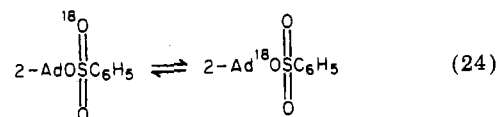


values of γ^+ for particular substituents according to the substrate used in eq 19, but, nevertheless, it appears that these parameters will be quite useful in the interpretation of reaction mechanisms. Only a small portion of the development work needed to establish the limits of this correlation has been done, but some of the comparative data available at this early stage are listed in Table I.

When a similar calculation of γ^+ for the cyano moiety ($\sigma_p^+ = 0.66$) was carried out for five different systems, values of 2.77, 3.14, 3.26, 3.49, and 4.00 were obtained.¹⁹ The most likely explanation of this relatively large variation in γ^+ is that the balance that exists between inductive destabilization and mesomeric stabilization for the cyano group is a function of the stability of the incipient carbocation. As a result, there is no single value for γ^+ that would fit all situations. A similar circumstance should exist for the α -carbonyl group.

The results discussed above are relevant to several important recent studies of solvolysis theory. Bentley et al. have carefully examined the rate dependence on solvent of many solvolytic reactions and have concluded that relatively few (but including 2-AdOTs and 7a) react by k_c routes.²⁴ Other systems such as cyclooctyl and *endo*-norbornyl tosylates that have been claimed to react by k_c processes are proposed by the authors to react with solvent participation.²⁴ The value of ^{18}O -labeling studies has been demonstrated again by Par-

adisi and Bunnett,³⁸ who have shown that, even in 2-adamantyl benzenesulfonate solvolysis, scrambling of the ^{18}O label occurs during solvolysis (eq 24). One



interpretation of this result is that reversible formation of an ion pair occurs before the rate-limiting step in this solvolysis. Finally, there is the conclusion of Knier and Jencks³⁹ that even typical secondary cations are not sufficiently stable in the presence of "reasonably good nucleophiles" to form intimate ion pairs but must react through one-step processes. It appears certain that further study of destabilized carbocations will be a powerful tool for the clarification of these new theories of carbocation behavior.

We thank the National Science Foundation (U.S.) and the Natural Science and Engineering Research Council (Canada) for financial support, and Drs. J. F. Bunnett, X. Creary, and T. W. Bentley for sharing their unpublished results. Our special gratitude goes to the contributions of our co-workers mentioned in the footnotes.

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 (39) Jencks, W. P. *Acc. Chem. Res.* 1980, 13, 161-169. Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* 1980, 102, 6789-6798. See also Richard, J. P.; Jencks, W. P. *Ibid.* 1982, 104, 4689-4691, 4691-4692.

Catalysis of Photochemical Reactions

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"The process resembles the creation of a work of art, which is firmly guided by the final whole even though the whole can be definitely conceived only in terms of its yet undiscovered particulars".¹

There is no reason why a reaction originating in an excited state cannot be catalyzed. Catalysis of ground-state reactions, both homogeneous and heterogeneous, is of course a well-developed concept; it enables us to explain many natural phenomena² and has fostered chemical changes of commercial value.³ Perhaps owing to the lack of a clear definition, catalysis of excited-state reactions has not emerged as an identifiable field of study, despite significant activity in this and related areas and conspicuous progress in understanding of photochemical reaction mechanisms.⁴ In this Account we propose a definition of a catalyst of a photochemical reaction and examine and classify according to the definition a variety of reported acceleratory

phenomena for photochemical reactions.

Chemists have applied a bewildering assortment of terms to reactions exhibiting enhanced quantum yields, examples of which include catalyzed, sensitized, promoted, accelerated, enhanced, stimulated, protonated, induced, and assisted. These words are often joined to the words light or photo or to a word designating a substance. The manifest lack of clear terminology in this area indicates that the chemistry being reported has outstripped the conceptual basis for describing it and that some new attention to definitions is needed. This Account is prompted by that recognition and by the conviction that a new phenomenon clearly recognizable as homogeneous catalysis in photochemistry is

(1) Polanyi, M. "Science, Faith, and Society"; University of Chicago Press: Chicago, 1964; p 32.

(2) Bender, M. L. "Mechanisms of Homogeneous Catalysis from Proteins to Proteins"; Wiley: New York, 1971.

(3) Thomas, C. L. "Catalytic Processes and Proven Catalysts"; Academic Press: New York, 1970. Wittcoff, H. A., and Reuben, B. G. "Industrial Organic Chemistry in Perspective"; Part I; Wiley: New York, 1980.

(4) (a) Neckers, D. C. "Mechanistic Organic Photochemistry"; Reinhold: New York, 1970. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin-Cummings: Menlo Park, CA, 1978.

Gene G. Wubbels was born in Preston, MN, in 1942. He received his B.S. from Hamline University and his Ph.D. from Northwestern University. In 1968 he joined the faculty of Grinnell College and in 1979 became Professor of Chemistry. He was a Visiting Professor at the University of Leyden, 1981-1982 (NSF Science Faculty Professional Development awardee).

now evident in the literature.

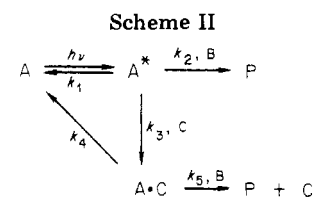
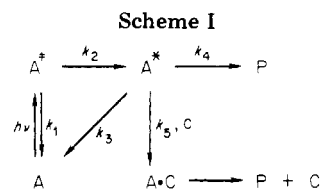
The relationship of this Account to the intensive efforts now occurring in the area of "photocatalysis" may be of interest to several readers. Investigators in photocatalysis aim to use mainly heterogeneous systems such as organized assemblies⁵ in solution or photoelectrodes⁶ to carry out photoreactions. Of particular interest is the aim of using solar energy to split water into hydrogen and oxygen.⁷ A dichotomy of heterogeneous and homogeneous systems has thus emerged for catalyses involving excited states, which parallels that for catalyses in the ground state. We shall deal here almost entirely with homogeneous systems; the problems of definition will cause us to look briefly at the heterogeneous systems.

