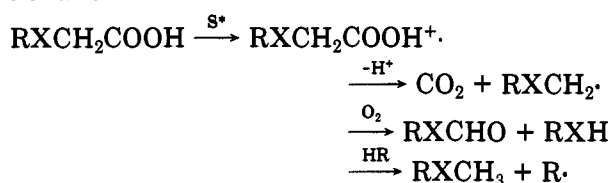
The photosensitized radical chain dehalogenation of several organic compounds implicates an inner-sphere type of electron transfer,<sup>1025a</sup> as does an interesting case of photosensitized dehydrogenation.<sup>330</sup> These and foregoing results suggest that some earlier elimination reactions<sup>1026-1031</sup> deserve thorough mechanistic investigation. It is indeed generally accepted that when a catalyst (here e) catalyzes a reaction it is able to catalyze also its reverse, and it seems that the number of examples given in this section is astonishingly small when compared with that reported in section III6b. The old dilemma  $E_{2H}-E_{2C}$  elimination<sup>986b</sup> deserves new experimental studies: the weak bases<sup>966a</sup> used to induce eliminations were indeed also good reducing agents, and electron transfer on halogens displays weak sensitivity to steric effects.<sup>43,979,1027</sup> Further studies in this direction could bear connection with biological examples.<sup>1032</sup>

### b. Loss of Fragments

The ejection of fragments<sup>1033</sup> highly stabilized by resonance (CO, CO<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, SO, S) may provide a good driving force in some electron-transfer-catalyzed reactions. We were unable to find clearcut photoelectron-transfer-catalytic examples of induced loss of CO. The radical chain reaction between tin hydride and triphenylacetyl chloride in xylene where the decarbonylation indeed occurs:<sup>913</sup>

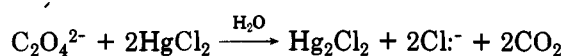


points, however, to the existence of such a possibility. The thermal electron-transfer-catalytic decarboxylation<sup>1034</sup> is well documented; the electron-transfer sensitization of the reaction.<sup>1035-1038</sup>



$\text{S}^*$  = redox sensitizer (quinone)

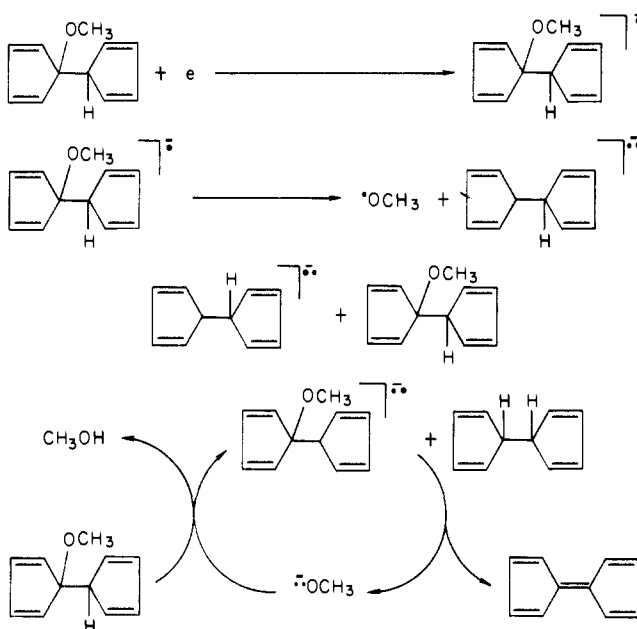
therefore does not come as a surprise. Photochemical decarboxylation of amino acids and peptides in solution<sup>1039</sup> or in frozen glass<sup>1040</sup> appears to follow the same basic principle: generation of an oxidant able to oxidize the carboxylates. Incidentally, the ancestor of photoelectron-transfer catalysis (class I) is the photochemical decarboxylation of oxalates.<sup>1041-1043a</sup> After discussions



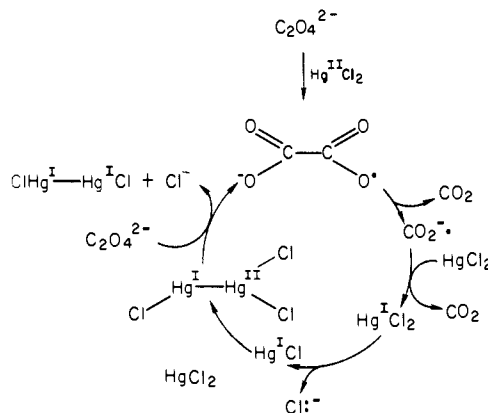
with J. Hershberger, we propose the cycle in Scheme XL.

The thermal<sup>987a,1005b,1044b-1048</sup> and electrochemical<sup>1022</sup> aspects of electron-transfer catalysis applied to di-

Scheme XXXIX

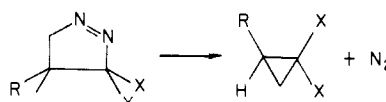


Scheme XL



azonium salts suggest that photoelectron-transfer catalysis<sup>1049</sup> could meet with success for this class of compound. This is indeed the case. Catalytic amounts of anthraquinone or benzophenone (S) photosensitize the radical chain decomposition of aryl diazonium salts (Scheme XLI).<sup>1050</sup> More recently Jirkovsky<sup>1051</sup> induced the same reaction using the couple of sensitizers 1,4-benzoquinone-2,4,6-tri-*tert*-butylphenol, which under irradiation leads to the semiquinone able to reduce the diazonium salt in a rate-determining step. The pH of the medium may train variations in rate constants covering 5 orders of magnitude. A natural question that arises after these results is: Are photo-Mervein,<sup>1052-1054</sup> photo-Gatterman,<sup>1055</sup> and photo-Pschorr<sup>1055</sup> reactions feasible?

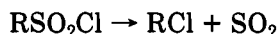
The thermal decomposition of 1-pyrazolines in the presence of small amounts of Ce<sup>IV</sup>.<sup>1056</sup>



advocates for photochemical attempts at the same result (cf. ref 1057, 1058). Tin hydride molecular-assisted homolysis<sup>1059</sup> of various azo compounds falls in the same

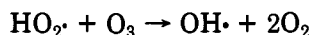
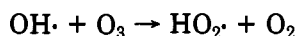
line. The susceptibility of diazo linkage to reductive electron-transfer catalysis is clearly demonstrated by a series of electrochemical works,<sup>1060-1063</sup> but some mechanistic aspects of the process are still under discussion.<sup>1006a,1064,1065</sup> Furthermore, diazoalkanes<sup>1066,1067</sup> and ketones<sup>1068</sup> also undergo oxidative electron-transfer catalysis. These data and others open up the photochemistry of azo compounds: the most recent report<sup>1069</sup> on photoeliminations of azo compounds contains no information relevant to photoelectron-transfer catalysis that testifies to how rarely this scheme is still discussed for this class of compounds.<sup>1070</sup>

Loss of SO<sub>2</sub> leading to a chain reaction has been reported in the decomposition of cyclohexanesulfonyl chloride in the presence of O<sub>2</sub> (solvent cyclohexane):<sup>1071</sup>



This class of reaction could probably be realized under milder conditions using class III photoelectron-transfer catalysis.

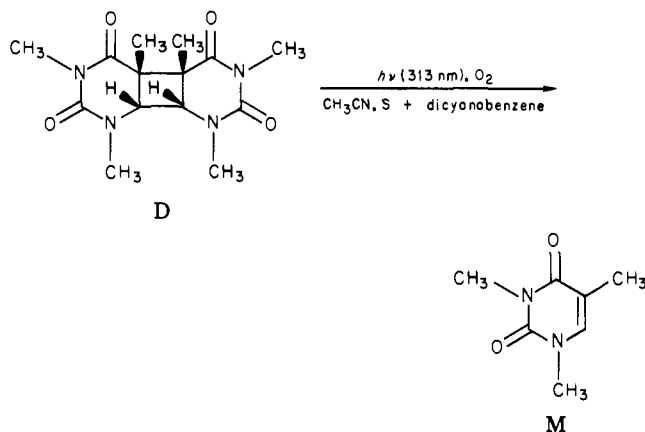
Loss of other fragments such as OH,<sup>1072</sup> S,<sup>1073,1074</sup> (CH<sub>3</sub>)<sub>2</sub>CO,<sup>1044a</sup> and SO<sup>1075</sup> could be profitably reexamined within the photoelectron-transfer-catalysis scheme for the search of milder conditions. When the loss of fragment is followed by addition, the overall result is equivalent to a substitution; therefore, further examples relevant to this section may be found in section III.1. Loss of O<sub>2</sub> from O<sub>3</sub> is known<sup>1076</sup> to occur in a chain reaction whose carrier is OH·:



therefore, any photochemical reaction generating OH· radicals (e.g., photo-Fenton<sup>1008</sup>) would be able to act as an initiator of this O<sub>2</sub> loss.

