84473-40-5; **3e**, 84473-41-6; **3f**, 69690-79-5; **3g**, 69690-88-6; **3k**, 69690-84-2; **3l**, 69690-82-0; **3m**, 69690-85-3; **3n**, 84473-42-7; **3o**, 69690-83-1; **3r** (R′ = H), 40630-94-2; **4f**, 69862-37-9; **4g**, 69690-90-0; **4k**, 69690-89-7; **5p**, 84473-43-8; **5q**, 84473-44-9; **13**, 84473-45-0; **15**, 84473-46-1; **19**, 84473-47-2; **20**, 60010-88-0; **22**, 84498-68-0; **23**, 84473-48-3; **24**, 72060-97-0; **26** (isomer 1), 84473-49-4; **26** (isomer 2), 84473-56-3; **27**, 84473-50-7; **28**, 16409-43-1; **29**, 84473-51-8; **30**, 84473-52-9; **31**, 1786-08-9; **32**, 84473-53-0; **33**, 77744-03-7; **34**, 84473-54-1; (±)-**36**, 84498-69-1; (±)-**37** (isomer 1), 82335-15-7; (±)-**37** (isomer 2), 82335-14-6; (±)-**38**, 82293-67-2; (±)-**39**, 69690-91-1; **39** (monochloro derivative), 84473-55-2; **40**, 69690-92-2; (±)-**41**, 65371-24-6; (±)-**42**, 69447-14-9; (±)-**43**, 67400-99-1.

Photohydration of Aromatic Alkenes. Catalytic Phenomena and Structure–Reactivity Studies

Peter Wan and Keith Yates*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received July 14, 1982

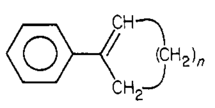
The photohydrations of aromatic alkenes **3–14** have been studied in aqueous sulfuric acid. Aromatic alkenes with substituents that have electron-donating effects equal to or greater than that of hydrogen (**3–7** and **14**) undergo photohydration via S_1 if other photoprocesses do not compete favorably. The electron-donating or -withdrawing abilities of substituents in S_1 do not necessarily reflect their ground-state σ values. For example, the meta-fluoro group is strongly electron withdrawing ($\sigma^+ = 0.35$) in the ground state, but evidence presented in this work suggests it is much less electron withdrawing (or in fact even becomes electron donating) in S_1. The opposite appears to be true for the para-fluoro substituent. It is shown that photohydration can be water, hydronium ion, or general acid catalyzed. The observation of general acid catalysis supports the proposed mechanism involving rate-limiting proton transfer to S_1. The individual catalytic rate constants for photoprotonation obey the Brønsted catalysis law, with an α value of $\sim$0.15, suggesting early transition states in these photoprotonations.

The photochemistry of alkenes has been a topic of continued interest to organic photochemists, offering a rich and fruitful area for study. A recent review[1] summarizes the present understanding of the photobehavior of this functional group in solution.

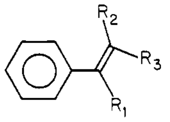
Of special interest to us is the photoprotonation of alkenes (eq 1). The photoprotonation process for aliphatic

$$>\mathrm{C{=}C}< \underset{\text{photoprotonation}}{\xrightarrow[\mathrm{H}^+]{h\nu}} >\mathrm{HC{-}C}^+< \underset{\text{photohydration}}{\xrightarrow{\mathrm{H_2O}}} >\mathrm{CHC(OH)}< \quad (1)$$

alkenes is reasonably well understood. For those aliphatic alkenes that undergo observed photohydration, it has been proposed that the mechanism involves nucleophilic trapping of the Rydberg state of the molecule by the solvent.[2] For nonaromatic cyclic alkenes, the mechanism is believed to involve nucleophilic trapping both of the Rydberg state and of the highly reactive *trans*-alkene intermediate, the mechanism followed depending on the ring size.[3] The situation for aromatic alkenes is less well understood. Phenylcycloalkenes **1** where n = 3–5 undergo photoprotonation via a mechanism involving the reactive trans intermediate (from either direct or sensitized excitation).[4] 1-Phenylcyclopentene (**1**, n = 2), being incapable of undergoing cis to trans isomerization, does not undergo photoprotonation.[4] To our knowledge, there have been no attempts at a systematic study of the protonation process for acyclic styrenes (**2**), although several styryl systems with electron-releasing substituents have been found to undergo Markovnikov addition of methanol and acetic acid.[5] We recently reported[6] our initial exploratory results on the



1



2

---

(1) Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1.

(2) (a) Kropp, P. J.; Reardon, E. J., Jr.; Gaibel, Z. L. F.; Williard, K. F.; Hattaway, J. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7058; (b) Fravel, H. G., Jr.; Kropp, P. J. *J. Org. Chem.* **1975**, *40*, 2424.

(3) (a) Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Am. Chem. Soc.* **1965**, *87*, 934. (b) Corey, E. J.; Shulman, J. I. *Tetrahedron Lett.* **1968**, 3655. (c) Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1965**, *87*, 2052. (d) Kropp, P. J. *Ibid.* **1966**, *88*, 4091. (e) Kropp, P. J.; Kraus, H. J. *Ibid.* **1967**, *89*, 5199. (f) Marshall, J. A.; Carroll, R. D. *Ibid.* **1966**, *88*, 4092. (g) Okada, T.; Shibata, K.; Kawanisi, M.; Nazaki, H. *Tetrahedron Lett.* **1970**, 859. (h) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783. (i) Kawanisi, M.; Kato, H. *Tetrahedron Lett.* **1970**, 721. (j) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635. (k) de Marcheville, H. C.; Beugelmans, R. *Tetrahedron Lett.* **1969**, 1901. (l) Marshall, J. A. *Acc. Chem. Res.* **1969**, *2*, 33.

(4) (a) Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 6383. (b) References 3h and 3g. (d) Fujita, S.; Hayaski, Y.; Nomi, T.; Nozaki, H. *Tetrahedron* **1971**, *27*, 1607. (e) Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329. (f) Bonneau, R.; Joussot-Dubien, J.; Yarwood, J.; Pereyre, J. *Tetrahedron Lett.* **1977**, 235.

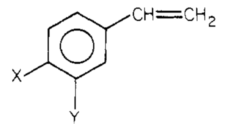
(5) (a) Miyamoto, N.; Kawanisi, M.; Nozaki, H., *Tetrahedron Lett.* **1971**, 2565; (b) Nozaki, H.; Otani, I.; Noyori, R.; Kawanisi, M. *Tetrahedron* **1968**, *24*, 2183. (c) Hixson, S. S. *Tetrahedron Lett.* **1973**, 277. (d) Hornback, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6773.

(6) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509. The photochemistry of alkynes in general has not been extensively investigated. Some recent papers are as follows: (a) Inoue, Y.; Ueda, Y.; Hakushi, T. *J. Am. Chem. Soc.* **1981**, *103*, 1806. (b) Nishio, T.; Omote, Y. *Chem. Lett.* **1976**, 103. (c) For a review, see: Coyle, J. D. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 15 pp 523–551.

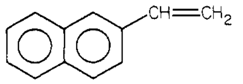
photohydration of some aromatic alkenes (mostly acyclic styrenes) and alkynes, which significantly extended the understanding of the photoprotonation behavior of these compounds. In this paper we report our further results on catalytic phenomena and structure–reactivity studies for the photohydration of aromatic alkenes in aqueous media. The results give insight into the nature of the transition state as well as the electron demand of the photoprotonation process for acyclic styrenes.

