

SUBSTITUENT EFFECTS IN THE PHOTOHYDRATION OF STYRENES AND PHENYLACETYLENES. AN ATTEMPT TO ESTABLISH A σ^{hv} SCALE FOR EXCITED-STATE REACTIONS

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The acid-catalysed rate constants (k_H^+) for the photohydration of 18 *meta*- and *para*-substituted styrenes and phenylacetylenes were determined in H_2SO_4 solutions by means of fluorescence quenching measurements and the standard Stern–Volmer approach. Singlet lifetimes of the substrates were determined in the reference solution (water at pH 7) by single photon counting. The $\log k_H^+$ values obtained did not correlate well with any previously reported σ scales, and were used to try to establish a σ^{hv} scale (for H-, *p*-F, *m*-F, *p*-Me, *m*-Me, *p*-Et, *m*-Et, *p*-OMe and *m*-OMe substituents) for possible use in other photochemical reactions. Correlation of all available literature data versus the new σ^{hv} scale gave reasonable correlations ($r = 0.957$ – 0.966). The problems associated with establishing linear free energy relationships for photoreactions are discussed.

INTRODUCTION

There have been numerous attempts to establish quantitative linear free energy relationships (LFERs) of the Hammett type for photochemical reactions, but none has been particularly successful. Part of the problem has been that all the attempted correlations of reactivity versus structure to date have been based on equilibria rather than rates, that is, on measurements or calculations of pK_a^* for excited-state acid–base reactions. Such values are very difficult to obtain precisely. Jaffé and Jones¹ carried out an extensive study of pK_a^* values for substituted phenols and other aromatic acids and bases using the Förster cycle approach.² They attempted to correlate their pK_a^* values against whichever ground-state substituent constants (σ , σ^- or σ^+) gave the best fit for particular series of acid–base equilibria. However, these correlations were at best only fair, and they concluded that exalted substituent constants would be generally required for excited states, and that *meta* and *para* substituents showed behaviour different to that expected on the basis of their ground-state σ values. Baldry³ used a different approach, although it too was based on phenol pK_a^* determinations. He first correlated pK^* versus ground-state σ values to obtain an approximate ρ value, then defined

a σ_{ex} scale based on the doubtful assumption that ρ^* would have the same value as ρ . The derived σ_{ex} scale was then used to try to establish correlations with several other reaction series, but again the results were fair to poor. Baldry³ also noted a greater electron-donating effect of *meta* substituents in excited-state processes. Sengupta and Lahiri⁴ used pK_a^* values for benzoic acids to establish a σ^* scale, because of the significance of this system in the original Hammett treatment. They then used this scale to calculate pK_a^* values for phenols, which were in very poor agreement with reported experimental values based on Förster cycle measurements.

Wehry and Rogers⁵ carefully determined pK_a^* values for substituted phenols, using both ultraviolet absorption and fluorescence measurements, and again found only a fair correlation with ground-state σ values. They did not attempt to use the data to establish an excited-state σ scale, but instead used the Taft equation⁶ to show that conjugative effects are much more important than inductive effects in electronically excited states, and that direct resonance interactions between *meta* substituents are considerably more significant than they are for ground states.

More recently, Shim *et al.*⁷ determined σ^* values, again based on phenol pK_a^* by defining ρ^* arbitrarily as unity, and showed that these correlate reasonably well with other series of pK^* values for both acids and bases

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and much better than do ground-state σ or σ^* values. They subsequently⁸ modified this approach by defining the dissociation of excited state benzoic acids as the reference reaction with ρ^* as unity (actually as -1.0 since they correlate pK^* rather than $\log K^*$ values) and derived a set of 'standardized' substituent constants σ^* .

The major problems with all of the above treatments are twofold. One is the inherent difficulty of determining accurate and reliable pK^* values using the Förster cycle method. These are based on precise location of the O–O transition frequency between the ground and excited states of both forms (acid and conjugate base) involved in the pK_a^* expression. Even when both species are fluorescent, which is not always the case, averaging of ν_{max} (absorption) and ν_{max} (emission) to obtain the O–O band frequency is subject to considerable error, even when the two bands relate to corresponding transitions. Since each band usually consists of a broad envelope, errors of only 200 cm^{-1} in averaging the two maxima can be serious. For example, at 286 nm this corresponds to an error of only 2 nm , which in turn leads to an error of 0.42 in the estimated pK^* value, or a factor of 2.6 in the equilibrium constant. Most if not all of the authors^{1–4} who have attempted to determine pK^* values have discussed this and other problems associated with the Förster cycle approach in some detail. Although there are other methods available in principle to determine accurate pK^* values, such as fluorescence titration⁹ and photopotentiometry,¹⁰ they are neither sufficiently generally applicable nor experimentally straightforward enough to make them feasible as a basis for excited-state LFERs.