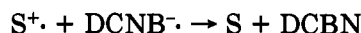
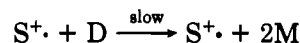
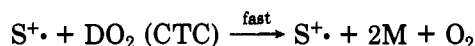
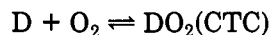
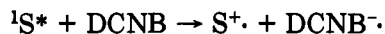
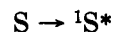
### c. Rupture of C-C Bonds

As we have met several examples of C-C bond formation involving photoelectron-transfer catalysis, we could wonder if the reverse reaction possibly undergoes this kind of activation. Recent work by Sakurai's group<sup>1077,1078</sup> gives a positive answer:



S = phenanthrene

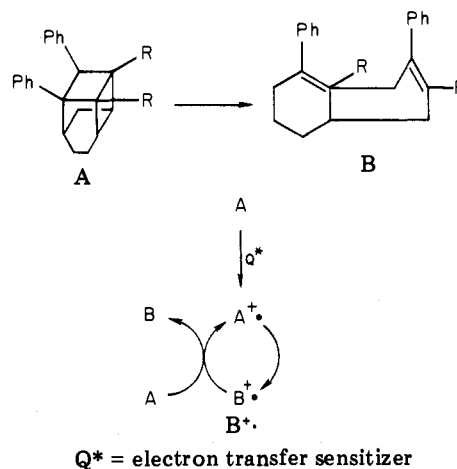
Quantum yield for air-saturated solution is 205, and both phenanthrene and *p*-dicyanobenzene are completely recovered. The authors put forth the following scheme for this catalytic monomerization:



It is not yet totally clear why CTC between D and O<sub>2</sub> makes the dimer much more susceptible to monomerization in the presence of the radical cation S<sup>·+</sup> and why a step with S<sup>·+</sup> oxidizing D, thus activating it toward monomerization, is dismissed. This interesting reaction does not take place with the *cis-anti* dimer but applies to the indene and cyclobutane dimers.<sup>312</sup> The ability of indole to split the dimers of pyrimidine is correlated with its electron-donor capacity.<sup>1025b</sup> One of the cleanest examples of photosensitized C-C bond cleavage has recently been provided by Mukai:<sup>1043b</sup>

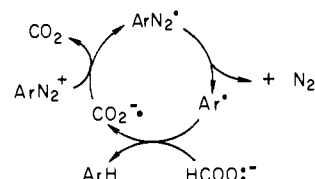
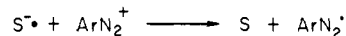
It would be interesting to check if unzipping<sup>1385</sup> of some polymers could be induced along this line of activation. At this point, it is interesting to note that H. G. Viehe recently proposed an efficient trapping agent for trapping carbon-centered radical [CH<sub>2</sub>=C(CN)SBU-*t*]-TBMA,<sup>1079,1080</sup>  $\alpha$ -(*tert*-butylthio)acrylonitrile.

Electrochemical chain reaction in the carbon-carbon bond cleavage of conjugated bases of 9-hydroxybifluorenyl or 9,9'-dihydroxybifluorenyl<sup>1022</sup> and the



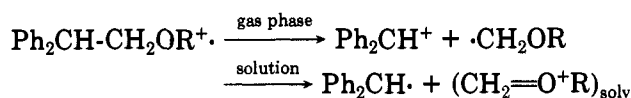
smooth cleavage of  $\alpha$  glycols<sup>1081</sup> involving redox catalysis suggest other interesting applications of photoelectron-transfer catalysis. The same conclusion transpires from several other examples: devitrification of ma-

### Scheme XLI

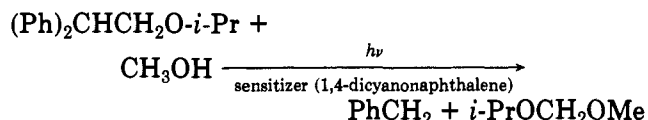


trixes<sup>1082</sup> and photofragmentation of methylene cyclopropane.<sup>1083</sup>

Some isomerizations given in section III5 are also pertinent to the present section. A. Albini<sup>76</sup> noticed the importance of solvation in the direction of cleavage:



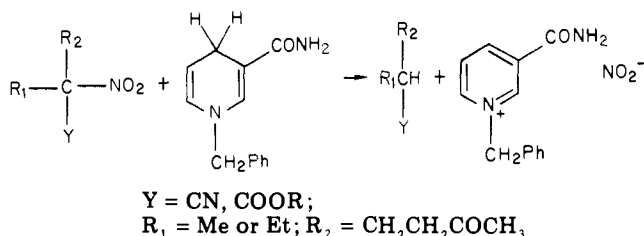
Arnold<sup>1084</sup> discovered that the photosensitized (electron-transfer) irradiation of some  $\beta$ -phenethyl ethers leads to cleavage of the  $\alpha$ -carbon-carbon bond:



Reductive photosensitization may also be used to induce C-C bond cleavage. Griffin recently reported that for homogeneous series of vicinal diaryl-substituted oxiranes, the activation smoothly passes from the oxidative mode to the reductive one.<sup>1101b</sup>

## 8. Reductions

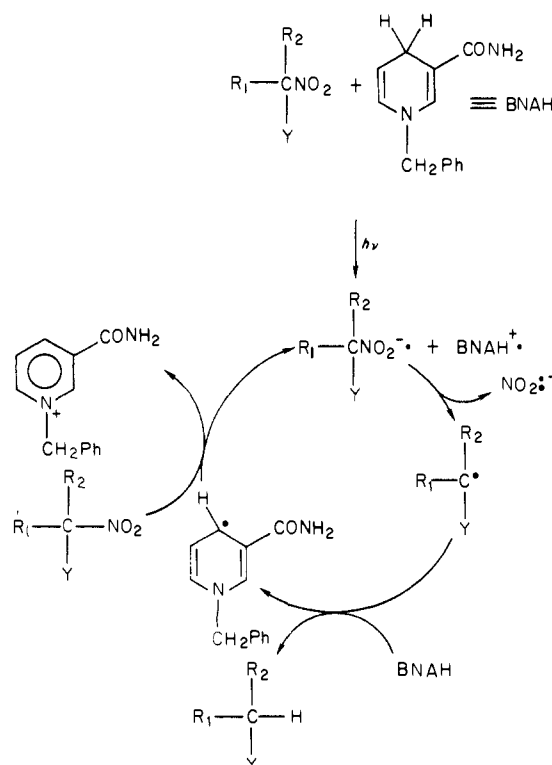
Because of their biochemical relevance,<sup>1085-1087</sup> the reduction by 1-alkyl-1,4-dihydronicotinamide derivatives has raised up a great deal of mechanistic work. The main mechanistic propositions are: hydride transfer,<sup>1088</sup> nonchain free radical,<sup>1089-1093</sup> and electron-transfer chain processes.<sup>1094</sup> N. Ono gave a very clear example of class I photoelectron-transfer catalysis in the reaction:



The evidences supporting the mechanism in Scheme XLII are strong effect of the light,<sup>1094</sup> inhibition by di-*tert*-butyl nitroxide and *m*-dinitrobenzene, and induction of the reaction by addition of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to a DMF solution of reagents kept in the dark. The radical pathway is probably favored by the fact that captodative radicals are generated in this reaction. This system<sup>1095</sup> would be particularly interesting to study with respect to the combination<sup>1097-1099</sup> of both electron-transfer catalysis and acid-base catalysis to active a given process. A. Kitani<sup>1096</sup> has indeed studied the catalytic effect of Mg<sup>2+</sup> and Li<sup>+</sup> ions on this class of reactions.

The role of light is essential in the foregoing mechanism: Blankenhorn,<sup>1100</sup> and later de Boer<sup>1101a</sup> and co-workers, showed that in most cases of thermal reduction involving NADH, a one-electron transfer as primary step is not thermodynamically feasible, whereas fluorescence-quenching studies indicate that 1,4-dihydropyridines in the excited state act as efficient one-electron donors toward a variety of substrates.<sup>1102</sup> From what we have seen in other sections, a continuum of situations<sup>43,1103</sup> probably exists with BNAH as re-

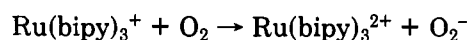
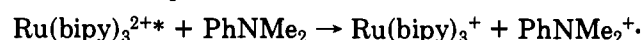
Scheme XLII



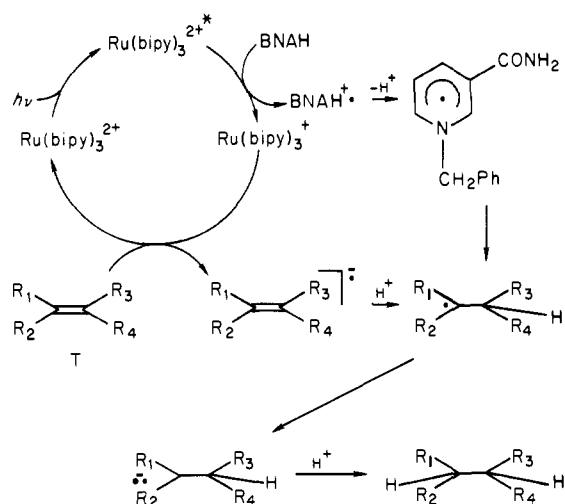
ducing agent depending upon the acceptor ability of the opposed substrate.<sup>1093,1104</sup> This continuum is not necessarily linear and could explain the existence of an optimal dependence of the overall rate of some other reductions<sup>1105</sup> involving NADH in a way reminiscent of what is observed for some proton-transfer-catalytic schemes.<sup>1106</sup> The recent report by Nonhebel<sup>1107</sup> uses free-radical clocks<sup>545</sup> to dismiss the radical participation in typical reactions catalyzed by horse liver alcohol dehydrogenase. Very recently, Bruce carefully studied the one- and two-electron reduction of oxygen by 1,5-dihydroflavins,<sup>1109</sup> Heelis reviewed the photoreduction of flavins,<sup>1140a</sup> and Yoneda reported on oxidations of alcohols or amines efficiently catalyzed by 5-deazaflavins and analogues.<sup>1132</sup>

Dye-sensitization of this class of reductions has been demonstrated by the early Krasnovskii work.<sup>1110</sup> More recently, C. Pac and H. Sakurai<sup>1099</sup> devised an elegant photoreduction of olefins by 1-benzyl-1,4-dihydronicotinamide mediated by Ru(bpy)<sub>3</sub><sup>2+</sup> in methanolic solutions (Scheme XLIII).