Definition of a Catalyst of a Photochemical Reaction

Catalysis in the ground state results from the action of a catalyst, "a substance which appears in the velocity expression to a power greater than its coefficient in the stoichiometric equation".⁸ One observes catalysis by a change in rate but explains catalysis by identifying a new reaction pathway made available by the catalyst.² In the simple case, reaction through the catalytic pathway, which involves a unique set of intermediates and rate constants, proceeds at a greater rate than does the uncatalyzed reaction and is evidenced in the rate expression by a term containing the catalyst concentration.

Efficiency for a photochemical reaction is the quantity analogous to rate for a ground-state reaction. Efficiency is measured by the quantum yield, which is the number of moles of a particular species formed or reacted divided by the number of einsteins of photons absorbed.⁹ In practice, the two measurements comprising the quantum yield are usually rate measurements, moles per unit of time and einsteins per unit of time. Rationalization of the quantum yield, however, in terms of photophysical and photochemical processes, requires a quantum yield expression, which is analogous to the rate expression for a ground-state reaction. The quantum yield expression relates efficiency to concentration terms and elementary rate constants for the system.

We propose that a catalyst for a photochemical reaction be defined as a substance that appears in the quantum yield expression for reaction from a particular excited state to a power greater than its coefficient in the stoichiometric equation.¹⁰ As will be shown below, it is often convenient to invert the quantum yield expression in order to isolate the catalyst concentration variable. In the inverted form a catalyst will appear with a negative exponent, the absolute value of which must exceed its coefficient in the stoichiometry.



General Reaction Schemes and Quantum Yield Expressions

Photochemical kinetic expressions may be conveniently derived through use of the steady-state assumption for excited states or reactive intermediates. Considering Scheme I, for the moment in the absence of catalyst, C, the efficiency of reaching the excited state, A*, from the excited state, A*, populated on initial excitation of A, is given by $\phi_i = k_2/(k_1 + k_2)$. The efficiency of reaching the product, P, from A* is $\phi_{ii} = k_4/(k_3 + k_4)$. If A* were a reactive intermediate in the ground state capable of decay to A, the same expressions would obtain. The overall efficiency is the product of ϕ_i and ϕ_{ii} . In the presence of catalyst, C, which in this case reacts irreversibly with A* to form A·C,¹¹ the quantum yield expression is as shown in eq 1. Inversion of eq 1 gives a convenient working expression, eq 2.

$$\Phi = \phi_i \left(\frac{k_4 + k_5[C]}{k_3 + k_4 + k_5[C]} \right) \quad (1)$$

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left(1 + \frac{k_3}{k_4 + k_5[C]} \right) \quad (2)$$

Equation 2 allows the prediction that a plot of the experimental numbers, $1/\Phi$ vs. $1/[C]$ will approach straight lines in two regions if two boundary conditions are achieved experimentally. If $k_4 \gg k_5[C]$, eq 2 is approximated by eq 3, which indicates that the quantum yield will not vary appreciably with changes in the catalyst concentration. For the region in which $k_4 \ll k_5[C]$, eq 4 applies, which predicts a linear relationship

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left(1 + \frac{k_3}{k_4} \right) \quad (3)$$

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left(1 + \frac{k_3}{k_5[C]} \right) \quad (4)$$

between $1/\Phi$ and $1/[C]$. Scheme I and eq 2-4 represent a simple form of the important category, general acid or base catalysis.¹² In that instance, the term $k_5[C]$ would be the sum, $\sum_i k_{5i}[C_i]$.

Although Scheme I includes an uncatalyzed route to product, a common occurrence in real systems, this is not a necessary feature of a catalyzed photoreaction. A

(5) Calvin, M. *Acc. Chem. Res.* **1978**, *10*, 369-375.

(6) (a) Bard, A. J. *J. Photochem.* **1979**, *10*, 59-75. (b) Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154-162.

(7) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376-384.

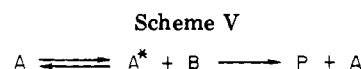
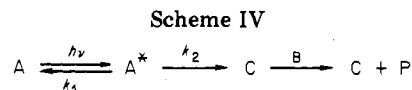
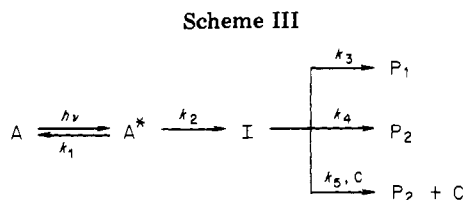
(8) Bell, R. P. "Acid-Base Catalysis"; Oxford University Press: Oxford, 1941. This definition does not apply without modification to chain reactions. For further discussion of the concept of catalysis in ground states, see ref 2 and 13.

(9) Reference 4b, pp 243-245; an einstein is an Avogadro's number of photons.

(10) Wubbels, G. G.; Celander, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669-7670; correction, *Ibid.* **1982**, *104*, 2677.

(11) A·C in this and the following schemes may be variously, an exciplex, a conjugate acid or base of A*, a pair of ions or radicals, a σ -complex, or a coordination complex.

(12) The distinction between general and specific acid (or base) catalysis for ground-state systems is discussed in detail in ref 2 and 8.



system is catalytic if the requirement stated in the definition is met.