Results

Product Studies. The substrates chosen for this structure–reactivity study (**3**–**14**) were available commercially or synthesized via dehydration of the corresponding 1-arylethanols.[7] Compounds **3**–**13** were distilled and **14** was sublimed prior to use. We have previously shown[6] that alkenes **3**, **5**, and **14** gave the corresponding Markovnikov products (1-arylethanols) when irradiated in water or dilute aqueous sulfuric acid (10^{-3} M substrate or less), while both the *m*- and *p*-nitrostyrenes (**12** and **13**) afforded anti-Markovnikov addition products (2-arylethanols). When substrates **4**, **6**, and **7** were irradiated under similar conditions, the products were the corresponding Markovnikov alcohols, as indicated by ^{1}H NMR and GLC analyses (by comparison with authentic alcohol samples). However, the results for alkenes **8**–**11** were disappointing. Photolysis of very dilute solutions (10^{-4} M) of **8** or **9** in water or dilute aqueous acid (~10% w/w) at 254 nm resulted in rapid formation of a precipitate film on the reaction wall. The ^{1}H NMR of the isolated product mixture showed broad uncharacterizable peaks, with complete loss of starting material, as indicated by the absence of vinyl proton resonances in the δ 5–7 region. GLC analysis showed only minor amounts of the expected alcohol products, even in low-conversion experiments; most of the material did not elute out of the column. We suspect the major products to be comprised of oligomers. The product study for these two styrenes is further complicated by the fact that irradiation of the expected alcohol products also results in extensive photopolymerization. However, since the extinction coefficient at λ_{max} for the styrene chromophore (10^4) is very much larger than that for the alcohol product (100–400), secondary photochemistry should not be important unless high-conversion experiments are performed.



	X	Y		X	Y
3	H	H	**9**	Cl	H
4	CH_3O	H	**10**	CN	H
5	CH_3	H	**11**	H	CF_3
6	F	H	**12**	NO_2	H
7	H	F	**13**	H	NO_2
8	Br	H			



14

Styrenes **10** and **11** also did not undergo clean photohydration. Irradiation of 10^{-3} M solutions of **8** in ~10% H_2SO_4 for 18 h at 254 nm resulted in the formation of six products as indicated by GLC. The expected alcohol comprised 20% of the product mixture. A similar experiment for **11** resulted in four products, 10% of which was the expected alcohol. Since the expected alcohol products were found to be photochemically inert under the above photolytic conditions, these results indicate that other primary photochemical processes are competing with photoprotonation. No attempts were made to indentify the nonalcohol products formed in these experiments.

Table I. Product Quantum Yields (Φ_p) as a Function of Medium Acidity for Substrates **3**–**7** and **14**

$-H_0$ (% H_2SO_4)	Φ_p **3**[a]	**4**	**5**[a]	**6**	**7**	**14**[a]
pH 7	0.025	0.036	0.037	0.0077	0.015	0.022
−0.32 (3.05)	0.032	0.081		0.011	0.049	0.18
−0.08 (5.08)	0.042		0.12			0.30
0.40 (10.54)	0.046		0.19			0.44
0.76 (15.50)	0.077	0.29	0.28	0.016	0.29	0.49
1.10 (20.35)	0.11		0.46			0.54
1.40 (24.72)	0.15		0.94	0.029	0.47	0.60

[a] Taken from ref 6.

Table II. Quantum Yield for Loss of Substrate (Φ_l) for Alkenes **10** and **11** as a Function of Medium Acidity

$-H_0$ (% H_2SO_4)	Φ_l **10**	**11**
pH 7	0.0059	0.044
0.76 (15.50)	0.0086	0.053
1.40 (24.72)	0.0094	0.062

Table III. Fluorescence Lifetimes[a]

condition	τ, ns **3**[b]	**4**	**5**[b]	**6**	**7**	**14**[b]
pH 7	7.5	~1	4.5	4.9	4.3	58
15.50% H_2SO_4	6.3	~0.7	3.3	4.0	3.7	40

[a] Measured by single-photon counting. [b] Taken from ref 6.

Multiplicity of the Reactive State. Pertinent to any structure–reactivity study of these photohydrations is a knowledge of the multiplicity of the reactive excited state since comparisons of substrate reactivity are only valid for those substrates reacting via states of the same multiplicity. We have previously shown[6] that nitrostyrenes **12** and **13** react via T_1. On the other hand, alkenes **3**, **5**, and **14** were shown to react via S_1. Employing the same experimental criteria previously reported[6] (i.e., fluorescence quenching by added sulfuric acid and triplet sensitization experiments), we have found that alkenes **4**, **6**, and **7** also photohydrate via S_1. Thus a total of six aromatic alkenes (**3**–**7** and **14**) are available for a structure–reactivity study in the S_1 photohydration process. Since the techniques available for the study of alkenes **3**–**7** and **14** (i.e., fluorescence quenching and single-photon counting) cannot be applied to the nitrostyrene reactions, we did not pursue the structure–reactivity study for the triplet photohydration.

Product Quantum Yields and Fluorescence Lifetimes. Product quantum yields (Φ_p) were measured via UV spectrophotometry, the experimental details being identical with those previously reported.[6] Listed in Table I are the product quantum yields for photohydration as a function of medium acidity for substrates **3**–**7** and **14**. Φ_p depends strongly on the medium acidity, indicative of an acid-catalyzed process. This can be readily seen from Table I by the magnitude of the ratio $\Phi_{24.72\%}/\Phi_{pH\,7}$, which ranges from 2 to 27 (most values are 8 or greater) depending on the substrate. The quantum yield for substrate loss (Φ_l) as a function of medium acidity was also measured

---

(7) (a) Hamer, G. K.; Peat, I. R.; Reynolds, W. F., *Can. J. Chem.* **1973**, *51*, 897. (b) Hamer, G. K. Ph.D. Thesis, University of Toronto, 1973.

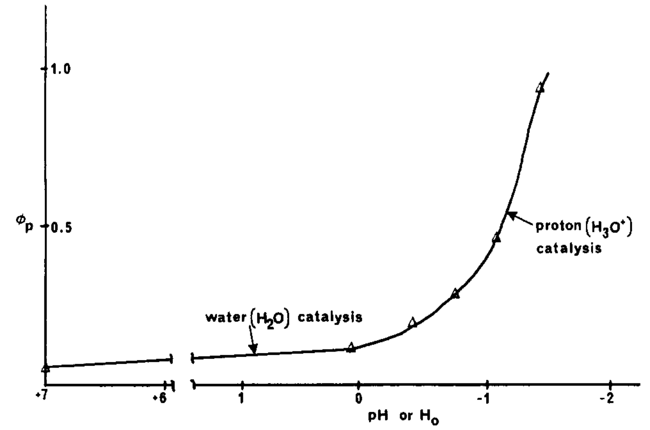


Figure 1. Φ_p as a function of medium acidity for aromatic alkene 5 (taken from ref 6).