Robinson and Yocum<sup>1111</sup> results showing that 5-deazariboflavin is a convenient catalyst for the photoreduction of low potential redox compounds in anaerobic medium illustrate the biological importance of this kind of process. The use of Ru(bpy)<sub>3</sub><sup>2+</sup> extends by more than 0.5 V the lower limit of reduction potential for olefins reducible by NADH. The electron-transfer properties of Ru(bpy)<sub>3</sub><sup>2+</sup> have been utilized for driving reactions transiently in the nonspontaneous direction: dimethylaniline is indeed "obliged" to transfer one electron to O<sub>2</sub> in the presence of light and of this ruthenium complex.<sup>1112</sup>



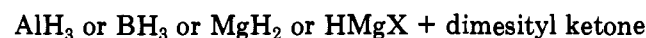
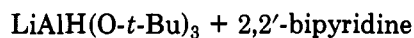
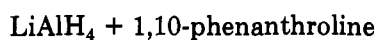
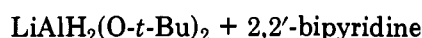


Scheme XLIII<sup>a</sup>

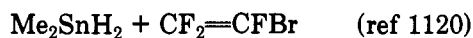
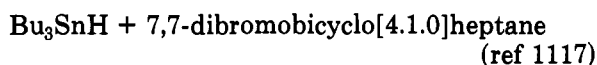
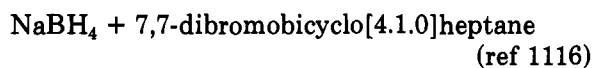
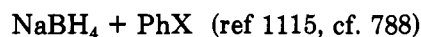
<sup>a</sup>  $R_1CR_2=CR_3R_4$  should have a reduction potential  $\geq -2.2$  V.

The dilemma hydride transfer versus  $eH^+$  mechanism pervades the field of reductions. Along this line, electron-transfer mechanisms may take place for the following couples of donor-acceptors:

*nonchain reactions*<sup>1017-1019</sup>



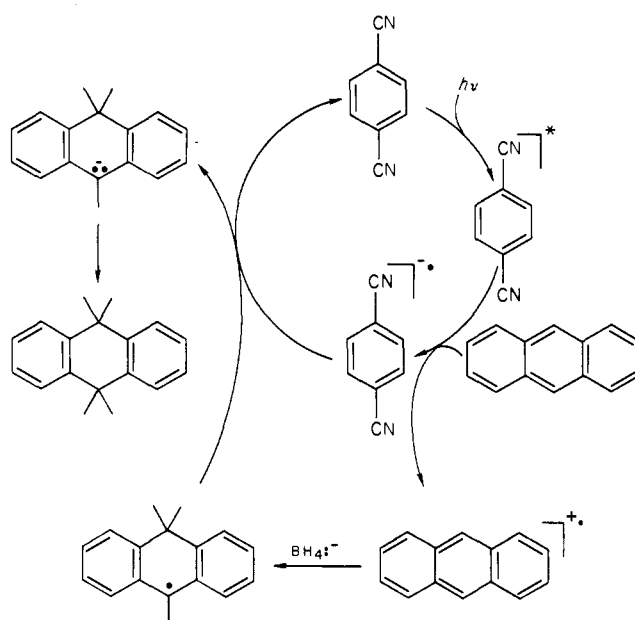
*chain reactions* (see also 1113b)



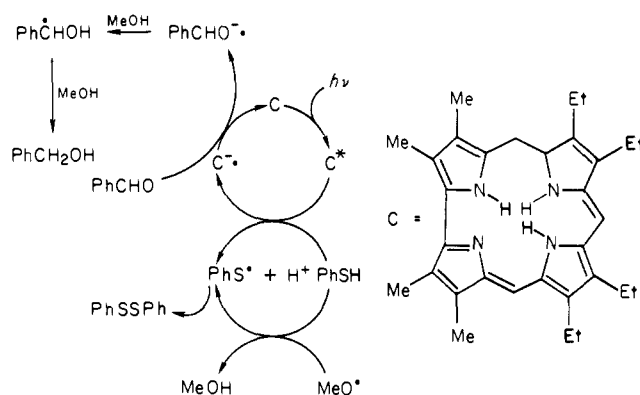
Although the oldest references do not discuss the possibility of electron transfer as an initiating step, the reported reactions are probably related to electron-transfer catalysis: this implies that for the less favorable DA couples photoelectron-transfer catalysis would probably induce the reaction of thermally inert couples.

The fact that no special section in the good G. L. Geoffroy review<sup>1121</sup> on "photochemistry of transition metal hydride complexes" deals with electron-transfer processes, while some papers<sup>227,1122</sup> reported in this review could be viewed through this scheme, testifies that

Scheme XLIV



Scheme XLV



much mechanistic work remains to be done in this direction opened by the pioneering works of Ashby,<sup>254</sup> Otsuka,<sup>1123</sup> Kochi,<sup>1124</sup> and Bergman<sup>1125</sup> groups. This is an immense territory when one realizes that thousands of metal hydrides have been prepared and characterized.<sup>227,1122</sup> Furthermore, class III PETC still widens this scope, as shown in Scheme XLIV<sup>1127</sup> where 1,4-dicyanobenzene sensitizes the photoreduction of anthracene by sodium borohydride (class III).

This principle of using a sensitizer to mediate electron (hydrogen; see section I5c) transfer from an electron (hydrogen) donor to an acceptor via a redox process of the excited sensitizer has been used for several other reducible substrates; some examples are gathered in Table XIX, and a typical catalytic cycle is shown in Scheme XLV.<sup>1128</sup>

Several variations<sup>1133,1134</sup> of this kind of catalytic cycle allow substantial yield improvements. The photoreduction of quinones illustrates the versatility of these systems: the electron-transfer step may either occur to the carbonyl in the ground state, a pigment in its excited state being the donor,<sup>1135</sup> or more frequently, to the carbonyl in its excited state (usually  $T_{n,\pi^*}$ ),<sup>1136</sup> a molecule in the ground state being the donor.<sup>1137,1138</sup>

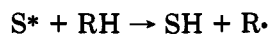
Twenty-five years ago Bridge and Porter<sup>141</sup> raised the most fundamental question: it concerns the outer-sphere vs. inner-sphere (H-abstraction) character of the

Table XIX. Examples of Photosensitized Reductions

overall reaction	photosensitizer	solvent	ref
PhCHO + 2 PhSH <sup>a</sup> → PhCH <sub>2</sub> OH + PhSSPh	corrole (1/280)	MeOH + AcOH	1128
dyes + ethyl chlorophyllide → reduced dyes <sup>b</sup>			1129
azobenzene + ethyl chlorophyllide → reduced azobenzene <sup>b</sup>			1129
riboflavins + ascorbic acid → reduced riboflavin <sup>b</sup>			1130
nitrobenzene + <i>N</i> -methylpyrrolidine →	Sn(IV) tetraphenylporphyrin dichloride	benzene	1131
aniline + azobenzene + azoxybenzene + <i>N</i> -methylpyrrole			1132
quinones			

<sup>a</sup> 6[PhSH] ≈ [PhCHO]. Other examples may be found in A. V. El'tsov, O. P. Stuzinskii, and V. M. Grebenkina, *Russ. Chem. Rev. (Engl. Transl.)*, 46, 93 (1977); J. C. Scaiano, *J. Photochem.* 2, 81 (1973); J. M. Bruce in "The Chemistry of the Quinoid Compounds", S. Patai, Ed., Wiley, London, 1974, Chapter 9; M. Julliard, J. Le Petit, *Photochem. Photobiol.*, 36, 283 (1982). <sup>b</sup> Deserves further mechanistic studies.

primary act when the excited state oxidizes or reduces its partner.

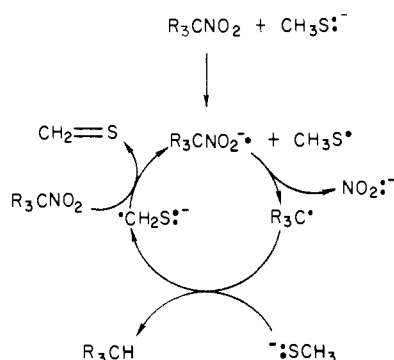


or



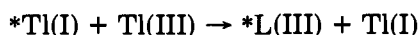
S. K. Wong<sup>142</sup> gave a well-documented account of this problem, and we discussed this question in section I5c.

N. Kornblum<sup>363,395a</sup> demonstrated that CH<sub>3</sub>S:<sup>-</sup> may behave as a reducing agent according to the following chain:

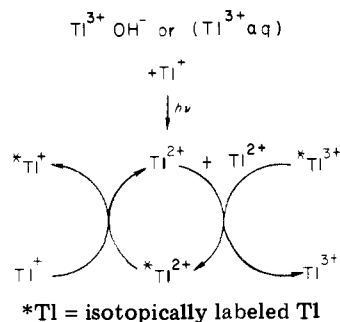


This reaction takes place under remarkably mild conditions (25 °C) compared with the far stronger conditions usually required for this kind of reduction.<sup>1141</sup> KI may, under appropriate conditions,<sup>1142a</sup> induce reduction of halodinitromethanes. The reduction of nitro groups by electron transfer has biological implications.<sup>1140b</sup>

Stranks and Yandell<sup>233</sup> thoroughly studied the photochemical Tl(I)–Tl(III) exchange:



At room temperature, the thermal electron exchange proceeds with half-lives of several hundred hours, whereas photoinduced exchange (2537 Å) exhibits half-lives of about 30 min. Their quantitative study is discussed in section I9, and their proposition of chain is:



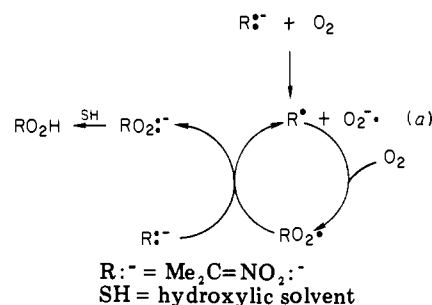
The initiation is attributed<sup>1143b</sup> to a charge transfer from ligand to metal excitation; we take it, however, to show the kind of chain which could be met for some 2-equiv exchange reactions<sup>1144</sup> (Sn<sup>II</sup>–Sn<sup>IV</sup>, Pt<sup>II</sup>–Pt<sup>IV</sup>, Sb<sup>III</sup>–Sb<sup>IV</sup>, As<sup>III</sup>–As<sup>IV</sup>) under appropriate medium and structural conditions.