Scheme I could also apply to the case where A^* is a bimolecular complex or adduct formed by reaction of A^* with coreactant B . In that case, k_2 in the term ϕ_1 would be replaced by $k_2[B]$.

Scheme II represents a case in which the product-forming step is bimolecular and the catalyst complex $A \cdot C$ decays to starting materials. The quantum yield expression is shown in eq 5, where f represents the

$$\Phi = \frac{k_2[B] + fk_3[C]}{k_1 + k_2[B] + k_3[C]} \quad (5)$$

partitioning of $A \cdot C$, i.e., $f = k_5[B]/(k_4 + k_5[B])$. Under the condition $fk_3[C] \gg k_2[B]$, the inverted quantum yield expression is approximated by eq 6.

$$\frac{1}{\Phi} = \frac{1}{f} \left(1 + \frac{k_1 + k_2[B]}{k_3[C]} \right) \quad (6)$$

It is often observed, as shown in Scheme III, that a rather stable intermediate partitions between two photoproducts. If the catalyst acts on the intermediate, in the limit $k_5[C] \gg k_4$, the quantum yield expression for P_2 is eq 7, which resembles eq 4. The system may

$$\frac{1}{\Phi} = \left(1 + \frac{k_1}{k_2} \right) \left(1 + \frac{k_3 + k_4}{k_5[C]} \right) \quad (7)$$

be easily distinguished, however, from Scheme I since the quantum yield for reactant disappearance in Scheme I is dependent upon the catalyst concentration, whereas in Scheme III it is independent.

As anticipated by the definition, catalyst concentration appears in the denominator of the inverted quantum yield expression for each of these schemes. The schemes by no means exhaust the possibilities for catalytic photochemistry, but they will provide a basis for the ensuing discussion of real systems.

Phenomena Distinguishable from Catalysis of a Photoreaction

Acceleration of thermal or photochemical reactions may have several causes. Noncatalytic causes already well-defined^{2,13} such as initiation of a chain reaction, temperature effects, and general solvent or salt effects need not be discussed here. We note in passing, moreover, the long-standing proscription¹³ of terming any light-induced reaction, "catalyzed by light". The term is a nonsequitur if catalysis is considered to be the action of a substance. In our opinion, the term "photocatalyzed" and its variants share this shortcoming, and we recommend that their use be discontinued (see below).

Sensitization by electronic energy transfer, an important and well-studied photochemical technique,¹⁴

(13) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961.

often causes a photoproduct to be formed with a quantum yield greater than that of the direct photo-reaction. In these cases the sensitizer increases the quantum yield by increasing the efficiency of reaching the reactive excited state; the efficiency from that state to the product is unchanged. Since it is in the latter stage that a catalyst must act, the well-recognized category sensitizer is excluded from the category catalyst.

Substances such as heavy-atom-containing solvents¹⁵ and compounds that make donor-acceptor complexes with excited states¹⁶ are known in several cases to enhance the efficiency of reaching a particular excited state, usually a triplet. These too would be excluded from the category catalyst because they affect only the efficiency of reaching the reactive state.

The term "photocatalysis" has been applied to two cases that should be distinguished from catalysis of a photochemical reaction. The first, outlined in Scheme IV, involves photochemical production of a catalyst in its ground state that catalyzes a ground-state reaction such as hydrogenation or isomerization of an olefin.¹⁷ In such a case, the rate of formation of the product, P , depends upon the catalyst concentration, which in turn depends upon the partitioning of A^* . There is, however, no photochemical reaction being catalyzed.

A second general case termed photocatalysis involves light absorption by a species, which causes a chemical change in another species while returning itself to its original state. A simple system is illustrated by Scheme V. This scheme applies to a number of solar energy conversion and storage systems and to "photocatalytic" semiconductor devices and photoelectrochemical cells.⁶ Photochemists will recognize Scheme V as a kind of photosensitization process, which we think suggests the chemistry more accurately than does the term photocatalytic or the alternative term photoassisted.¹⁸ The criterion for the "catalytic" part of the designation is that the absorbing species acts more than once (usually repeatedly) to effect the chemical change taking place.^{6,19} This aspect does indeed evoke catalysis, but a photosensitizer also may perform its function repeatedly, whether it causes chemistry elsewhere by electronic energy transfer or by direct dissociation of a bond in the quencher.²⁰ The distinction rests on

(14) Lamola, A. A.; Turro, N. J. "Energy Transfer and Organic Photochemistry"; Wiley: New York, 1969.

(15) (a) Horrocks, A. R.; Kearvill, A.; Tickle, K.; Wilkinson, F. *Trans. Faraday Soc.* 1966, 62, 3393-3399. (b) Fleming, R. H.; Quina, F. H.; Hammond, G. S. *J. Am. Chem. Soc.* 1974, 96, 7738-7741.

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(17) (a) Nasielski, J.; Kirsch, P.; Wilputte-Steinert, L. *J. Organomet. Chem.* 1971, 27, C13-14. (b) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 173-189. (c) Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.* 1981, 103, 977-978.

(18) Wrighton, M. S.; Ginley, D. S.; Wolczanski, P. T.; Ellis, A. B.; Morse, D. L.; Linz, A. *Proc. Natl. Acad. Sci. U.S.A.* 1975, 72, 1518-1522.

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whether the reactant or the unchanging species is initially excited.

We will not treat here the many photoreactions of organic substrates mediated by metal ions^{17b,21} beyond noting that most are difficult to classify cleanly as either catalyzed or sensitized. Typically the metal ion is not changed by the photoreaction, but the absorbing chromophore is a complex in which both the metal ion and the substrate are necessary.