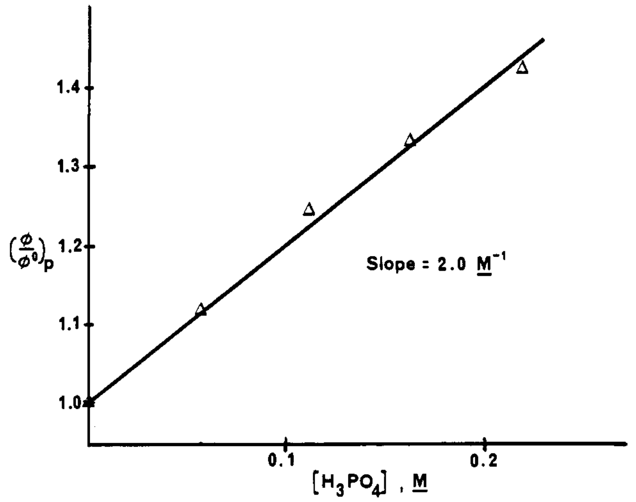


Figure 2. Plot of $(\Phi/\Phi^0)_p$ vs. H_3PO_4 concentration for the photohydration of *p*-methylstyrene (5).

for two of the alkenes (10 and 11) that did not display clean photohydration. These are tabulated in Table II. The quantum yields are very low for these two alkenes, and $\Phi_{24.72\%}/\Phi_{pH\,7}$ is approximately 1.5, indicative of at best a weakly acid-catalyzed process. This result is in agreement with the finding that photohydration is only a minor pathway for these two substrates.

Fluorescence lifetimes (τ) were measured at pH 7 and in 15.5% H_2SO_4 by using the single-photon counting technique[8] on deaerated samples for alkenes 3–7 and 14 (Table III). These will be employed in the Discussion for photokinetic analyses.

Table IV. Dependence of $(\Phi/\Phi^0)_p$ on General Acid (H_3PO_4-NaH_2PO_4) Concentration for 5 and 7 at pH 2.2

condition	$(\Phi/\Phi^0)_p$[a] 5	7
HCl, 0.56 M NaCl	1.00[b]	1.00[b]
0.055[c]	1.12	1.18
0.11	1.25	1.36
0.16	1.33	1.54
0.22	1.42	1.72

[a] Φ_0 = quantum yield at pH 2.2, 0.56 M NaCl. All experiments were performed at pH 2.2 at constant ionic strength (0.56 M). (However, Φ_p was found to be invariant with added salt of up to 3 M.) [b] By definition. [c] Indicates concentration of H_3PO_4 (general acid) in the H_3PO_4-NaH_2PO_4 buffer.

Table V. Dependence of $(\Phi/\Phi^0)_p$ on General Acid (NaH_2PO_4-Na_2HPO_4) Concentration for 5 and 7 at pH 5.2

condition	$(\Phi/\Phi_0)_p$[a] 5	7
$HClO_4$, 1.0 M NaCl	1.00[b]	1.00[b]
0.25[c]	1.13	1.13
0.50	1.17	1.27
0.75	1.35	
1.00	1.48	1.47

[a] Φ_0 = quantum yield at pH 5.2, 1.0 M NaCl. All experiments were performed at pH 5.2 at constant ionic strength (1.0 M). [b] By definition. [c] Indicates concentration of NaH_2PO_4 (general acid) in the NaH_2PO_4-Na_2HPO_4 buffer.

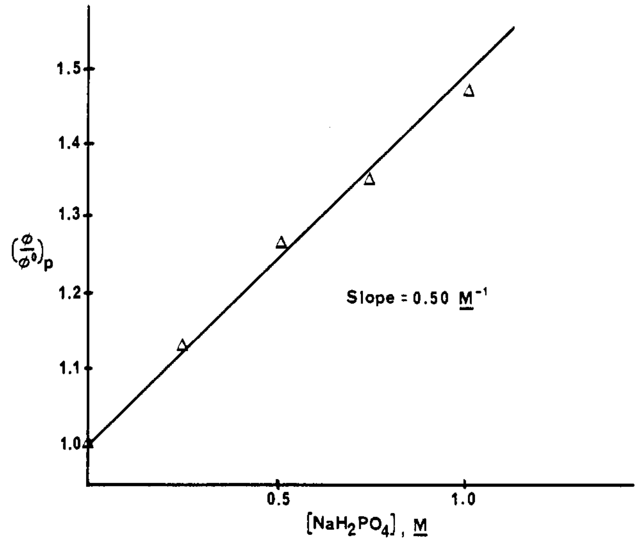
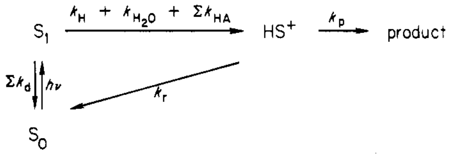


Figure 3. Plot of $(\Phi/\Phi^0)_p$ vs. NaH_2PO_4 concentration for the photohydration of *m*-fluorostyrene (7).

Scheme I



General Acid Catalysis of Photohydration. The following picture has emerged regarding catalytic phenomena in photohydration. In the dilute acid region (pH 7–1), water catalysis dominates. This is manifested by a flat region in the Φ_p vs. acidity plot in which Φ_p remains essentially constant. The proton-catalyzed process is manifested by a sharp increase of Φ_p with medium acidity (see Figure 1 for a representative example). This usually occurs at acidities greater (i.e., more negative) than H_0 = 0 for most of the alkenes studied. A recent report by Wubbels and Celander[9] on a general base catalyzed photoreaction prompted us to investigate the possibility of general acid catalysis in these photohydrations.[10] Employing UV spectrophotometry to monitor the photohydration, we have found that photohydration is a general

---

(8) Ware, W. R. In "Creation and Detection of the Excited State"; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 264.

(9) Wubbels, G. G.; Celander, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669.

(10) The observation that water can catalyze these photohydrations is in fact evidence that other general acids can catalyze the reaction. Water can be regarded as a "general acid", with a pK_a of 15.7. General acid catalysis has been observed in the ground-state hydration of styrenes: Schubert, W. M.; Keefe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559.

Table VI. Values of Photoprotonation Rate Constants for Water, Phosphoric Acid, Sodium Dihydrogen Phosphate, Boric Acid, and the Hydronium Ion

	photoprotonation rate constants (k_{HA}), M^{-1} s^{-1}				
substrate	k_{H_2O} (15.7)[b]	$k_{H_3BO_3}$ (9.23)[b]	$k_{NaH_2PO_4}$ (7.19)[b]	$k_{H_3PO_4}$ (2.15)[b]	k_H[a] (−1.74)[b]
5	1.5×10^5	2×10^6	3.9×10^6	1.6×10^7	3.6×10^7
7	6.3×10^4	1×10^6	1.8×10^6	1.2×10^7	3.4×10^7

[a] Calculated by using log ($k_H/k_H{}^0$) values (vide infra) where $k_H{}^0$ is an averaged value of k_H for styrene (**3**).[6] [b] pK_a of the catalyzing acid, taken from ref 16.

acid catalyzed process. Alkenes **3**–**7** and **14** exhibited buffer catalysis in two different phosphate buffers[11] (H_3PO_4–NaH_2PO_4 and NaH_2PO_4–Na_2HPO_4) and in boric acid (H_3BO_3–NaH_2BO_3), as indicated by the increasing $(\Phi/\Phi^0)_p$ values, where Φ^0 is the quantum yield without added buffer, with increasing buffer concentration, at constant pH and ionic strength (see Tables IV and V for substrates **5** and **7**). Moreover, plots of $(\Phi/\Phi^0)_p$ vs. general acid concentration were linear (see Figures 2 and 3 for examples). The photokinetic consequences of these results in terms of catalytic phenomena in photoprotonation will be discussed in the next section.