The reduction of various organic radicals<sup>1139</sup> catalyzed by the radical cation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine calls for parallel photochemical experiments. For the photodebromination of 5-bromo-2-methoxypyrimidine in methanol accelerated by triethylamine, the amine acts as an electron donor in the initiation step and as a base in a propagation step of the chain reaction.<sup>235b</sup>

## 9. Oxidations

The recent book "Metal Catalyzed Oxidation of Organic Compounds" gives a detailed account of mechanistic schemes involved in thermal catalytic oxidation reactions.<sup>319</sup> It covers more than 1,400 references, which gives an idea about the extent of this area. This section will therefore deal only with selected examples specifically illustrative with respect to photoelectron-transfer catalysis.

G. A. Russell<sup>1145</sup> was the first searcher to propose that even in the absence of any other reagent, a couple of donor (carbanion from 2-nitropropane)–acceptor (O<sub>2</sub>) could react according to an electron-transfer-catalytic mechanism. One out of several possible chains is<sup>1146</sup>

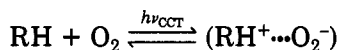


<sup>a</sup> For complications in mechanisms involving O<sub>2</sub><sup>-</sup> in the presence of proton sources, see ref 1143a.

This mechanism was extended<sup>1031</sup> to fluorene, other polyarylmethanes, substituted toluenes, benzhydrols, polyarylethanes, and ketones; furthermore, it shed new light on the oxidation of benzoin,<sup>1147</sup> hindered phenols,<sup>1148</sup> and, perhaps, nitrile,<sup>1151,1152</sup> hydroxylamine, and

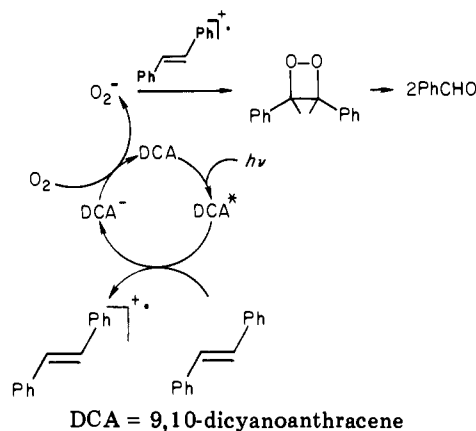
azo compounds.<sup>1153,1154</sup> Its photochemical aspects (class I) are only beginning to be investigated,<sup>1142b</sup> and its connections with spontaneous inflammability of some organometals or photooxidation of tertiary aryl-phosphines<sup>1155</sup> deserve further study. The  $E^\circ$  value of  $O_2/O_2^-$  couple ( $-0.15$  V)<sup>1149,1150</sup> allows the expectation of a good number of donors able to transfer their electron.

M. Tamres and R. L. Strong<sup>684</sup> recently wrote an excellent review where a section specifically deals with the evidence brought for contact charge-transfer complexes from organic compounds to  $O_2$ , and their possible role in reactivity. The first remarkable information is that if  $O_2$  does form contact charge-transfer spectra with a large variety of organic compounds (amines, alkanes, toluene, aromatics, ethers; see Table C, ref 684), it does not form definite complexes even with good electron donors; Tamres rationalizes this fact by noticing that the vertical electron affinity of  $O_2$  is possibly negative<sup>1160</sup> (cf. ref 1150). These contact charge-transfer complexes are thought to play an active role in the photooxidation of aliphatic, olefinic, and aromatic hydrocarbons:<sup>1157</sup>



Studies carried out at  $-30$  °C indicate that radical cations are formed after irradiation of ethers in the presence of  $O_2$ ,<sup>1158</sup> and irradiation in the contact charge-transfer band of  $O_2$ -diethyl ether at 77 K produces an ESR signal<sup>1159</sup> ( $CH_3$  or  $CH_3CH_2$ ). The same type of spectroscopic evidence has been obtained<sup>1159,1160</sup> in the reaction between amines and  $O_2$ , and Jefford recently proposed a charge-transfer mechanism for the photooxygenation of enamines.<sup>1190b</sup> Although it is difficult to devise totally unambiguous experiments in these photooxidation experiments because of the multiple roles (energy-transfer quencher of fluorescence and phosphorescence,<sup>1161</sup> enhancement of the singlet-triplet band for many organic compounds<sup>1156,1162</sup>) possibly played by  $O_2$ , the foregoing data, completed by Brewer's demonstration<sup>1163</sup> that  $O_2$  fluorescence quenching rates for alkyl and fluorobenzenes are inversely dependent on the ionization potentials of the aromatic molecules, strongly suggest that type I photoelectron-transfer catalysis is indeed of importance in the direct photooxidation of many organic compounds. Picosecond spectroscopy will no doubt clarify this point in the future: the very short lifetime ( $<2 \times 10^{-10}$  s)<sup>1164</sup> of some intermediate complexes involved demand its intervention.

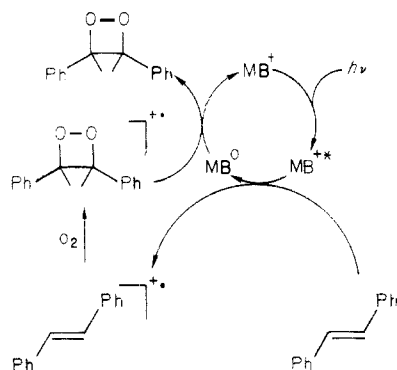
Most of the photosensitized<sup>1165-1168</sup> photooxygenation reactions are believed to involve promotion of  $O_2$  to an excited singlet state<sup>1169-1172</sup> or the formation of a "transitory complex" between the excited state of the sensitizer and oxygen in its ground state.<sup>1173-1179</sup> Recently, however, several electron-deficient sensitizers have been found to promote the oxygenation of electron-rich olefins which, with standard singlet oxygen conditions, give no oxygenated products. Foote<sup>1180</sup> observed that *trans*-stilbene in  $CH_3CN$  reacts with  $O_2$  in the presence of 9,10-dicyanoanthracene (DCA) employed as a sensitizer, to yield 2 mol of benzaldehyde. He proposed a mechanism,



where the olefin transfers an electron to an excited state of DCA for the production of radical ions, to be compared with the classical mechanism, where the sensitizer transfers its excess energy to oxygen, henceforth transformed into a singlet oxygen (note also that  $O_2$  ( $^1\Delta_g$ ) is a better oxidizing agent ( $E^\circ \approx 0.67$  V) than the ground state ( $E^\circ \approx 0.33$  V).<sup>1167a</sup>

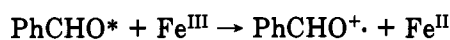
The quenching rate constants of fluorescence for cyano aromatic sensitizers by electron-rich olefins were demonstrated<sup>1181</sup> to agree with those expected from Weller's<sup>29</sup> treatment of photoexcited electron-transfer processes, and laser flash photolysis even allowed direct observation of the generation of  $DCA^-$  and its reaction with  $O_2$ .<sup>1182</sup> These photophysical studies fall in line with the ESR observation of  $DCA^-$  upon irradiation of a solution containing 1,1-diphenylethylene and DCA in deoxygenated  $CH_3CN$ .<sup>1183</sup> Furthermore, Schaap was also able to show that the oxygenating species involved in the last step is indeed superoxide and not molecular oxygen (cf. 1101b). Superoxide reacts 30 times faster with chemically generated radical cation of olefin than does oxygen. Therefore, the foregoing catalytic cycle involving superoxide ion<sup>1184,1185</sup> seems well established and has other applications.<sup>1186-1189</sup> However, in some cases part of the overall oxygenation products could arise from the reaction of singlet oxygen. A. J. Bard<sup>1190a</sup> indeed showed that superoxide and various radical cations annihilate to produce low yields of singlet oxygen. With the radical cation of thianthrene these yields are drastically increased.<sup>1191b</sup> On the other hand, the high quantum yields measured (20) for the photosensitized (DCA) oxygenation of methyl 1,2-diphenylcyclopropene-3-carboxylate<sup>1192</sup> suggest that under some conditions both class I and class III (see section II2) photoelectron-transfer catalysis may contribute to the overall disparition of reagents. The example given in section II2c shows that other electron-transfer-photosensitized oxygenations do not include the participation of superoxide. Foote discovered recently another such example in the photosensitized (methylene blue  $MB^+$ ) oxygenation of *trans*-stilbene,<sup>1193</sup> where the use of Weller's equation<sup>29</sup> dismisses the possibility of superoxide production in the medium. The mechanism in Scheme XLVI is supported by the experimental observations. Some electron-transfer-photosensitized oxygenation may also be sensitized with  $\alpha$ -diketones,<sup>1194</sup> or carbon tetrachloride, or tetrabromide.<sup>1195</sup> The whole set of preceding results leads unavoidably to the question:<sup>1193</sup> What degree of overlapping may exist between the photogeneration of singlet oxygen (energy

Scheme XLVI



transfer) and peroxide generation (electron transfer)? D. G. Whitten and C. Gianotti<sup>205</sup> have shown that during the quenching of porphyrin and metalloporphyrin excited states by oxygen, both superoxide ion and singlet oxygen are formed. The latter dominates with this class of photooxygenation sensitizers,<sup>1196</sup> but the authors stress the point that for other sensitizers the reverse situation<sup>1184</sup> could be met as well. An elegant and simple experimental tool to evaluate the eventual involvement of singlet O<sub>2</sub> in photooxidations has recently been proposed by Foote:<sup>1197</sup> it rests on the fact that the lifetime of singlet O<sub>2</sub> is 10 times longer in CD<sub>3</sub>CN than in CH<sub>3</sub>CN. More recently Farid<sup>1198</sup> described an electron-transfer-sensitized photooxygenation of 1,1-dimethylindene that yielded products with regiochemistry opposite to that of products from comparable singlet-oxygen reaction. The photosensitized tris(2,2'-bipyridine)ruthenium(II) oxidation of ascorbic acid<sup>1199</sup> in an aqueous solution illuminated with visible light shows that attractively cheap processes could emerge from these studies. Chemical trapping using the high reactivity of superoxide ion<sup>1200,1201</sup> should also be feasible under certain conditions. The problem, however, is that this anion radical is also highly reactive towards some of the transients (radical cations) formed in these reactions.<sup>1191</sup>