Certain complex photoreactions and some sensitized ones may, however, include catalytic steps. If the reaction is the process $(A-B)^* \rightarrow A-P$, where P is product, the conversion is often effected by transfer of an electron or an electron hole of A^* to a mediating species, which causes chemistry while it returns to its original state.⁷ Such species are catalysts of the photochemical reaction. Species postulated to mediate proton or electron transfers in the photosynthetic unit²² are thus catalysts or catalytic groups. Whereas opsin makes a covalent complex with its substrate, if it does indeed mediate proton transfers in the photoisomerization of 11-*cis*-retinal,²³ it exemplifies an enzymic catalyst of a photoreaction.

Related to but distinguishable from catalysis of photoreactions are the "photostimulated" radical chain substitution reactions.^{24,25} These reactions, when caused by light, are known to occur by a free-radical chain mechanism, the photochemistry serving only to generate chain-propagating radicals. These processes are not catalytic just as ground state initiations of chain reactions are not considered to be catalytic.¹³ The distinction is implied by the term photostimulated,²⁵ but in the interest of consistency we prefer the term photoinitiated. The recent characterization of these reactions as "electron transfer catalysis"²⁶ seems wholly unjustifiable.

Acid and Base Catalysis

Base Catalysis. Possibly the earliest base-catalyzed photoreaction to be reported is the photoreduction of benzophenone to benzhydrol in 2-propanol containing sodium 2-propoxide.²⁷ In this case benzopinacol is formed with unit efficiency in the absence of base, and benzhydrol forms with nearly the same efficiency when the base is present.^{27b} The mechanism thus resembles Scheme III since the catalyst increases the product quantum yield at the expense of a competing product, the quantum yield of reactant disappearance remaining constant. The catalytic step probably corresponds to specific base catalysis.

Photo-Smiles rearrangements of ω -anilinoalkyl nitrophenyl ethers in acetonitrile or methanol are catalyzed by triethylamine,²⁸ and those of ω -aminoalkyl

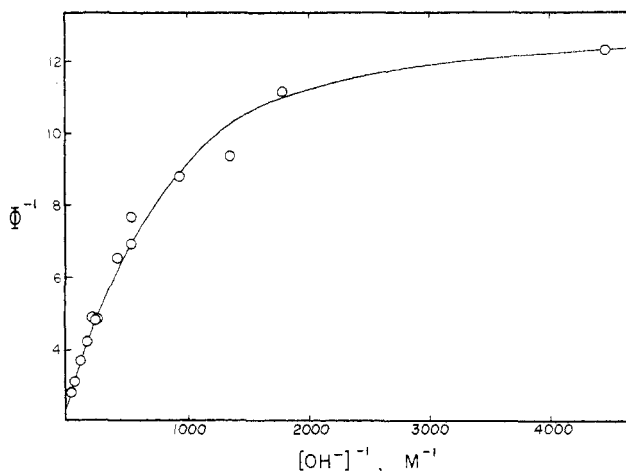
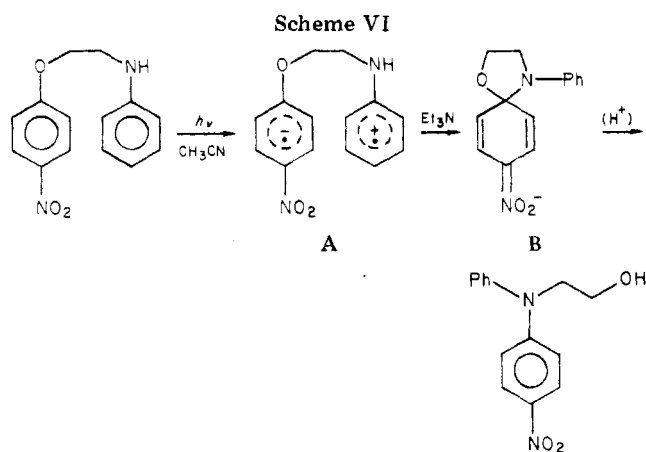


Figure 1. Quantum yield of photo-Smiles rearrangement of $m\text{-O}_2\text{NC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{NH}_2$ at various concentrations of NaOH.

nitrophenyl ethers in water are subject to general base catalysis.¹⁰ When the ω -amino group is NHPh ,²⁸ the systems are highly regiospecific for rearrangement or cyclization para to the nitro group. When the ω -amino group is NH_2 ,²⁹ strong meta regiospecificity is found. In the former case the mechanism shown in Scheme VI has been formulated on the basis of nanosecond flash photolysis studies. Radical ion pair A is believed to be responsible for a transient (λ_{max} 450 nm) formed within 10 ns of the laser flash whose lifetime (65 ns in acetonitrile) is shortened to 25 ns by 0.1 M Et_3N . The σ -complex B is assigned to a long-lived transient ($\tau > 1$ ms), which shows a diffuse maximum near 400 nm. That triethylamine is a catalyst rests on the demonstration that it interacts with transient A and also that it increases the efficiency of product formation. Quantitative efficiency data are not yet available for this system.

The effect of sodium hydroxide on the efficiency of photo-Smiles rearrangement of $m\text{-O}_2\text{NC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{NH}_2$ in water is shown in Figure 1.¹⁰ The plot indicates that an uncatalyzed reaction ($\Phi = 0.08$) occurs at low base concentration and that reaction catalyzed by hydroxide occurs at high base concentration ($\Phi_{\text{lim}} = 0.42$). Determination of the quantum yields at constant pH in the presence of the bases acetate,

(28) (a) Mutai, K.; Kanno, S.; Kobayashi, K. *Tetrahedron Lett.* 1978, 1273-1276. (b) Yokoyama, K.; Nakagaki, R.; Nakamura, J.; Mutai, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* 1980, 53, 2472-2475. (c) Mutai, K.; Yokoyama, K.; Kanno, S.; Kobayashi, K. *Ibid.* 1982, 55, 1112-1115.