Discussion

General Acid Catalysis and the Brønsted Catalysis Law. The proposed mechanism[6] for the photohydration of alkenes **3**–**7** and **14**, which takes water and general acid catalysis into account, is shown in Scheme I. Assuming a steady state for HS^+, Φ_p is given by eq 2, where k_{HA} is

$$\Phi_p = \left(\frac{k_p}{k_p + k_r}\right) \times \left(\frac{k_H[H^+] + k_{H_2O}[H_2O] + \sum k_{HA}[HA]}{\sum k_d + k_H[H^+] + k_{H_2O}[H_2O] + \sum k_{HA}[HA]}\right) \quad (2)$$

the photoprotonation rate constant due to general acid HA.

It has been shown[13] in the ground-state hydration of styrenes that the rate of nucleophilic attack on the intermediate carbonium ion is much more rapid than its return (via loss of a proton) to substrate. This finding is also true for the hydration of many other alkenes.[14] Therefore, if HS^+ is a ground-state species, then $k_p \gg k_r$. However, we have no direct and easily accessible way of determining the exact nature of HS^+ other than to assume its reactivity is equal to (or more likely greater than) a ground-state carbonium ion. Thus we make the reasonable assumption that $k_p \gg k_r$.

In the dilute acid region, where general acid catalysis experiments were performed, $(\sum k_{HA}[HA] + k_{H_2O}[H_2O])$ $\gg k_H[H^+]$. Assuming the employment of only one general acid, eq 2 simplifies to eq 3. It can be shown that $(\Phi/\Phi^0)_p$,

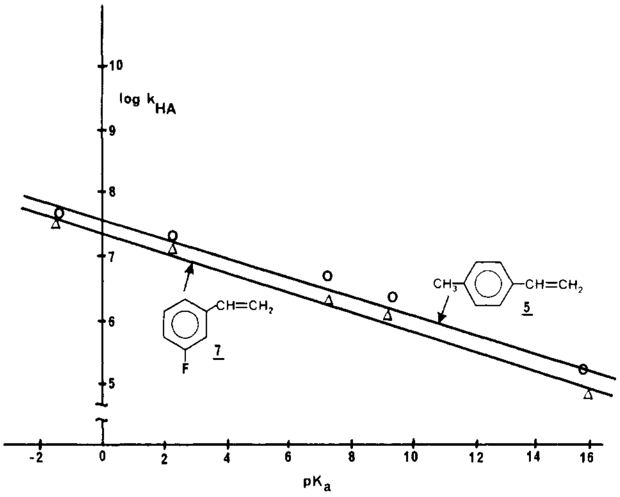


Figure 4. Brønsted plot of log k_{HA} vs. pK_a for substrates **5** and **7**.

$$\Phi_p = \frac{k_{HA}[HA] + k_{H_2O}[H_2O]}{\sum k_d + k_{HA}[HA] + k_{H_2O}[H_2O]} \quad (3)$$

$$\left(\frac{\Phi}{\Phi^0}\right)_p = \left(1 + \frac{k_{HA}[HA]}{k_{H_2O}[H_2O]}\right)\left(\frac{\sum k_d + k_{H_2O}[H_2O]}{\sum k_d + k_{H_2O}[H_2O] + k_{HA}[HA]}\right) \quad (4)$$

$$\left(\frac{\Phi}{\Phi^0}\right)_p \cong 1 + \frac{k_{HA}[HA]}{k_{H_2O}[H_2O]} \quad (5)$$

where Φ^0 is the quantum yield in the absence of HA, is given by eq 4. Since $(\sum k_d + k_{H_2O}[H_2O]) \gg k_{HA}[HA]$ under the experimental conditions,[15] a further simplification results in eq 5. We have already seen that plots of $(\Phi/\Phi^0)_p$ vs. [HA] are linear (Figures 2 and 3). Using values of k_{H_2O} calculated from eq 6 (derived from rearrangement of eq

$$k_{H_2O} = \Phi_{pH\,7}/\tau_{pH\,7}[H_2O] \quad (6)$$

3, with [HA] = 0) and setting $[H_2O]$ = 55.5 M, the individual photoprotonation rate constants were calculated and are summarized in Table VI for substrates **5** and **7**.

Many general acid (or base) catalyzed reactions in the ground state are found to obey the Brønsted catalysis law

---

[11] The observation of buffer catalysis is an experimental test for general acid catalysis in these photohydrations.[12] For practical reasons, buffer catalysis experiments can only be performed in the dilute acid region. We presume general acid catalysis can take place in the whole acidity region. Phosphate buffers were chosen because of their lack of UV absorption at wavelengths longer than ~220 nm, thus enabling photolysis to be carried out at 254 nm and the use of UV spectrophotometry to monitor the progress of the photohydration. The use of acetic acid–sodium acetate as a buffer (pK_a = 4.75) proved to be unsuccessful since even 0.25 M solutions of the buffer absorbed significantly at 254 nm (OD ~0.25). On irradiation, it was found this absorption increased, thus indicating the buffer is photochemically labile.

[12] Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; Chapter 3.

[13] Schubert, W. M.; Lamm, B. *J. Am. Chem. Soc.* **1966**, *88*, 120.

[14] (a) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 5372. (b) Taft, R. W., Jr.; Purlee, E. L.; Riesz, P.; DeFazio, C. A. *Ibid.* **1955**, *77*, 1984. (c) Purlee, E. L.; Taft, R. W., Jr. *Ibid.* **1956**, *78*, 5807, 5811. (d) Boyd, R. H.; Taft, R. W., Jr.; Wolf, A. P.; Christman, D. R. *Ibid.* **1960**, *82*, 4729. (e) Deno, N. C.; Kish, F. A.; Peterson, H. J. *Ibid.* **1965**, *87*, 2157.

[15] Maximum [HA] used in the experiments was 1.0 M. Since $\sum k_d + k_{H_2O}[H_2O] \sim 10^8$–$10^9$ s^{-1}, a simple calculation using the observed quantum yields with and without added general acid in the dilute acid region (pH 7–1) shows that $(\sum k_d + k_{H_2O}[H_2O])/k_{HA}[HA] \sim 10^2$.

[16] (a) Meites, L. "Handbook of Analytical Chemistry"; McGraw-Hill: New York, 1963; pp 1–21. (b) For the pK_a's of H_2O and H_3O^+, see: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 264 and 280.

(eq 7),[12] where k_{HA} are the individual catalytic rate con-

$$k_{\mathrm{HA}} = G_{\mathrm{A}}K_{\mathrm{a}}^{\alpha}$$

$$\log k_{\mathrm{HA}} = \alpha \log K_{\mathrm{a}} + \text{constant} \qquad (7)$$

stants, K_a are the corresponding dissociation constants for the acid, and G_A is a constant for the reaction. Plots of log k_{HA} vs. pK_a for alkenes **5** and **7** are shown in Figure 4. A good linear plot was obtained in each case over a pK_a range of 17 logarithmic units (correlation coefficients 0.991 and 0.996 for **5** and **7**, respectively), indicating that the Brønsted relationship is obeyed, with a Brønsted α of ca. 0.15 for both substrates. To our knowledge, the results presented here are the first reported examples of the Brønsted catalysis relationship applied to a photoreaction. Using the value obtained for α as an approximate measure of the development of the proton transfer in the photoprotonation process,[17] we conclude that the proton is much less than half transferred at the transition state. This situation is depicted by structure **15** as opposed to **16**,

$[\mathrm{Ar}\text{—}^{\delta+}\mathrm{CH}{=}\mathrm{CH_2}\text{- - - -}\mathrm{H}\text{- -}\mathrm{A}^{\delta-}]^*$