Recent work<sup>1202</sup> on the photoinitiated oxidations of benzaldehyde<sup>1203,1204</sup> and sulfite<sup>1205,1206</sup> by oxygen brings a new view of old reactions<sup>1207,1208</sup> and provides a possible example of class II photoelectron-transfer catalysis. Veprek-Siska's group provides evidence to back the proposition that the role of light in this reaction is to generate a catalyst for the thermal reaction. This occurs by the reducing action of excited benzaldehyde on traces of transition-metal ions, e.g.,

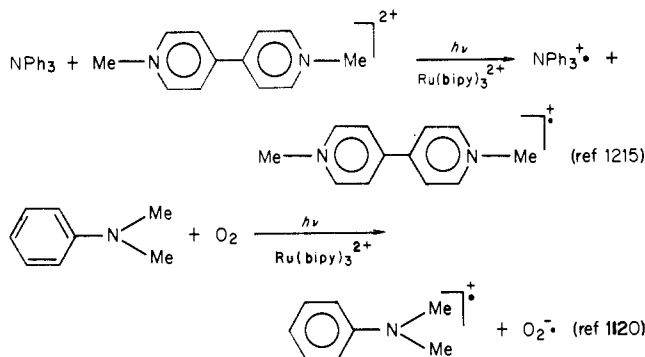


The exact mechanism of thermal oxidation catalyzed by Fe<sup>II</sup> is unknown; therefore, at the moment there is some ambiguity for classing this example in type II or type III photoelectron-transfer catalysis.

The photooxidation of chloride to chlorine in aqueous solution catalyzed by anthraquinone derivatives<sup>1209a</sup> in the presence of O<sub>2</sub> proceeds via electron transfer from the chloride to the anthraquinone triplet state. These results bear some analogy with the corresponding redox-catalyzed thermal reaction.<sup>1210</sup>

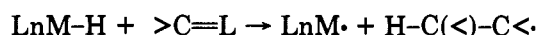
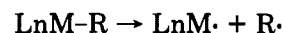
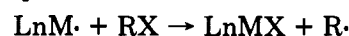
Some oxidizing agents are highly promoted when catalytic amounts of 1-e oxidants are present (catalysis by silver(I),<sup>1211</sup> ruthenium(III),<sup>1191a</sup> copper(III),<sup>1212,1213</sup> cerium(IV)<sup>1214</sup>); it would be interesting to know if ap-

propriate stable photosensitizers could play the same role. The Ru(bipy)<sub>3</sub><sup>2+</sup>-photoinduced reduction of NPh<sub>3</sub> which goes in the nonspontaneous direction has been discussed thoroughly with other oxidation reactions of the same type in the good review<sup>335</sup> by T. J. Meyers:



## 10. Relations with Ionic Coordination Catalysis

As pointed out by J. Halpern,<sup>1216a</sup> research in the field of homogeneous catalysis during the past several decades has mainly focused on processes<sup>1217</sup> such as hydrogenation,<sup>1218</sup> carbonylation, hydroformylation,<sup>1219</sup> metathesis,<sup>1220,1221</sup> and certain oxidation<sup>1222</sup> reactions that proceed through nonradical mechanisms. Halpern then gives some examples where the foregoing type of catalyzed reactions involve radical species; as a starting point, he enumerates the three main classes of processes in which free radicals are generated through reactions of metal complexes



Although the first of these three processes<sup>1223,1224</sup> may be viewed as an S<sub>H</sub>2 mechanism and therefore possibly (section I5c) as inner-sphere electron transfer,<sup>1225</sup> nothing is said in this paper<sup>1216a</sup> about the possibilities offered by electron transfer to generate free radicals. From the preceding sections it should be clear that, under appropriate conditions, the second process (see section III1b) and the third one (see section III8) may involve electron-transfer mechanisms. This is particularly true when photochemical and electrochemical methods are used to generate the catalyst. In our opinion, the actual importance of electron-transfer catalysis in the so-called "ionic" homogeneous catalysis will be realized only when searchers working in this field connect more systematically their photochemical results with electrochemical ones and vice versa. That this is not yet recognized is shown by the following examples where we tie together references where an electron-transfer mechanism is not even discussed and where another work (reference given) not yet connected to it could suggest such an interaction: reaction<sup>1226</sup> between PhCH<sub>2</sub>Mn(CO)<sub>5</sub> and HMn(CO)<sub>5</sub> where the thermal homolysis of Mn-C bond is induced by the diamagnetic hydride (MAH<sup>730</sup>). In organic molecular-assisted homolysis there are not many ways<sup>740,1227</sup> to escape the electron-transfer scheme to explain the production of paramagnetic species from diamagnetic ones. It should be noticed that with inorganic transition-metal com-

plexes there is one more degree of liberty: the possibility of internal transition low spin  $\rightarrow$  high spin<sup>1228</sup> before the reaction occurrence or that of thermal intramolecular electron transfer between the ligands and the metal;<sup>1229,1230</sup> photochemical hydroformylation of olefins with ionic cobalt catalysts in the presence of  $P(n\text{-Bu})_3$ <sup>1231</sup> (possible electron donor under irradiation, see section III1c1), to be connected with the radical mechanism proposed by J. Halpern<sup>1216a</sup> for the thermal hydroformylation of styrenes and Marko's studies on the role of  $\text{Co}_2(\text{CO})_8$  in these reactions;<sup>1216b</sup> photoinduced metathesis of olefins<sup>1232-1235</sup> where the irradiation of a mixture of  $\text{W}(\text{CO})_6$  (good electron donor in excited state) and  $\text{CCl}_4$  (good acceptor, see section III2a) allows the production of an active catalyst for the thermal reaction, to be connected with the observation of paramagnetic species in the thermal reaction catalyzed by  $\text{WCl}_6$  (acceptor),  $\text{AlEtCl}_2$  (donor)<sup>1236</sup> and with the recent electrochemical generation of metathesis catalysts;<sup>1237</sup> photochemical hydrogenation with direct modification of rate and selectivity of Wilkinson catalyst,<sup>1238</sup> or iridium complexes catalysts,<sup>1239</sup> to be connected with the good electron-donor properties of some M-H bonds.<sup>1124</sup> These examples are only a small sampler among many more; they converge with Halpern,<sup>1216</sup> Khidekel,<sup>1240</sup> Kochi<sup>1241</sup> reviews to discourage the proposition of simple ionic mechanisms in this field without any experimental attempt (ESR, CIDNP, free-radical clocks, pulse radiolysis, flash photolysis) at detecting the presence of paramagnetic species. The following electrochemical results (for which photochemical germane experiments are still to be carried out) still strengthen this warning: electrochemical hydrogenation<sup>1242</sup> and electrochemical generation of iron dinitrosyl that is a powerful catalyst for C-C bond formation from dienes.<sup>1243</sup> It may be stressed that the electron-transfer hypothesis is not limited to semantic mechanistic interpretations. For example, if it is proven that in the photocatalyzed metathesis involving  $\text{W}(\text{CO})_6$  and  $\text{CCl}_4$  a photoredox reaction is involved, then new couples of catalysts involving donor-acceptor couple will possibly be devised.

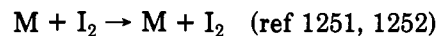
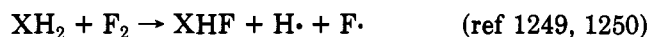
### 11. A Classification of Reactions Assisting the Search of New Activation Processes

To make skimming through the review easier, we retained a classical division of reactions in the foregoing sections. We would like to suggest that another classification of richer heuristic value may be conceived. It follows from two basic principles: most of the reactions may be viewed as starting by a donor-acceptor interaction (not necessarily spectroscopically identified); therefore, DD, AA, and AD couples are possible to devise a reaction. For the first two categories a third umpolung reagent or catalyst must be added (see section II1); for the third one, when the DA interaction is not intrinsically strong enough, it can be increased by acid-base catalysis (in its larger sense) and its improvements,<sup>1244</sup> by electron-transfer catalysis,<sup>42</sup> or by a combination of both types of catalysis. Photochemical excitation may enhance the activation in any of these three situations or even increase the DA interaction without any other catalyst present (in this sense *photochemical umpolung* exists and is important). The

second principle is that electron transfer (oxidative or reductive) is associated with two main kinds of activation: dissociative (including simple weakening of bonds leading to stereoisomerizations) and associative. This converges with the R. D. Guthrie proposition of classification,<sup>1245</sup> which parallels some inorganic approaches,<sup>1246</sup> and with the lucid Ebersson treatment of electroorganic synthesis.<sup>278</sup> The combination of these two basic principles leads to the matrix shown in Table XX. Heuristic matrixes are usually richer in possibilities than the actual world simply because they do not include a critical examination of what boxes should be crossed out on "logical grounds." We feel, however, that in this field the molecular logics are not mature enough to allow such a crossing: Alder's logical attempts to predict some impossible electron-transfer-catalyzed mechanisms led him to propose that  $S_{\text{RN}}2$  (cf. ref 543) and oxidation-reduction mechanisms (cf. sections III8 and III9) should not exist. On the other hand, we did not include a further dimension in this matrix: namely, the possibility of adding mixtures of E designed to allow the operation of both acid-base and electron-transfer activation. With this in mind, it should be clear that *electron-transfer catalysis and, more specifically, photoelectron-transfer catalysis probably has a bright future in the design of new reactions and rational explication of old ones.*