(29) Wubbels, G. G.; Halverson, A. M.; Oxman, J. D. *J. Am. Chem. Soc.* 1980, 102, 4848-4849.

(21) (a) Srinivasan, R. *J. Am. Chem. Soc.* 1964, 86, 3318-3321. (b) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *Ibid.* 1982, 104, 998-1007. (c) Lewis, F. D.; Oxman, J. D. *Ibid.* 1981, 103, 7345-7347.

(22) Brace, J. G.; Fong, F. K.; Karweik, D. H.; Koester, V. J.; Shepard, A.; Winograd, N. *J. Am. Chem. Soc.* 1978, 100, 5203-5207.

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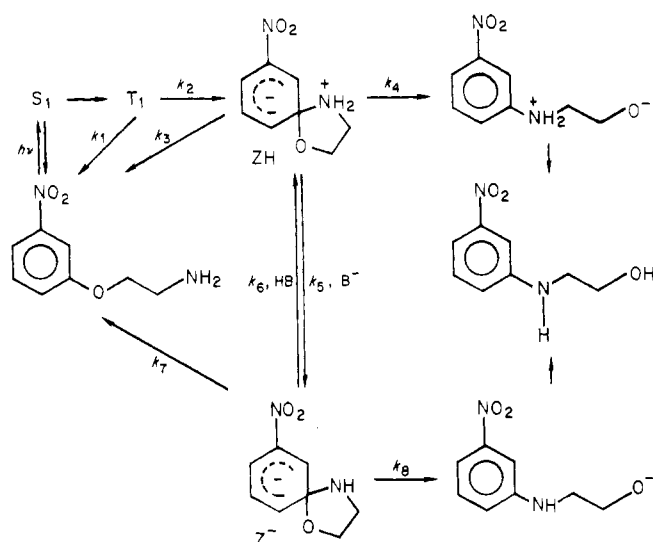
(24) (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* 1966, 88, 5663-5664. (b) Kornblum, N.; Michel, R. E.; Kerber, R. C. *Ibid.* 1966, 88, 5662-5663. (c) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 734-745.

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(27) (a) Bachman, W. E. *J. Am. Chem. Soc.* 1933, 55, 391-395. (b) Cohen, S. G.; Sherman, W. V. *Ibid.* 1963, 85, 1642-1647.

Scheme VII

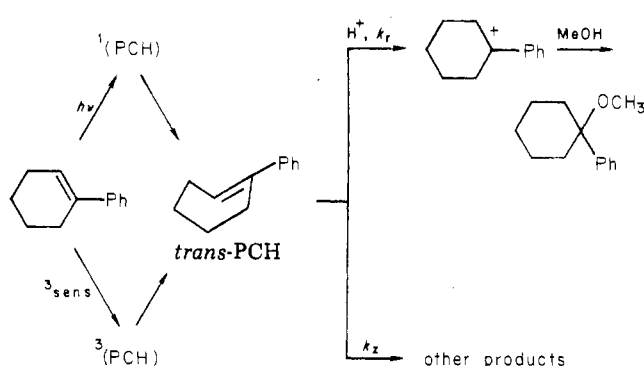


carbonate, phosphate, ethanolamine, and morpholine revealed that all are, to varying extents, effective catalysts. This demonstration, apparently the first, of general catalysis of a photoreaction was rationalized by the mechanism shown in Scheme VII (cf. Scheme I). General base catalysis requires that $k_7 + k_8 \gg k_6[\text{HB}]$. A nanosecond flash photolysis study in progress³⁰ indicates that k_8 is $1.4 \times 10^7 \text{ s}^{-1}$ and that, in contrast to the *N*-phenyl systems,²⁸ no exciplex intermediate intervenes between the triplet and the first σ -complex, ZH. It now seems obvious that electron transfer, as in the *N*-phenyl cases, should result in substitution ortho or para to nitro, whereas direct attack of a nucleophile on the triplet π, π^* nitrophenyl moiety should occur preferentially at the meta position due to the excited-state electron distribution or the small energy gap separating the meta encounter complex from the meta σ -complex.³¹

Quantitative studies show that amines are potent proton-transfer catalysts of photocyclization of 1-(α -naphthyl)-1-phenylethylenes to 1-phenyl-acenaphthenes^{32a} and of 1,4-diarylbutenyne to 1-phenylphenanthrenes.^{32b}

Acid Catalysis. One of the earliest reports of an acid-catalyzed photoreaction is that of Stoll and Schlientz,³³ who found that the endocyclic alkene moieties of ergotamine and lysergic acid diethylamide underwent Markovnikov photoaddition of water when irradiated in aqueous acetic acid solution. The closely related acid-catalyzed photoaddition of protic solvents to endocyclic alkenes was developed as a useful synthetic reaction in the late 1960's.³⁴ Whereas a rich variety of structural studies strongly suggested that these reactions proceeded from the excited alkene to a highly strained *trans*-cycloalkene, which underwent

Scheme VIII



protonation followed by solvent addition, quantitative evidence for the proposed mechanism has appeared only recently.³⁵ 1-Phenylcyclohexene (PCH) was found to react according to Scheme VIII. Plots of $1/\Phi_{\text{ether}}$ vs. $1/[\text{H}^+]$ were made for the direct irradiation (singlet reaction) and the sensitized reaction (triplet). The slope to intercept ratios of these plots represent the product of k_t and the lifetime, τ , of *trans*-PCH. That these ratios were identical for the singlet and triplet routes indicated that a common intermediate that reacted with acid was involved.^{35a} That the values also matched the product of τ for an intermediate assigned in a flash photolysis study^{35b} to *trans*-PCH and k_t from the same study strongly supported the findings. The mechanistic scheme (and associated quantum yield expression)^{35a} for this system is similar to the general case outlined in Scheme III. Since protonation of *trans*-PCH is probably irreversible, the catalysis in this system is likely to be general acid catalysis.