15

$[\mathrm{Ar}\text{—}^{\delta+}\mathrm{CH}{=}\mathrm{CH_2}\text{- -}\mathrm{H}\text{- - - -}\mathrm{A}^{\delta-}]^*$

16

where α is close to unity (i.e., an "early" as opposed to a "late" transition state). This is reasonable in terms of the rates of proton transfer to S_1 we have reported previously[6] and in this work, which are in the range 10^5–10^7 M^{-1} s^{-1} for a number of the substrates. Such unusually fast proton transfer to carbon would be expected to be associated with a low value of α.[21]

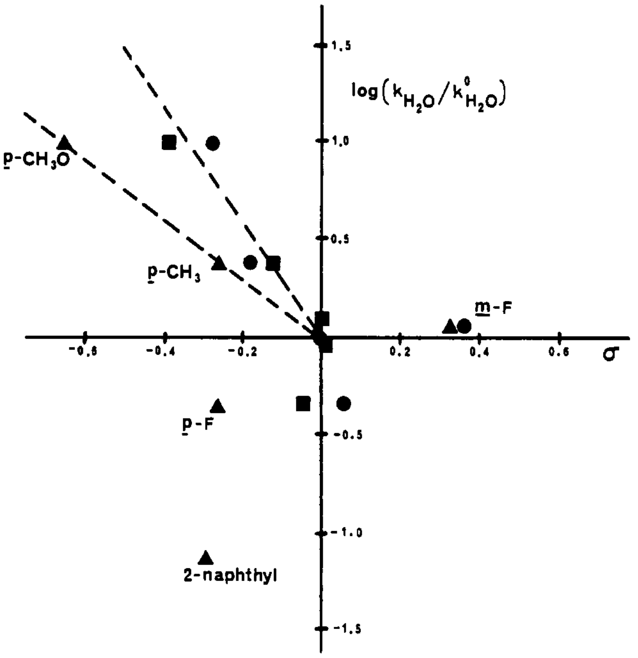


Figure 5. Plot of log ($k_{\mathrm{H_2O}}/k_{\mathrm{H_2O}}{}^0$) vs. σ for alkenes **3–7** and **14** (▲ vs. σ^+; ● vs. σ; ■ vs. σ_{exc}). The σ^+ value for **14** is taken from ref 32; σ and σ_{exc} values are not available for this compound.

Sensitivity of Photoprotonation to Ring Substituents. We have found that only certain aromatic alkenes undergo clean photohydration (hence photoprotonation). Substrates **8–11** photohydrate inefficiently, and other photochemical processes dominate in the deactivation of the excited state. A simple rationalization is available to explain this observation in the case of **10** and **11**.[24] The cyano and trifluoromethyl groups are strongly electron withdrawing at both the meta and para positions in the ground state (σ^+ values range from 0.52 to 0.67).[25] It would appear that these two groups are also electron withdrawing in S_1. The proposed electron-withdrawing character would explain the inefficient photoprotonation of these substrates since S_1 would take on a less polarized (or even diradicaloid) structure (e.g., **17**) as opposed to an essentially

${}^{\delta\delta+}\mathrm{Ar}{=}\mathrm{CH}{=}\mathrm{CH_2}{}^{\delta\delta-}$ **17** ${}^{+}\mathrm{Ar}{=}\mathrm{CH}{=}\mathrm{CH_2}{}^{-}$ **18**

charge-transfer structure (e.g., **18**) for electron-donating substituents.[26] A treatment of excited-state substituent effects by Baldry,[28] based on the singlet excited-state pK_a's of substituted phenols, gives additional support for the electron-withdrawing character of the m-CF$_3$ and p-CN groups. In this treatment Baldry reports $\sigma_{\mathrm{exc}}(m\text{-CF}_3) = 0.74$ and $\sigma_{\mathrm{exc}}(p\text{-CN}) = 1.6$.

A straightforward rationalization is available to explain the behavior of the halo-substituted styrenes **6–9**. The dissociation energy for the Ph–X bond (where X = Br, Cl, F) is 72, 94, and 116 kcal mol^{-1}, respectively.[29] Since the

---

[17] The value of the Brønsted α may be used as a measure of the development of the transition state of an acid- or base-catalyzed reaction.[18] The validity of this interpretation is based on the Hammond postulate.[19] Thus an α value near zero implies a very exothermic process, and the transition state closely resembles the starting materials. An α value near unity indicates a very endothermic process, and the transition state closely resembles the products. For an interpretation of α values greater than unity, see ref 20.

[18] (a) Reference 16b, pp 254–257. (b) Leffler, J. E.; Grunwald, E. "Rates and Equilibria in Organic Reactions"; Wiley: New York, 1963; pp 156–168, 238–242. (c) Gregory, M. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1967**, *89*, 2327. (d) Kosower, E. M. "Physical Organic Chemistry"; Wiley: New York, 1968; p 18. (e) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

[19] (a) Reference 16b, pp 197–199. (b) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (c) Le Noble, W. J.; Miller, A. R.; Hamann, S. C. *J. Org. Chem.* **1977**, *42*, 338. (d) Miller, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 1984.

[20] Bordwell, F. G.; Boyce, W. J., Jr.; Hautala, J. A.; Yee, K. C. *J. Am. Chem. Soc.* **1969**, *91*, 4002.

[21] Protonation rates to styrenes in the ground state are in the range 10^{-5}–10^{-7} M^{-1} s^{-1}.[22] Due to their low reactivity α values have not been determined for the protonation process but would be expected to be much greater than 0.5 (the reaction is quite endothermic, with $\Delta H^* \sim 20$ kcal mol^{-1}).[22] A trend in decreasing α values with increasing protonation rates in vinyl ether hydrolysis, which involves rate-limiting protonation on carbon, has been reported.[23] In addition, it can also be shown from a consideration of idealized potential-energy surfaces for proton transfer from a ground-state acid to an excited-state base, that in a thermoneutral process, α should be significantly less than 0.5, unlike the case of thermoneutral proton transfers between ground-state acids and bases, which would be expected to have α values close to 0.5. Therefore in the present case, involving proton transfer from ground-state H_3O^+ to an excited styrene system, one would expect a low value of α, since the proton transfer is clearly more exothermic (or less endothermic) than the corresponding ground-state process.

[22] Schubert, W. M.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559.

[23] Kresge, A. J.; Chen, H. L.; Chiang, Y.; Murrill, E.; Payne, M. A.; Sagatys, D. S. *J. Am. Chem. Soc.* **1971**, *93*, 413.

[24] We are aware of one other report[5c] that shows the deactivating effect of the para-cyano substituent on photoadditions to β-*tert*-butylstyrenes. In this paper it was shown that methanol adds efficiently to p-methoxy-β-*tert*-butylstyrene while the para-cyano compound was inert to photoaddition.

[25] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

[26] The nitrostyrenes **12** and **13** are exceptions. Although the nitro group is very electron withdrawing in both the ground[25] and excited states,[27] these substrates photohydrate efficiently nevertheless,[6] but via a different mechanism (through T_1), taking advantage of the *reverse* polarization due to the nitro group.

[27] (a) Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922. (b) Havinga, E.; Kronenberg, M. E. *Pure Appl. Chem.* **1968**, *16*, 137.

[28] Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 951.