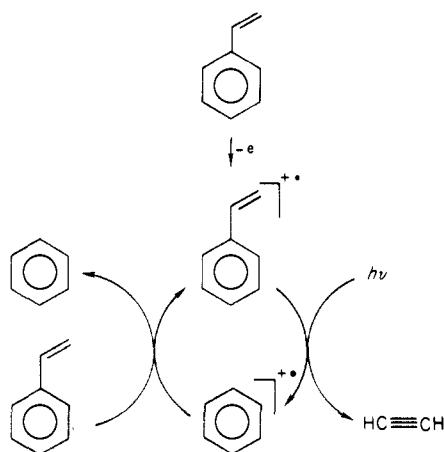
### IV. Examples of Photoelectron-Transfer Catalysis In the Gas Phase

Although the notion of chain reaction was born from the gas-phase study<sup>1247</sup> of the reaction  $\text{H}_2 + \text{Br}_2$  and this class of reaction is still under study, it does not seem that chain reactions initiated by an electron transfer are recognized in classical gas-phase studies.<sup>1248</sup> The direct homolytic reaction is by far the most usual initiating act, although in the reaction  $\text{H}_2 + \text{F}_2$  and  $\text{H}_2 + \text{I}_2$  the initiating step involves an interaction between several species:

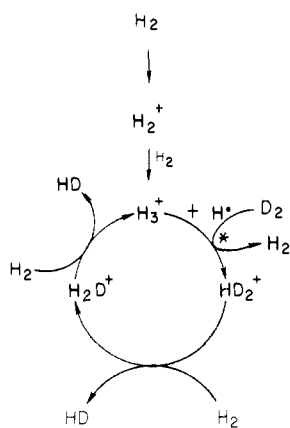


This interaction, however, has never been viewed as an electron transfer and is difficult to study experimentally. The same have bearing with Rice-Herzfeld mechanisms of pyrolysis.<sup>1253</sup> In some cases the same overall kinetic law is insufficient to discriminate between a first-order<sup>1254</sup> initiation step and a second-order one.<sup>1255</sup> Furthermore, photochemical initiation is considered to be necessarily a unimolecular event.<sup>7</sup> All these data would suggest that electron-transfer catalysis is nonexistent in the gas phase; the so-called ionic mechanisms discussed by Benson<sup>1309</sup> closely parallel electron-transfer mechanisms. Furthermore, electron-transfer catalysis in the gas phase seems sensible because proton-transfer catalysis<sup>1256</sup> is known in this phase and also because clustering seems to play an important role in the reactivity of species studied in a flowing afterglow apparatus<sup>1257</sup> and in gas-phase (<1 torr) radiation chemistry.<sup>1258,1259</sup> We, therefore, made a superficial search of processes studied in the gas phase and for which the proposed mechanism involves electron-transfer catalysis.

An interesting example of electron-transfer-induced chain reaction comprising photochemical stimulation was recently reported in ICR studies:<sup>1260-1262</sup>

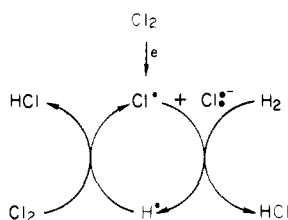


Radiation chemistry in the gas phase<sup>1263</sup> provides the simplest possible electron catalytic scheme: it concerns the radiation-induced exchange reactions in the system  $H_2/D_2$  or  $H_2/I_2$  or  $o\text{-}p\text{-}H_2$  conversion. Schaeffer and Thompson indeed proposed that the initiation started with oxidation of  $H_2$  by the radiation according to the following scheme:<sup>1264,1265</sup>

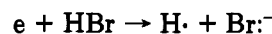


\*for this step see ref 1266

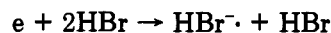
The initiation step ( $H_2^+ + H_2$ ) may be viewed as an inner-sphere ( $S_H2$ ) electron-transfer process; the chain is rather long ( $>10^4$ ) (cf. ref 1267). In contrast with this example where oxidative associative activation is involved, reductive dissociative activation explains part of the overall reaction observed in the radiation-induced reaction between hydrogen and chlorine:<sup>1268</sup>



Armstrong<sup>1269a</sup> made an interesting contribution to the problem of reductive dissociative activation in the gas phase; he proposed that the two-body reaction:



is not tenable and that three-body reactions better explain his experimental results:

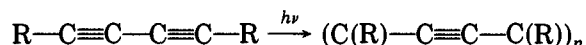


Possible examples of such photoelectron-transfer catalysis may be found in A. R. Anderson and G. G. Meisel's chapters in the book (ref 1270) (vinyl acetate polymerization,<sup>1271</sup> N exchange in  $N_2O$ ,<sup>1272</sup> ethylene polymerization<sup>1273,1274</sup>). Now that bimolecular gas-phase reactions of anions are experimentally traceable,<sup>1275,1276</sup> it would be interesting to check if the chain character of some solution reaction (e.g., *p*-nitrobenzyl halides +  $N_3^-$ ) is conserved in the gas phase.

## V. Examples of Photoelectron-Transfer Catalysis in the Solid State

In a review dealing with intermolecular interactions in organic molecular crystals, Ponte Goncalves<sup>1277</sup> gives clear evidence for electron-donor-acceptor complexes and excimers<sup>1278</sup> in organic molecular crystals (see also ref 1279). It is, however, uneasy to evaluate their role in the photochemical activity in the solid state.<sup>1280,1281</sup> This is particularly true because the spectroscopic evidences for complexes originate from an overall view of the crystal, whereas lattice imperfections that present very probably the initiating sites for reaction<sup>1282,1283</sup> are in such a small concentration that their structural characteristics are beyond the grasp of spectroscopy. Keeping this restriction in mind, we can only pick up some selected examples that suggest that electron-transfer catalysis and its photochemical implications could play a role in the solid state.

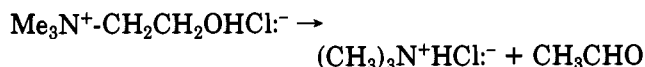
The solid state polymerization of diacetylene<sup>1284-1289</sup> with high-energy radiation corresponds to the overall reaction:



The rates of polymerization on either radiation or thermal annealing<sup>1289</sup> cover a wide range<sup>1290</sup> according to the value of R, and a proper choice of solvent allows the obtention of active or inactive phase. Recently Patel<sup>1291</sup> was able to measure values of quantum yield higher than 50 when  $R = (CH_2)_4OCONHCH_2COO(C-H_2)_3CH_3$ . The initiation step of this reaction is not well understood but could involve electron transfer for the radiation-induced examples.

Cationic polymerization of vinylcarbazole induced by gaseous halogens, boron trifluoride, stannic chloride, or sulfur dioxide in a solid state could be viewed either as an acid- or an oxidant-catalyzed reaction.<sup>1292,1293</sup>

A long free-radical chain has been proposed to explain<sup>1294</sup> the radiation-induced decomposition of chlorine chloride:<sup>1295</sup>



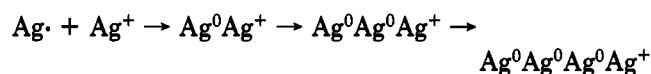
One of the best known (but not necessarily best understood<sup>1296</sup>) photoelectron-transfer-catalytic reactions occurring in the solid state is the silver halide photography. A drastically simplified picture of the phenomenon is that the light induces an electron transfer from

Table XX. Matrix of Electron-Transfer Activation Modes for Searching New Reactions<sup>a</sup>

type of reaction	dissociative, type of activation	associative, type of activation
substitution	R.A.: D + A; D + A + E <sup>b</sup>	R.A.: D + A; D + A + E
	O.A.: D + A; D + A + E	O.A.: D + A; D + A + E
addition	R.A.: D + A; D + A + E	R.A.: D + A; D + A + E
	O.A.: D + A; D + A + E	O.A.: D + A; D + A + E
metathesis	R.A.: D + A; D + A + E	R.A.: D + A; D + A + E
	O.A.: D + A; D + A + E	D.A.: D + A; D + A + E
elimination	R.A.: D + A; D + A + E	
	O.A.: D + A; D + A + E	
oxidation	R.A.: D + A; D + A + E <sup>c</sup>	
	O.A.: D + A; D + A + E	
rearrangement	R.A.: D + E; A + E	
	O.A.: D + E; A + E	
stereoisomerization	R.A.: D + E; A + E	
	O.A.: D + E; A + E	

<sup>a</sup> R.A. = reductive activation, O.A. = oxidative activation, D = donor, A = acceptor. The table may be extended to D + D or A + A, but in that case E becomes a necessity (cf. the dimerization or polymerization of olefins). <sup>b</sup> D + A corresponds to electron-transfer catalysis developing without light, and/or catalyst; E means either electron-transfer catalyst (thermal inner- or outer-sphere), photon in type I photoelectron-transfer catalysis, photocatalyst or photosensitizer, respectively, in type II and III photoelectron-transfer catalysis, cathode (anode) giving (taking) catalytic amounts of electrons, cathode (anode) + mediator giving (taking) stoichiometric amounts of electrons but with a decreased overpotential. <sup>c</sup> One can think of reductive activation of an oxidation if an initial electron transfer to the substrate being oxidized in the overall stoichiometric equation transforms it into an active species more susceptible to oxidation and able to enter a catalytic cycle (e.g., RX + O<sub>2</sub> + reductive photosensitizer). Although this matrix stressed catalytic activation, it should be clear that it can be used also for stoichiometric activation and umpolung (see ref 278); it could shed fresh light on some old mechanisms (oxidative duplication of thiolates, chemistry of so-called arynes, etc. . .).

the halide to Ag<sup>+</sup> (or to a delocalized conduction band of Ag<sup>+</sup>). This electron migrates to the nearest defect in the crystal, and there a beginning of clusterification occurs:



This is equivalent to an associative activation; the quantum yield<sup>1297</sup> of the process is about 0.9, and 3 atoms is the minimum size<sup>1298</sup> to be reached by the cluster to allow a subsequent development of the latent image. This development is a reduction<sup>1299</sup> of the host silver halide crystal, efficiently catalyzed (10<sup>-8</sup> g of cluster for 1 g of BrAg are sufficient<sup>1300</sup>) by the foregoing clusters of Ag (called latent image center). As the reduction is more efficient where the catalyst is present and as the catalyst is very near to the point where the photo met the crystal, parts that received high amounts of photons appear as rich in Ag<sup>0</sup> (black) after the development.