Related to these reactions are the acid-catalyzed photoadditions of protic solvents³⁶ and other neutral molecules³⁷ to benzene or toluene. In the former case, strong qualitative evidence supports the conclusion that benzvalene is formed photochemically and is then protonated and attacked by solvent to form bicyclo-[3.1.0]hexene photoadducts. The photoadditions of neutral molecules such as maleic anhydride, *p*-benzoquinone, α, α, α -trifluoroacetophenone, diethyl ether, and tertiary amines to benzene³⁷ appear to involve polar exciplex intermediates, which are captured by protonation of the acceptor portion thereof and thus prevented from decay to starting materials. The former case³⁶ corresponds to Scheme III, whereas the latter³⁷ corresponds to Scheme I (bimolecular version where A^* is an intermediate).

A variety of substituted aromatic alkenes and alkynes have recently been found to undergo efficient acid-catalyzed Markovnikov photohydration in sulfuric acid-water solutions.³⁸ For seven substrates lacking a nitro substituent group, a reaction scheme involving

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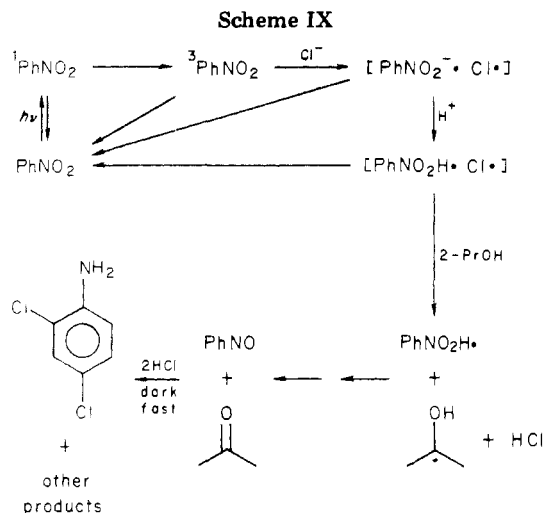
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protonation of the singlet excited state ($k_H = 1-4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the alkynes, $2-6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the alkenes) was proposed. The evidence consisted of linear plots of $1/\Phi$ vs. $1/[H^+]$, Stern-Volmer plots of fluorescence quenching by acid, effect of acid on directly observed transients in flash photolysis experiments, and solvent deuterium isotope effects. That the protonation step appeared to be irreversible suggests that the systems would show general-acid catalysis^{38b} (Scheme I with a single excited state). The nitro-substituted styrenes and phenylacetylenes underwent anti-Markovnikov photohydration from triplet excited states and displayed complex dependencies of efficiency on acid concentration. In these cases, efficiency-determining attack of water on the triplet state was suggested.

Nitrobenzene was found in 1966 to undergo a novel acid-catalyzed photoreduction-chlorination reaction with hydrochloric acid to give 2,4,6-trichloroaniline³⁹ and in 1967 to undergo HCl-catalyzed photoreduction by 2-propanol.^{40a} Uncatalyzed photoreduction occurs, but it is inefficient. The effect of HCl on photoreduction of nitrobenzene and other nitroaromatics^{40bc} was attributed to protonation of the $^3n,\pi^*$ state associated with the nitro group. We questioned this interpretation and showed that sulfuric acid was ineffective as a photoreduction catalyst.⁴¹ It was demonstrated that chloride ion played a critical role in the catalysis and that acid catalysis at constant chloride ion concentration did indeed occur but that a hydrogen ion concentration of 0.06 M in 50% 2-propanol-water containing 6 M chloride ion exhausted the catalytic effect of acid.⁴¹ These results were interpreted by the mechanism shown in Scheme IX. Subsequent microsecond flash photolysis experiments⁴² confirmed the sequence of electron transfer followed by protonation. The system corresponds in part to Scheme II, though there are two catalysts active in Scheme IX, hydronium ion and chloride ion (see below).

Our detailed study of the aqueous, acid-catalyzed photoreduction-chlorination reactions⁴³ (giving tri-