[29] (a) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 113. (b) Fox, M. A.; Nichols, W. C., Jr.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 8164. For a recent review of the photochemistry of aryl halides, which includes an extensive discussion of photoinduced aryl-halide bond fragmentations, see: Grimshaw, J.; de Silva, A. P. *Chem. Soc. Rev. (London)* **1981**, *10*, 181.

estimated singlet energy is about 98 kcal mol^{-1} for these compounds, based on the parent styrene,[25] excitation to S_1 gives sufficient energy to cause Ph–X bond fragmentation for *p*-bromo- and *p*-chlorostyrenes (**8** and **9**). The evidence suggests that it is probably this additional process that competes favorably with photohydration for these two alkenes. On the other hand, due to the much greater strength of the Ph–F bond, bond cleavage does not compete favorably for both *m*- and *p*-fluorostyrenes (**6** and **7**), hence these substrates photohydrate cleanly.

Photoprotonation Rate Constants and the Hammett Relationship. In the dilute acid region (pH 7–1), in the absence of general acid, the expression for the quantum yield is given by eq 8. It can be shown that the expression

$$\Phi_p = \frac{k_{H_2O}[H_2O]}{\sum k_d + k_{H_2O}[H_2O]} \qquad (8)$$

for $k_{H_2O}/k_{H_2O}{}^0$, where k_{H_2O} are the water-catalyzed photoprotonation rate constants for a substituted aromatic alkene and for the parent styrene (**3**), respectively, is given by eq 9, where $\Phi_{pH\,7}$, $\Phi_{pH\,7}{}^0$, $\tau_{pH\,7}$, and $\tau_{pH\,7}{}^0$ are the re-

$$\frac{k_{H_2O}}{k_{H_2O}{}^0} = \left(\frac{\Phi}{\Phi^0}\frac{\tau^0}{\tau}\right)_{pH\,7} \qquad (9)$$

spective product quantum yields and singlet lifetimes for the substituted aromatic alkene and the parent styrene. Thus a Hammett correlation treatment results in eq 10, where σ are the appropriately chosen substituent constants.

$$\log\left(\frac{k_{H_2O}}{k_{H_2O}{}^0}\right) = \log\left(\frac{\Phi}{\Phi^0}\frac{\tau^0}{\tau}\right)_{pH\,7} = \sigma\rho \qquad (10)$$

The quantum yield expression at high acidities ($k_H[H^+] \gg k_{H_2O}[H_2O]$), in the absence of general acids, is given by eq 11. A Hammett correlation treatment for the hydro-

$$\Phi_p = \frac{k_H[H^+]}{\sum k_d + k_H[H^+]} \qquad (11)$$

$$\log\left(\frac{k_H}{k_H{}^0}\right) = \log\left(\frac{\Phi}{\Phi^0}\frac{\tau^0}{\tau}\right)_{15.5\%} = \sigma\rho \qquad (12)$$

nium ion photoprotonation rate constants is given by eq 12 (data in 15.5% H_2SO_4 were employed for this acidity region). With use of the quantum yield results given in Table I and the lifetimes reported in Table III, plots of log ($k_{H_2O}/k_{H_2O}{}^0$) and log ($k_H/k_H{}^0$) vs. three different σ parameters (σ, σ^+, and σ_{exc}[28]) are shown in Figures 5 and 6, respectively. No readily discernible correlation was found for k_H and k_{H_2O} against any one of the three different sets of σ parameters, although both the *p*-CH_3O and *p*-CH_3 groups are *electron donating* if these points are correlated with the parent styrene (dashed lines in the figures). The k_H values correlate reasonably well with σ if one neglects the point for *m*-fluorostyrene (Figure 6), with $\rho(S_1) = -5.6$ compared to $\rho(S_0) = -3.6$.[22] The reasonable correlation observed for *p*-CH_3O and *p*-CH_3 and the parent styrene along with the results for *p*-CN and *m*-CF_3 styrenes reported above strongly suggests that photoprotonation is very sensitive to the electron-donating abilities of the substituents; i.e., *photoprotonation takes place only if the ring substituent has an electron-donating effect that is approximately equal to or greater than that of hydrogen.* Thus the meta-fluoro group, although strongly electron withdrawing in S_0 ($\sigma^+ = 0.35$),[25] is much less so in S_1 and may possibly be effectively electron donating (note the improved correlation observed in Figures 5 and 6 when σ_{exc} for this group is used). Assuming ρ for photoprotonation is between −3 and −5, our results suggest that the para-fluoro group is much less electron donating in S_1 than in the ground state ($\sigma^+ = -0.25$).[25] Reversals in electron-donating abilities of substituents in the excited state at the meta and para positions have been well documented by Zimmerman[27a,30] and Havinga.[27b] The present results for the fluoro substituent give an additional example of this apparently general phenomenon.

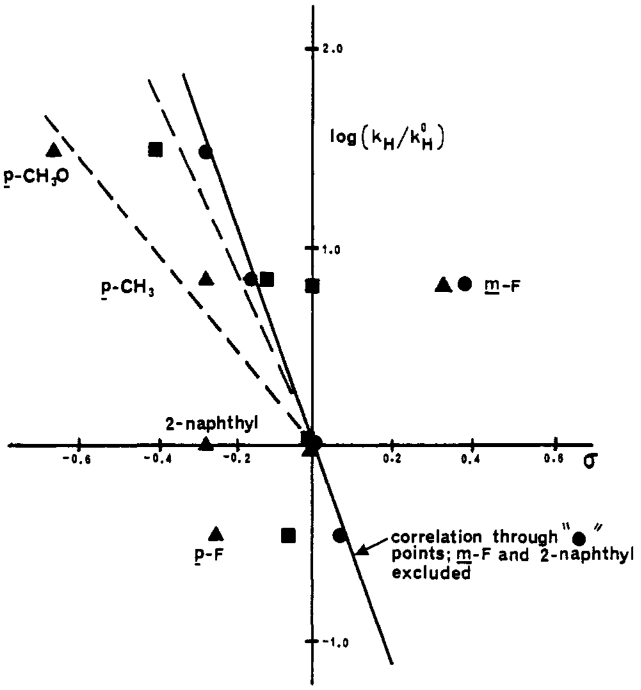


Figure 6. Plot of log ($k_H/k_H{}^0$) vs. σ for alkenes **3–7** and **14** (▲ vs. σ^+; ● vs. σ; ■ vs. σ_{exc}).

This work has shown that fruitful results may be obtained by employing classical physical organic analysis to photochemical structure–reactivity studies, although the quantitative treatment of substituent effects in photochemical reactions is at present more difficult than in analogous thermal reactions. Further work along these lines to establish a suitable scale of S_1 excited-state substituent constants is in progress in these laboratories.

Experimental Section

General Remarks. ^1H NMR spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$ with Me_4Si as internal standard, and UV spectra were recorded on a Unicam SP 1800 instrument. GLC analyses were performed on a Varian Aerograph Series 2700 instrument on either a 3% OV 17 on Chromosorb W/HP or a 5% Carbowax 20M column. Integrated peak areas were calculated by using a Varian CDS 111 processor. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer at room temperature.

Preparatory irradiations were carried out on a Rayonet RPR-100 reactor (254, 300, or 350 nm). Solutions were purged with argon for 30 min before irradiation. Stirring during irradiation was accomplished by a magnetic stirring bar. For quantum yield determinations, a GE 250-W medium-pressure lamp (General

---

(30) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 918.