A whole class of reactions that could involve electron-transfer-induced processes is that of solid-state explosives and propellants that detonate under pressure or flash of light (NCl<sub>3</sub>, KClO<sub>4</sub>, etc.);<sup>1301</sup> it has been shown indeed that conductivity of crystals made of electron-donor-acceptor complexes<sup>1302,1303</sup> or of mixed valence compounds<sup>1304</sup> shows drastic changes in conductivity by application of pressure.

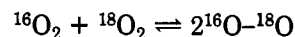
## VI. Photoelectron-Transfer Catalysis at Interfaces

One of the reasons why electron-transfer-catalyzed reactions should be studied with the utmost care in solution chemistry is the very great importance that they presumably have in interfacial systems and in heterogeneous catalysis where they are, however, more

difficult to experimentally demonstrate. This section will purposely be very concise; our only aim is to direct the reader to relevant reviews with the hope that it will make easier connections between apparently independent territories. A good introduction to the field is provided by Gerischer's review on interfacial reactions caused by excitation.<sup>1209b</sup>

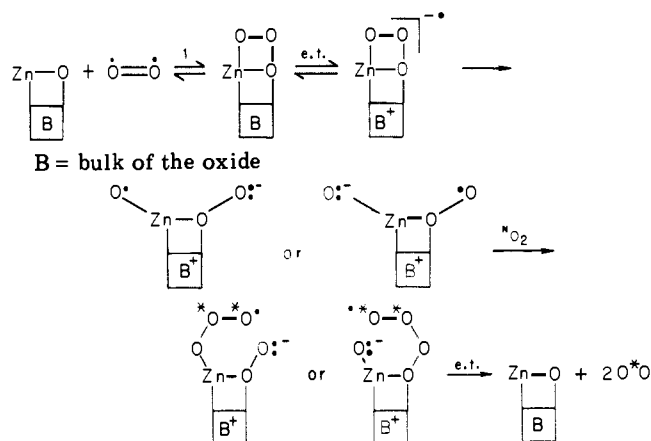
### 1. Heterogeneous Catalysis

As Volkenshtein<sup>1305</sup> mentions in his pioneering book, most of the heterogeneous catalysis deals with semiconductors because, besides the well-identified semiconductor oxides, many metals used as catalysts are covered with a semiconducting film. Furthermore, A. J. Bard and co-workers<sup>1306</sup> recently considered the catalytic activity of metal colloids under the angle of colloids acting as microelectrodes with a potential determined by the photoinduced mediator. We shall therefore summarize one very careful mechanistic work dealing with catalysis on semiconductors<sup>1307</sup> and treat it in a molecular approach to point out the similarities between solution electron-transfer catalysis and interfacial electron-transfer catalysis. More in-depth treatments may be found in ref 1305, 1308, and 1310b. J. Cunningham studied the rapid isotopic equilibration:<sup>1307</sup>



that takes place at room temperature under the catalytic influence of oxygen-deficient zinc oxides. Cunningham points out that occurrence of the overall reaction implies a sequence consisting of at least the following three processes: (a) adsorption onto ZnO with activation of the <sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sub>2</sub> probably on active sites, (b) surface exchange of oxygen isotopes, and (c) desorption of isotopically equilibrated oxygen back into the gas phase. A molecular description could be:





From the point of view of electron-transfer activation the first adsorption is necessary: if too weakly adsorbed  $O_2$  were to receive an additional electron the species would have a pronounced  $O_2^-$  character, and the bond in this radical anion is still strong enough to avoid dissociation.<sup>1311</sup> On the other hand, if the adsorption is strong enough, the double-bond character of  $O_2$  is significantly decreased on adsorption; therefore, if there is a bulk to surface charge transfer,<sup>1312</sup> the species formed will be of the type  $R-O-O-R^-$ , whose lability has been treated in section IIIId. The addition of  $O_2$  to the dissociated oxygen needs no special comment, but the last step deserves comparison with the classical electron-transfer-catalytic cycle that we have discussed in section IIII. We recall that in this catalytic cycle one important condition was that the redox potentials of the intermediate  $NuCH_2Ar^-$  and reagent  $ClCH_2Ar$  were to be such that the chain could go on.<sup>546</sup> Here the bulk of the catalyst  $B^+$  has to be such (expressed equivalently in terms of Fermi levels or local redox potentials) that it can accept the return of the initially borrowed electron, because this return conditions the desorption step (cf. ref 1313). The photocatalytic effects<sup>99,1314-1317</sup> reported in many heterogeneous catalytic processes, although experimentally demonstrated beyond any doubt<sup>1318</sup> in certain cases, is still a good way off the grasp of total rationalization;<sup>1319</sup> this may be understood from the preceding sections; in the preceding molecular mechanism there are at least four steps where light can play a role: adsorption,<sup>1320-1322</sup> change of relative redox properties<sup>1323-1325</sup> of the couple adsorbed reagent catalyst, direct photocleavage of an adsorbed bond, and desorption.<sup>1326-1328a</sup> In any case, we believe that understanding would go at an increased pace if results obtained in homogeneous solution and at interfaces were more systematically brought into relationship. Comparison of substituent effects<sup>1329</sup> for both classes of processes is an important step in this direction. The industrial importance of catalysis on metal oxides<sup>1330</sup> fully justifies such an effort. We treated one example where reductive dissociative electron-transfer activation was involved; it should be clear, however, that oxidative examples probably exist as do associative examples, too (see section IIII6). To set up an equivalence scale between the position of the Fermi potential (which can be modified either by doping or illumination) and the in-solution redox properties of systems involved in electron-transfer catalysis,<sup>42,326</sup> it would be interesting to quantitatively study the same reaction under both homogeneous and heterogeneous conditions. For ex-

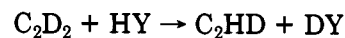
ample, the racemization of  $Co^{III}(en)_3^{3+}$  is catalyzed by electron transfer<sup>886</sup> in solution and occurs also on charcoal<sup>1331</sup> and carbon black acts as an ET catalyst in the two-phase dehydrogenation of hydrazo nitriles.<sup>1328b</sup> Many more examples may be found in the excellent Spiro essay,<sup>1332</sup> and work in this direction<sup>1333</sup> may provide interesting new synthetic openings.<sup>1334</sup> Mechanistic studies<sup>1269b</sup> on superbasic surfaces<sup>1310a</sup> should also contribute to this important stream.

## 2. Photoelectrochemistry

It transpires from the foregoing sections that the field from where most fundamental progress in understanding interfacial electron-transfer catalysis is coming is photoelectrochemistry. Furthermore, this field is experiencing impressive development because of its connections with the use of solar energy. The introductory lecture given by Professor Nozik for the 70th Faraday Discussions of the Royal Society in its 1980 meeting<sup>1335</sup> is of such quality that there is no need for us to write a section on this topic. The reader should therefore return to this account and more recent reviews<sup>1336-1338</sup> to gain a view of the importance of this field in relation to the understanding and practical application of electron-transfer catalysis.

## 3. Catalysis by Electron-Donor-Acceptor Complexes of Alkali Metals

In 1958 K. Tamaru<sup>1339</sup> started his series of studies dealing with the use of donor-acceptor couples as catalysts. In a typical experiment, phthalocyanine powder doped with small amounts of Na catalyzes the hydrogen exchange:



HY = phthalocyanine

at room temperature, whereas the same reaction does not occur at 200 °C with highly purified phthalocyanine.<sup>1340</sup> Many other reactions<sup>1341</sup> were then discovered to be catalyzed by such electron-donor-acceptor complexes (also called color centers by other workers<sup>1342</sup>):  $H_2-D_2$  exchange reaction,<sup>1267</sup> hydrogenation of unsaturated hydrocarbon,<sup>1343</sup> nitrogen,<sup>1344</sup> and carbon monoxide,<sup>1345b</sup> and dehydrogenation.<sup>1346</sup> Their industrial application has been hampered until now because their long-term stability was not sufficient.<sup>1353</sup> The illuminating paper written by A. J. Bard<sup>1338</sup> gives the fundamentals to understand the connections between this class of thermal catalysis by powders and photocatalysis. A simplified description follows from the foregoing sections: light may be able to transform any adsorbate on the powder into a reducing agent whose reducing ability challenges the one associated with alkali metals (although this reducing ability is enhanced<sup>1346</sup> for alkali metals themselves when they are in anionic vacancies). Another important aspect stressed in this *Science* publication is the gain in understanding fundamentals of heterogeneous catalysis when these results are analyzed in electrochemical terms.

This section on electron-transfer catalysis at interfaces purposely left aside other interesting aspects such as emulsions<sup>1347</sup> and organometallics,<sup>43</sup> we hope, how-



ever, to have shown the rich connections to be established between homogeneous electron-transfer catalysis and photocatalysis where a coherent mechanistic picture is beginning to emerge, and its heterogeneous counterpart where the mechanistic aspects are far less precise but the practical achievements considerable. A bunch of new processes could possibly result also from tighter connections between the field of ETC and the large class of intercalation compounds.<sup>1345a</sup>

## VII. Applications

The range of applications of photoelectron-transfer catalysis is amazingly wide. Even if we omit the photochemical applications aiming at a rational utilization of solar energy,<sup>1348,1401</sup> there remains a great variety of fields where photoelectron-transfer catalysis can bring new applications.