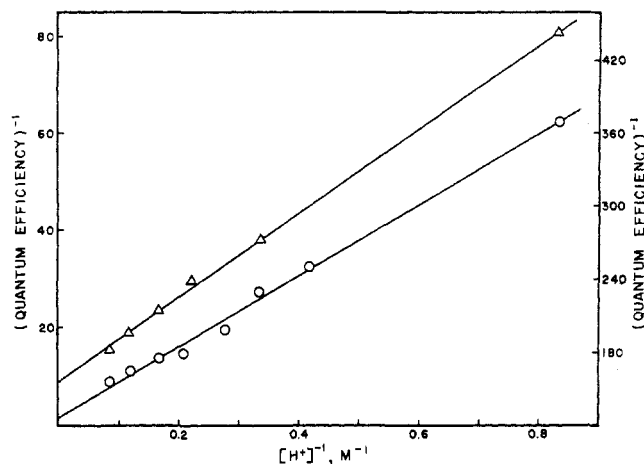
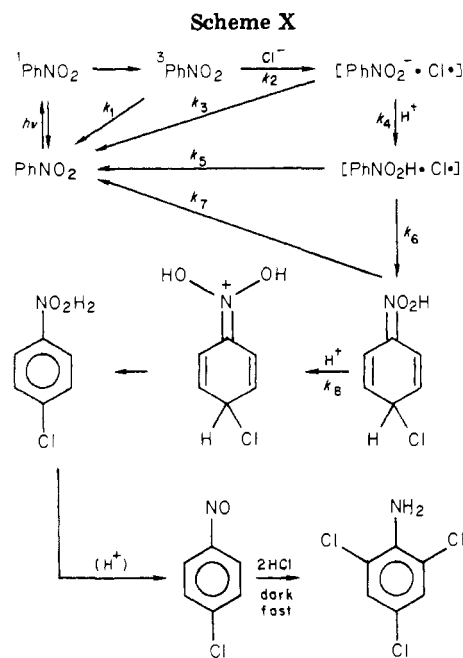
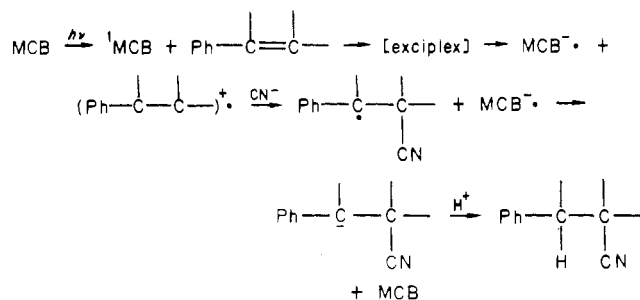


Figure 2. Quantum efficiency for disappearance of 3-bromonitrobenzene (Δ , read left ordinate) and 4-nitrophenol (\circ , read right ordinate) at various hydrogen ion concentrations in aqueous solutions of HCl and LiCl such that $[Cl^-] = 12 \text{ M}$.



Scheme XI



chloroanilines from nitrobenzenes) revealed that an additional acid-catalysis step was involved. For nitrobenzene and *m*-bromonitrobenzene, the quantum yields at constant 12 M chloride ion increase with increases in the acid concentration through the range 0.1–12 M, whereas for *p*-nitrophenol, the acid dependency ceases at about 5 M acid concentration. As shown in Figure 2, plots of $1/\Phi$ vs. $1/[H^+]$ at constant 12 M chloride ion

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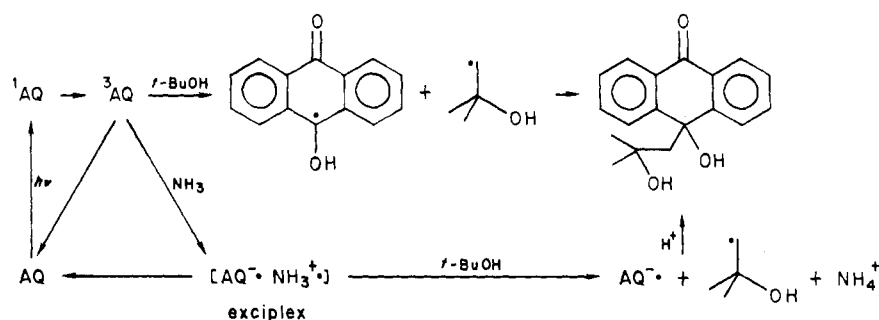
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Scheme XII



are linear, indicating clearly that acid catalysis is involved. Identification of the early reaction steps with those for HCl-catalyzed photoreduction follows from the observation that 1% 2-propanol diverted the reduction-chlorination almost entirely to reduction, presumably due to trapping of $[\text{PhNO}_2\text{H}\cdot, \text{Cl}\cdot]$.

The mechanism, shown in Scheme X, shows two distinct acid-catalysis steps. Step k_4 , capture of the anion radical partner of a putative exciplex, is similar to the process suggested for photoadditions to benzene³⁷ and recently postulated to explain the qualitative effect of acids on CIDNP of an aromatic ketone exciplex.⁴⁴ Step k_3 initiates acid-catalyzed tautomerization of a Meisenheimer adduct. The former catalysis is exhausted at proton concentrations above 0.1 M (observed in photoreduction),⁴¹ whereas the latter requires much higher acid concentrations. Chloride ion has a catalytic role in the photoreduction that will be discussed below as an electron hole transfer catalysis; its role in the reduction-chlorination reaction is not catalytic because it is consumed.

Other acid-catalyzed photoreactions whose kinetics have been studied more or less quantitatively include the acid-catalyzed photo-Wallach rearrangement of azoxybenzene⁴⁵ and the photocyclizations of diaryl-fumarates^{46a} and α -phenylcinnamates^{46b} to 9,10-dihydrophenanthrenes.

Electron-Transfer Catalysis

π -Orbital Donors and Acceptors. Clear examples of photoreactions caused by π -electron acceptors that suffered no overall chemical change were provided by Arnold and co-workers.⁴⁷ Anti-Markovnikov addition of alcohols and hydrogen cyanide to styrene derivatives caused by acceptors such as methyl *p*-cyanobenzoate (MCB) occurs according to Scheme XI.^{47b} Arnold designates these reactions electron-transfer photosensitized, a term we endorse in as much as reaction originates in an excited state of the acceptor. In one case, the exciplex and subsequent reactions were shown to occur by excitation of the olefin.^{47a} In this case the system should be designated a catalyzed photochemical reaction, the catalyst being the electron acceptor.