(31) For other examples, see: (a) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 805, 809. (b) Hixson, S. S. *J. Chem. Soc., Chem. Commun.* **1975**, 515. (c) Sengupta, D.; Lahiri, S. C. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 1097. (d) Wehry, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 41. (e) Ito, Y.; Nishimura, H.; Matsura, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1187. (f) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329 and references therein. (g) Johnston, L. J.; de Mayo, P.; Wong, S. K. *Ibid.* **1982**, *104*, 307.

(32) Pincock, J. A.; Yates, K. *Can. J. Chem.* **1970**, *48*, 3332.

Electric, England) was employed. Monochromatic light was obtained by using a Bausch & Lomb high-intensity monochromator. A Corning 7-54 band-pass filter (240–420 nm) was also employed to filter out scattered light from the monochromator.

Quantum Yield Measurements. The general method is described as follows. Solutions of the substrates (10^{-4} M) in the appropriate acid were prepared in Suprasil quartz cuvettes (Hellma, 1.00 cm) equipped with micro stirring bars (7 mm). After the solutions were purged with argon (5 min), the optical density (OD) at the exciting wavelength (254 nm) and at λ_{max} (240–255 nm, depending on the styrene) were measured on a Unicam SP 1800 spectrophotometer. After irradiation (typically 1–5 min for the reactive compounds, longer for substrate **10**) on the optical bench, the OD's were remeasured (conversion 5–10%), and the quantum yield for loss of substrate were calculated via

$$\Phi_l = \Delta A_\lambda/(10^3\epsilon_\lambda \Delta I_a)$$

where ΔA_λ is the loss of OD at λ_{max} of the substrate, ϵ_λ is the extinction coefficient at this wavelength, and ΔI_a is the number of photons absorbed per unit volume during the irradiation. Since for styrenes **3**–**7** and substrate **14** only one product is formed, it can be shown that $\Phi_l = \Phi_p$ for these cases.

For determination of whether the ground-state hydration reaction was significant or not during the irradiation, identical "blank" solutions were made and kept in the dark. Employing this technique, we found that the ground-state hydration becomes significant only at $-H_0 > 1.4$. For these acidities, Φ_l were calculated after substracting out the ground-state contribution to ΔA_λ.

Malachite green leucocyanide[33] (MGL) in acidic ethanol was employed for chemical actinometry. Since our lamp produced only 10^{-8}–10^{-9} einsteins min^{-1} cm^{-3} at 254 nm (10-nm bandwidth), we found this actinometer to be more appropriate than potassium ferrioxalate, MGL being ca. 10 times more sensitive. The compound was synthesized according to the method of Calvert and Rechen,[34] mp 174–176 °C (lit.[34] mp 176–177 °C). The actinometer solution was prepared by mixing 0.5 mL of acidic aqueous ethanol (10^{-3} M HCl) with 2.5 mL of a 10^{-3} M stock solution of MGL in ethanol in a quartz cuvette. The OD at 622 nm was measured before and after irradiation, and the change in OD (ΔA) was then used to calculate the light intensity of the source via

$$I \text{ (einsteins min}^{-1}\text{ cm}^{-3}) = 10^{-3}\Delta A/(\epsilon_{622}\Phi_{MGL}\Delta t)$$

where ϵ_{622} is the extinction coefficient of the blue dye produced at 622 nm (1.063×10^5 cm^{-1} M^{-1}),[33] Φ_{MGL} is the quantum yield for dye formation (0.91),[33] and Δt is the elapsed irradiation time. Since the OD's at 254 nm (λ_{exc}) for the substrates were kept >1, ΔI_a can be calculated reliably via

$$\Delta I_a = (1 - e^{-2.30\bar{D}_{254}})I\Delta t$$

where $\bar{OD}_{254}$ is the average OD at 254 nm and Δt is the irradiation time for the substrate.

Relative quantum yields for the general acid catalysis experiments were done in quartz cuvettes in a merry-go-round apparatus using an RPR-100 reactor equipped with 254-nm lamps. The relative yields $(\Phi/\Phi_0)_p$ were calculated by taking the relative OD changes at λ_{max} of a cuvette with the appropriate buffer and a reference cuvette with no buffer but with the same salt concentration (NaCl). The concentration of the substrate was 10^{-3} M, thus ensuring that the OD at λ_{exc} (254 nm) >1.0. Conversions were limited to 5–20%.

Steady-State and Transient Fluorescence Studies. Solutions for fluorescence studies were prepared by injecting a stock solution of the substrate (in CH_3CN) into the appropriate acid solution via a microliter syringe. After the solutions were purged with argon, fluorescence spectra were recorded under identical conditions. The fraction of fluorescence quenching (Φ_f/Φ_f^0) was obtained via

$$\Phi_f/\Phi_f^0 = (I_f/I_f^0)_{\lambda_{max}}$$

where I_f and I_f^0, are the fluorescence intensities at λ_{max} in the aqueous acid and water, respectively.

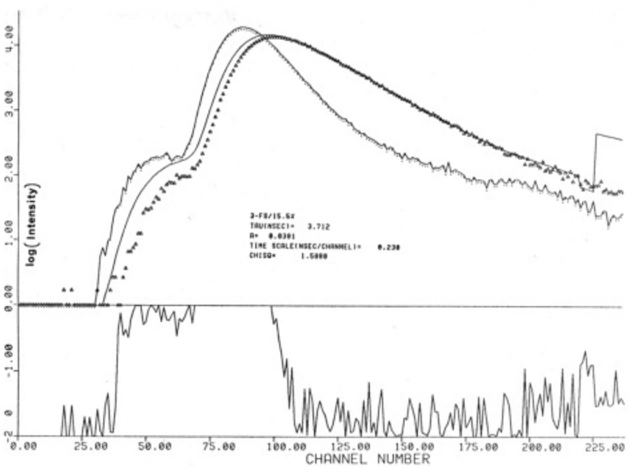


Figure 7. Fluorescence decay curve as determined by single-photon counting for *m*-fluorostyrene (**7**) in 15.50% H_2SO_4. The decay curve was analyzed by a computer-simulated deconvolution to give a lifetime of 3.7 ns ($\chi^2 = 1.588$; 0.230 ns/channel).

Fluorescence lifetimes were measured by single-photon counting.[8] Excitation was through a Jarrell-Ash monochromator (260–290 nm), and the emission was isolated by a combination of band-pass and cut-off filters. Solutions of the substrates (10^{-4} M) in quartz vessels were purged with argon prior to measurement. The data were collected on an Ortec multichannel analyzer and deconvoluted by using a computer program. A typical run is shown in Figure 7 for *m*-fluorostyrene (**7**).

Product Studies. The following experiments were typical of the procedures employed.

(a) *m*-Fluorostyrene (7, Direct Irradiation). A solution of 100 mg of the substrate (75 mL of CH_3CN and 400 mL of ~10% H_2SO_4) was outgassed with argon for 30 min in a quartz vessel. The solution was subsequently irradiated at 254 nm at ~10 °C (coldfinger) for 1.5 h with rigorous stirring (stirring bar or by a stream of argon). The photolyzed solution was saturated with NaCl and extracted twice with 2 × 100 mL of CH_2Cl_2. After drying over anhydrous $MgSO_4$ and removal of the solvent on a rotary evaporator, the photosylate was analyzed by GLC and ^1H NMR. Essentially pure (~90–95%) 1-(*m*-fluorophenyl)ethanol was obtained. The structure of the alcohol was confirmed by comparison with an authentic sample synthesized by $LiAlH_4$ reduction of *m*-fluoroacetophenone.