Section III should have shown that even with the remarkable achievements already obtained in synthetic chemistry, *the subject still seems full of potentialities for the design of new mild synthetic processes*. Among the less explored areas, we can cite: coenzyme photoregeneration,<sup>1349a</sup> design of polymer-supported<sup>1349b,1350,1415-1419</sup> redox photosensitizers allowing an easier workup of the obtained products, use of anchimeric<sup>1351,1352</sup> assistance to devise systems<sup>1354</sup> comparable with polyfunctional acid-base catalyst,<sup>1355,1356</sup> attempts to use electron-transfer catalyst or sensitizers<sup>1357,1358</sup> as a way of designing asymmetric catalytic reactions (this seems a priori a difficult aim because outer-sphere electron transfers display weak sensitivity to steric effects<sup>123a,1420</sup>) but some hope<sup>1359,1360,1418</sup> is still left with inner-sphere processes<sup>1361</sup> and even perhaps with some outer-sphere<sup>1362,1363,1421</sup> application of phase-transfer-catalytic conditions to photoelectron-transfer catalysis,<sup>1364</sup> and use of semiconductor powders with or without sensitizers. This last point deserves a special mention; A. J. Bard<sup>1338</sup> describes the application of photoelectrochemistry for the deposition of metals<sup>1365</sup> (Pt, Cu, ...) on semiconductors, the chemistry done by these catalysts being different from that observed at macroelectrode or classical heterogeneous catalysts. Applying this principle without barriers between organic and inorganic chemistry opens an immense territory to be explored, because one can imagine photodeposition of noble metal on organic powders but also photodeposition of organic or organometallic compounds on surfaces in such a way that *a new generation of tailor-made redox surfaces is going to appear*.<sup>1366</sup> A very difficult challenge with respect to this is the design of milder reduction processes for the activation of industrial catalysts.<sup>1367</sup> Photochemistry will play a role in both their design and utilization. One of the most challenging aspects of these synthetic applications is their intrinsically interdisciplinary character: they link such different fields as organic and inorganic, thermal and photochemical, homogeneous and heterogeneous, all fields that overspecialization had led to divergence and whose electron-transfer activation shows the intrinsic unity.

Another field of applications already well explored<sup>1366</sup> is the one of photographic systems where some of the reactions involved in the so-called free-radical photography<sup>1369</sup> are clearly ETC ones; this is still an important

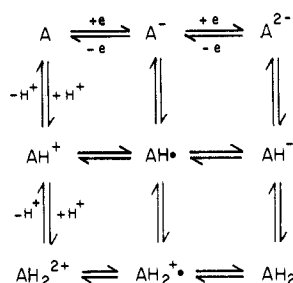
territory despite the fact that rather satisfactory systems are already available.<sup>1370</sup> In their recent review, Alfimov and Yakusheva<sup>1368</sup> draw attention to the fact that material whose employment is based on electron phototransfer have the highest energetic light sensitivity: up to  $10^{-7}$  J cm<sup>-2</sup>. On the other hand, a complete review<sup>1371</sup> is devoted to the role of donor-acceptor interactions in non-silver information recording processes. These two contributions show the definitive importance of photoelectron-transfer catalysis for the field of information recording processes. In a related field, the reprographic technique of diazography<sup>1372</sup> could benefit from better understanding of photoelectron-transfer catalysis (see section III7b).

Electron-transfer-induced dissolution of Fe<sup>III</sup> oxides and ferrites<sup>1373</sup> suggests interesting experiments to be tried in the field of photodissolution of corrosion pits. Photopolymerizations are one of the rare applications of photochemical methods to the heavy chemical industry (polyamides). We have seen that photoelectron-transfer catalysis could explain some of these reactions either in the liquid<sup>1374</sup> or solid state.<sup>1375</sup> This latter field with its associated possibilities of absolute asymmetric syntheses making chiral products<sup>1376</sup> from achiral precursors and of designing solid-state systems for information storage<sup>1377</sup> could take on more and more importance in the future. On the opposite side, the incorporation of dyes in some polymers could stabilize them by playing the role of electron trap or electron source under light irradiation.<sup>1378</sup> Graft polymerization on chemically modified wools<sup>1422</sup> could possibly be performed with visible light.

An indirect application of photoelectron-transfer catalysis could be to use it as an analytical tool,<sup>1379</sup> e.g., trace amounts of tin can be detected thanks to its catalytic effect<sup>1380</sup> on the oxidation of hydroxynaphthol blue by H<sub>2</sub>O<sub>2</sub>. This type of amplification has been reviewed,<sup>1379</sup> and many new applications issue every year.<sup>1381,1382,1423</sup>

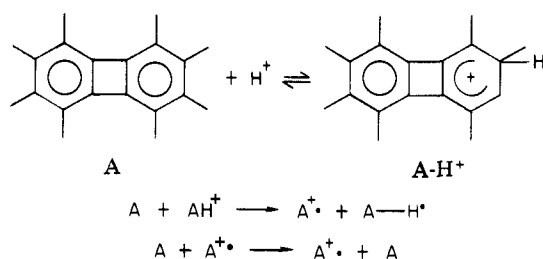
These applications should stimulate the design of new sensitizers or photocatalysts with improvements in the direction of stability,<sup>1383</sup> special stericity,<sup>1384</sup> and high chirality inducement power. More generally the search for new oxidizing and reducing structures<sup>1424-1426</sup> may lead to new achievements in the mechanistic understanding of ETC. All these studies will contribute to the full identification of the various mechanistic possibilities involved in simple model systems, possibly making easier the understanding of far more complex biological systems (photosynthesis,<sup>1385-1390</sup> electron-transfer proteins,<sup>1427</sup> mitochondrial electron-transfer chains<sup>1428,1429</sup>) in a way reminiscent of Jenck's approach to proton-transfer catalysis<sup>911</sup> (although it must be recognized that some biological effects<sup>1430</sup> are uneasy to stimulate on simple models). Although we did not treat the case of branched chains initiated by electron transfer, it should be stressed that there is no obvious reason why such a kind of initiation should be forbidden for these cases. As the actual nature of the initiation process does not in itself affect the kinetic treatment of the reaction, provided that radicals are produced during initiation at a constant rate, it seems that not much work has been devoted to this step in the field of explosives and propellants.<sup>1301</sup> Now that the conceptual mechanistic basis for electron-transfer catalysis

is better understood,<sup>42</sup> it would be interesting to investigate what the hypothesis electron or photoelectron-transfer-initiated branched chain brings to this field. This deeper understanding is also needed to disentangle one important mechanistic problem the surface of which until now has only been scratched by mechanistic chemists: namely, the successive occurrence of steps when both electron-transfer and acid-base catalysis (either  $H^+$ ,  $OH^-$ , or generalized Lewis<sup>1391</sup>) are involved. This problem was treated a long time ago by electrochemists: Cauquis recently represented it quite clearly for the reduction of A to  $AH_2$  (square diagram).<sup>1392</sup>



Although this square diagram involves a stoichiometric reaction, its implications for catalytic reactions have to be considered.

These implications are obviously dealt with in the electron-transfer chemistry of carbanions.<sup>1146</sup> Until now it does not seem that this type of analysis has been extended beyond the field of electrochemistry despite the fact that there are certainly systems in organometallic chemistry,<sup>915</sup> bioorganic chemistry, inorganic chemistry,<sup>121f,579</sup> and organic chemistry<sup>819,1393-1397</sup> where this analysis could be performed. A noticeable exception is provided by the elegant NMR studies reported by Hart.<sup>1431</sup> To explain the modification of NMR signals observed for octamethylbiphenylene solubilized in chloroform when trifluoroacetic acid is added to the solution, he proposed the following scheme:



These types of studies would help precisizing on simpler systems the chemiosmotic approach.<sup>1399</sup> Fast photochemical techniques seem indeed particularly able to resolve the old dilemma.<sup>1398</sup> When do Lewis acids act as acids and when do they act as oxidizing agents? The same kind of question arises with base catalysis<sup>1432</sup> of photoreactions (i.e., when base?, when reducing?, when both?).

Another direction in which fascinating results are expected and that we discussed in the first paper of this series is the use of magnetic fields<sup>1398</sup> to change the selectivity of the overall quantum yields of photoelectron-transfer catalysis or to induce anisotropic reactions in appropriate solids.<sup>1433</sup> The recent publication by

Neta<sup>1400</sup> that reports simultaneous flash photolysis and pulse radiolysis of metalloporphyrin opens the way to a deeper understanding of the interactions involved for electron-transfer reaction according to the multiplicity of a given state.

### VIII. Summary and Outlook

In this contribution we have tried to show that a large territory of photochemistry, rather neglected until now because it was overlapping with so-called dark reactions, deserves more in-depth studies because of its generality and potential applications. The main new information brought by this review is: set of new mechanistic scenarios covering a large variety of reactions that are generally not even discussed in most of the recent articles or reviews, the necessity of putting into perspective these photochemical results with their thermal and electrochemical counterparts, the importance of electron-transfer photosensitization (class III photoelectron-transfer catalysis) for the design of new processes, an extension of the EDA concept in the direction of catalysis, a set of reactions where fast techniques should lead to bright investigations, the recognition that a very important activation (dissociative or associative) may result from electron transfer (intramolecular or intermolecular), and the pervasiveness of the dilemma, "direct photochemical homolysis electron-transfer-induced one." This rich harvest of information was made possible when it was recognized that photoelectron-transfer catalysis is a topic by itself and not a balkanization of tiny islands associated with large territories of chemistry (inorganic, organic, organometallic; polymers and biochemical; electrochemical, photochemical, and thermal; experimental and quantum theoretical; solution, solid state, interfaces, and gas phase); it is precisely this positive overlapping with so many different areas that confers to it this strategic attractiveness.

One of the most fascinating aspects of the present topic is its ambivalent character: the preceding sections have shown that applied chemistry already uses photoelectron-transfer catalysis; on the other hand, the very roots of chemical reactivity seem to be closely enmeshed with it (1e-2e mechanistic dilemma in inorganic (ref 233, 1402-1404, 1434), organic (ref 42, 352a, 693, 786, 1405-1407, 1435-1437), organometallic (ref 43, 258, 1408-1410), biological (ref 1140, 1411, 1412, 1438), role of cages (ref 138), ion pair, and solvation in this reactivity (ref 1391, 1413, 1414)); from this point of view, it is very probable that in the future photochemists working in the picosecond range will contribute as much towards in-depth understanding of chemical reactivity as many "thermal" chemists.

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