Photoaddition of styrene derivatives to other olefins by a mechanism related to Scheme XI has also been reported,^{47c} as has photosensitization by an electron donor.^{47d} A variety of electron-transfer photosensitized oxidations⁴⁸ and cycloadditions⁴⁹ have now been reported.

n-Orbital Donors. The HCl-catalyzed photoreduction of nitrobenzene by 2-propanol⁴¹ discussed previously (Scheme IX) shows a unique form of catalysis by an n-orbital donor, chloride ion, that we have termed electron hole transfer catalysis.⁵⁰ Due to the rapid rate of radiationless decay of triplet nitrobenzene,⁵¹ direct photoreduction by neat 2-propanol is inefficient ($\Phi = 0.01$). By transferring to chlorine the electron hole on oxygen of nitrobenzene created by n, π^* excitation, a longer lived or more reactive hydrogen abstractor is created, which greatly increases the efficiency of photoreduction.

A further example is shown by the ammonia-catalyzed photoaddition of *tert*-butyl alcohol to 9,10-anthraquinone (AQ),⁵⁰ as shown in Scheme XII. In this case also, the direct hydrogen abstraction is inefficient, generating product (cleanly) with $\Phi = 0.0058$ in 4:1 *t*-BuOH:benzene. Ammonia strongly enhances the quantum yield. A linear plot is obtained for $1/\Phi$ vs. $1/[\text{NH}_3]$, which indicates a limiting quantum yield (at infinite ammonia concentration) of 0.43. The system is an example of Scheme II.

Electron hole transfer catalysis has also been found for the water-catalyzed photoisomerization of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid.⁵² Catalysis by water is indicated by a linear plot of $1/\Phi$ vs. $1/[\text{H}_2\text{O}]$ for mixtures of water and acetonitrile; the transfer agent derives from a water molecule oxidized by one electron. An electron hole transfer catalysis involving rapid hydrogen-atom transfers by thiols has been reported for photoreduction of benzophenone by amines.⁵³ The process also appears to be involved in the hydroxide ion catalyzed dealkylations of *N,N*-dialkylnitroanilines⁵⁴ and the chloride ion catalyzed solar photodecomposition of nitrates in sea water.⁵⁵

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Concluding Remarks

This subject is in its infancy. The potential for growth seems large because of the well-developed natures of the two adjacent fields, namely, ground-state catalysis and photochemistry and because the concepts are likely to be useful in understanding solar photochemistry and exploiting it.

Some specific research questions that need attention can be identified. For electron hole transfer catalyses, it is not known whether an exciplex itself or a dissociated species bearing the electron hole is responsible for the observed hydrogen abstractions; there is no reason in principle why an exciplex cannot participate in the normal bimolecular photoreactions common to other excited states. We also know little about the rates and transition-state structures for proton transfers to and from excited molecules or energy-rich intermediates. Moreover, there is currently no example of protonic catalysis in which the excited molecule interacts reversibly with the catalyst, so that the conjugate acid

or base retains excitation. Indeed, it is generally true that we know little about the detailed energetics of complex photoreactions, and studies of catalysis may contribute new insights in that area. Finally, we know next to nothing about applications of catalysis in photochemistry, which might be expected to improve efficiencies and obtainable yields of products as well as to foster much new photochemistry.

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Contribution of Theoretical Chemistry to an Understanding of Electronic Substituent Effects

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Hammett substituent constants have now become an integral part of chemistry. Such σ values provide a numerical scale of the electronic effect, on a property or reactivity, of a substituent located elsewhere in the molecule. Much recent interest has centered on the origins, transmissions, and magnitudes of the various component electronic substituent effects included in such values. One difficulty is that the behavior of many substituents is dependent on the particular solvent employed, but recent developments have allowed a wide range of reactivities to be measured in the gas phase. Such measurements not only allow the establishment of unperturbed scales of substituent effects but are also directly comparable with theoretical calculations.

It is now possible to use theoretical methods to obtain reasonable values for some molecular properties, particularly using ab initio molecular orbital theory where the necessary programs are readily available. For certain processes, such as proton-transfer equilibria, the energy can often be calculated to within 1-2 kcal of the experimental gas-phase results. Likewise, theoretical electron-density distributions have been shown to be in reasonable accord with experimental electron-distribution maps.

Ronald D. Topsom was born in Brentford, England, in 1933; he received his B.Sc., M.Sc. at the University of New Zealand and his Ph.D. at the University of London. He served as Lecturer and Senior Lecturer in Organic Chemistry at the University of Canterbury, New Zealand from 1958-1965; and in 1965 he became Professor of Organic Chemistry at La Trobe University, Victoria, Australia, where he remains. His principal interests are the use of theoretical and spectroscopic methods in the study of substituent effects in organic chemistry.

The level of agreement obtained between theory and experiment gives sufficient confidence to allow a theoretical approach to related model systems that may not be available or amenable to experiment. The discussion below shows that such results can greatly help our understanding of the mechanisms and magnitudes of substituent electronic effects.

Ab Initio Molecular Orbital Theory^{1,2}

Theoretical calculations of substituent effects using ab initio molecular orbital theory have mainly employed the models² developed by Pople and co-workers. For very small organic molecules, such computations involve a compromise between computational cost and accuracy while for somewhat larger molecules, the number of orbitals involved limits the level of calculation that can be employed.

The simplest level (the so-called minimal basis) represents each atom by just those functions that are necessary to accommodate all of its electrons while maintaining overall spherical symmetry. Thus, at the STO-3G level,^{3,4} hydrogen is represented by a 1s orbital and the elements Li to F by five orbitals (1s, 2s, 2p_x,

(1) See, for example, ref 2 and "Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum, New York, 1977; "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum, New York, 1977.

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(4) Each orbital is approximated by a 3-G expansion to Slater-type functions.