(b) *m*-Fluorostyrene (7, Sensitized Irradiation). A solution consisting of 50 mg of the substrate and 10 g of sodium 2-benzoylbenzoate (200 mL, CH_3CN and 800 mL of H_2O) was purged with argon for 30 min and subsequently irradiated in a 1-L Pyrex vessel at 350 nm (Rayonet RPR-100) for 12 h. The workup differs from the above only in that the CH_2Cl_2 extract was washed several times with 5% NaOH to remove the final traces of the sensitizer. The ^1H NMR spectrum showed the presence of no starting material and no alcohol product but only broad signals between δ 7–8 and 1–3.

(c) *m*-Fluorostyrene (7, Product Study in 0.22 M H_3PO_4). A buffer solution at pH 2.2 was prepared (0.22 M H_3PO_4 and 0.34 M NaH_2PO_4); 100 mg of the substrate was dissolved in a solution consisting of 50 mL of CH_3CN and 200 mL of the buffer. After outgassing with argon, the solution was irradiated in a quartz vessel at 254 nm with internal cooling for 1 h. After the standard workup procedure, the ^1H NMR showed a mixture consisting of ~40% alcohol and ~60% substrate. This experiment shows that the general acid acts only as a proton donor and does not interfere in the overall photohydration.

(d) *p*-Bromostyrene (8). A solution of 100 mg of **8** (100 mL of CH_3CN and 400 mL ~10% H_2SO_4) was prepared in a quartz vessel. After outgassing with argon, the vessel was irradiated for 30 min. Extensive polymerization was observed on the reaction vessel wall. A small sample of the homogeneous solution was worked up. The TLC of this indicated only starting material. The solution was irradiated for an additional 3 h. After workup, the ^1H NMR of the photosylate showed broad uncharacterizable peaks, with complete loss of starting material, as indicated by the

---

(33) Fischer, G. J.; LeBlanc, J. C.; Johns, H. E. *Photochem. Photobiol.* **1967**, *6*, 757.

(34) Clavert, J. G.; Rechen, H. J. L. *J. Am. Chem. Soc.* **1952**, *74*, 2101.

absence of vinyl proton resonances in the δ 5–7 region. GLC analysis showed only minor amounts of the expected alcohol product; most of the material did not elute out of the column. Photolysis of 1-(*p*-bromophenyl)ethanol, the expected photohydration product, under similar irradiation times as for **8** also resulted in extensive photopolymerization.

(e) *m*-(Trifluoromethyl)styrene (11). A solution of 60 mg of **11** (130 mL CH_3CN and 400 mL ~10% H_2SO_4) was irradiated (after outgassing with argon) at 254 nm for 18 h. After workup, the photosylate was analyzed by GC, which showed six major products (~97% conversion), one of which (~20%) was the expected alcohol. No attempts were made to identify the other products. Irradiation of 1-(*m*-(trifluoromethyl)phenyl)ethanol, the expected alcohol product, under identical conditions as for **11**, resulted in >95% recovery of the material. This experiment shows that the alcohol product, once formed, does not undergo secondary photochemistry. Thus it strongly suggests that other primary photochemical processes are competing with photoprotonation for **11**.

Acknowledgment. Grateful acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada (NSERC) for continued financial support and for a postgraduate scholarship to P.W.

Registry No. **3**, 100-42-5; **4**, 637-69-4; **5**, 622-97-9; **6**, 405-99-2; **7**, 350-51-6; **8**, 2039-82-9; **9**, 1073-67-2; **10**, 3435-51-6; **11**, 402-24-4; **12**, 100-13-0; **13**, 586-39-0; **14**, 827-54-3.

Complex-Base-Promoted Syn Eliminations from *trans*-1-Bromo-2-chlorocyclohexane[1]

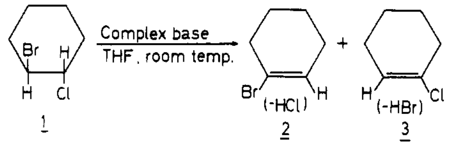
Alan P. Croft and Richard A. Bartsch*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

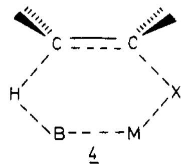
Received August 3, 1982

Syn eliminations from *trans*-1-bromo-2-chlorocyclohexane (**1**) induced by complex-base combinations of $NaNH_2$–NaOR(Ar) in tetrahydrofuran at room temperature favor dehydrochlorination (54–65%) over dehydrobromination. Under the heterogeneous reaction conditions, oxyanion bases derived from tertiary, secondary, and branched primary alcohols as well as phenols and 2-butanone are effective complex-base components, which suggests that $NaNH_2$ is the effective base species. Reactions of **1** with $NaNH_2$–NaO-*t*-Bu are not influenced by ultrasonic irradiation, but the propensity for loss of the normally poorer leaving group disappears in the presence of 15-crown-5. Transition states for complex-base-promoted syn eliminations are discussed.

Lee and Bartsch[2] have reported a reversal of the usual E2 leaving group ordering[3,4] for syn eliminations from several *trans*-1,2-dihalocycloalkanes induced by the complex base[5] $NaNH_2$–NaO-*t*-Bu. Thus, when treated with $NaNH_2$–NaO-*t*-Bu in tetrahydrofuran (THF) at room temperature for 24 h under heterogeneous conditions, *trans*-1-bromo-2-chlorocyclohexane (**1**) yielded 52–55% of 1-bromocyclohexene (**2**) and 30–31% of 1-chlorocyclohexene (**3**; eq 1). Analogous syn elimination from *trans*-1-bromo-2-fluorocyclohexane gave 85% of 1-bromocyclohexene (dehydrofluorination product) but no detectable 1-fluorocyclohexene (dehydrobromination product). The preferential loss of the normally poorer halogen leaving group in these syn eliminations was rationalized by Sicher's transition-state **4**[6] in which there is strong interaction of the base counterion M with the leaving group X.



(1)



4

To provide further insight into these unusual syn elimination reactions, we have examined the effects of added crown ether, ultrasonic irradiation, and oxyanion component variation within the complex base upon the relative yields of **2** and **3** in complex-base-promoted 1,2-eliminations from **1**. In addition, a qualitative assessment of the influence of such variations upon the activity of the complex-base combinations as dehydrohalogenation agents was made. The results of this study are now reported.

Experimental Section

Materials. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from lithium aluminum hydride under nitrogen immediately before use. Sodium amide powder (Fisher Scientific) was transferred and weighed in a nitrogen-flushed dry bag. Reagent grade alcohols from several commercial sources were distilled before use. The 15-crown-5 (Aldrich) was used directly. Other reagent grade inorganic and organic chemicals were used as received. *trans*-1-Bromo-2-chlorocyclohexane (**1**) was prepared by reaction of cyclohexene, *N*-bromoacetamide, and 16% aqueous HCl at -5 to -10 °C.[7] Compounds **2** and **3** were available from earlier work.[2,7]

Gas–Liquid Partition Chromatography. GLC analysis was conducted with a Varian Aerograph Series 2400 FID gas chro-

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] Lee, J. G.; Bartsch, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 228.

[3] Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 408–417.

[4] Bunnett, J. F.; Garbish, E. W., Jr.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385–391.

[5] Caubère, P. *Acc. Chem. Res.* **1974**, *7*, 301–308.

[6] Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200–214.

[7] Lee, J. G. Doctoral Dissertation, Texas Tech University, 1978.