The second problem is more of a theoretical than a practical nature. If the basic Hammett equations for equilibria and rates:

$$\begin{aligned}\log K_x/K_0 &= \rho\sigma \\ \log k_x/k_0 &= \rho\sigma\end{aligned}$$

where $K_x(k_x)$ refers to a substituted aromatic compound and $K_0(k_0)$ refers to the unsubstituted derivative, are redefined for analogous excited state processes, as in

$$\begin{aligned}\log K_x^*/K_0^* &= \rho^*\sigma^* \\ \log k_x^*/k_0^* &= \rho^*\sigma^*\end{aligned}$$

the problem remains of how to define a standard ρ^* value. Since excited-state reactions will have a different structure dependence in general to analogous thermal processes, then $\rho\sigma \neq \rho^*\sigma^*$ for any given reaction type. Since it has been shown frequently that excited-state pK^* values and $\log k$ values do not correlate at all well with ground-state σ scales, then in general $\sigma \neq \sigma^*$ for a particular substituent. In turn this means that $\rho \neq \rho^*$ for any analogous pair of thermal and photochemical

reactions. Therefore, attempts to define excited-state σ scales based on assumptions about ground-state ρ values are bound to be invalid. Similarly, definition of $\rho^* = 1.0$ for excited state benzoic acid ionizations, although a valid approach, bears no simple relation to the corresponding ground-state ionizations with $\rho = 1.0$. Therefore, any σ values derived on this basis cannot be directly related to, or compared quantitatively with, substituent effects in thermal reactions, although such a treatment may be applicable to other photochemical reactions.

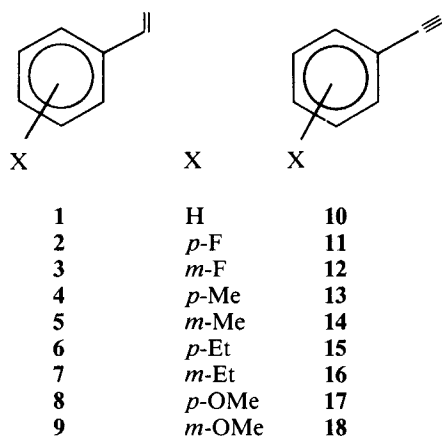
In other words, ground-state benzoic acid ionization and its substituent dependence (as quantified by its $\rho\sigma$ product) cannot be related directly to *any* excited-state equilibrium or reaction rate (in terms of its $\rho^*\sigma^*$ product), since we cannot separate the individual ρ - and σ -type dependences, except purely arbitrarily. Therefore, we may as well choose any photochemical reaction series whose equilibria or rates can be measured reasonably accurately, as the defining reaction series with $\rho^* = 1.0$ or $\rho^* = -1.0$ whichever is more convenient. It is already obvious that pK^* values are very difficult to determine reliably or accurately (see later). However, photochemical reaction rates based on the standard Stern–Volmer approach¹¹ are not as subject to such large inaccuracies or inconsistencies and therefore it is proposed that excited-state LFERs be based on photochemical rate constants, rather than equilibrium constants. It should be pointed out that although K_{SV} values can be obtained fairly accurately from linear Stern–Volmer plots, the derived k^q values are always subject to errors in determining the reference lifetimes τ^0 , particularly for short-lived singlet states, and therefore it is not expected that photochemical LFERs so based will necessarily be as precise or have the same predictive value as those well established for thermal reactions.

In connection with a recent study¹² of acid catalysis on photohydration reactions, we have measured the rate constants for hydronium ion quenching of the S_1 states of a number of substituted styrenes and phenylacetylenes. It is proposed to try to use these reaction series to test the above ideas and determine whether a viable σ scale can be set up for general use in photochemical reactions.

RESULTS

Product studies

The substrates selected for study are listed below (1–18). It has been shown previously¹³ that this type of substrate reacts cleanly via its lowest singlet state to give acid-catalysed addition of water across the multiple bond of the side-chain (or photohydration).



It has also been shown previously¹³ that although nitro-substituted styrenes and phenylacetylenes do photohydrate cleanly, they react exclusively via their lowest triplet state, owing to the fast intersystem crossing characteristic of nitroaromatics. [Since singlets and triplets normally show different photochemical reactivities, and have different charge distributions, it is necessary that any LFER for a photoreaction be based on a uniform set (i.e. singlet or triplet) of reactions. This does not mean that a σ -scale based on S_1 reactions would not be applicable to other reaction series based on T_1 reactions, provided that the latter series were uniformly of T_1 type. Other typical electron-withdrawing substituents could not be used either. Trifluoromethyl and cyano compounds photoprotonate so slowly that reaction is inefficient during the short S_1 lifetime. Less strongly electron-withdrawing groups such as bromo and chloro lead to competing homolytic cleavage and biphenyl-type products owing to the relative weakness of their C—halogen bonds. These factors limited our choice of substituents to hydrogen, fluoro, alkyl and alkoxy groups.]

Product studies were carried out as described previously,^{12,13} with similar results, i.e. the formation of mainly Markovnikov-type products (alcohols or ketones), with some polymeric material.

Reactions could be followed by monitoring the change in UV absorption in either the 245–252-nm region (styrenes) on the 233–250 nm region (phenylacetylenes). The λ_{\max} and ϵ_{\max} values of the substrates are listed in Table 1. The styrenes were easier to monitor in this way since the product alcohols have much lower molar absorptivities (ϵ) in this region ($\leq 400 \text{ l mol}^{-1} \text{ cm}^{-1}$) than do the ketone products from the phenylacetylenes (see Figure 1). However, even in the latter cases, approximate isosbestic points were obtained, as shown in Figure 1 for 13.

Product quantum yields (ϕ_{pdt}^0) were determined for all substrates in water at pH 7, since these values are needed to estimate $k_{\text{H}_2\text{O}}$ values for the 'uncatalysed'

Table 1. Absorption and emission maxima, quantum yields for substituted styrenes and phenylacetylenes^a

Compound	$\lambda_{\max}^{\text{abs.}}$ ^b (nm) ^b	$\epsilon_{\max}^{\text{abs.}}$ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\max}^{\text{excit.}}$ ^c	$\lambda_{\max}^{\text{F}}$ ^d	Φ_0^e
1	247	14 600	259	305	0.008
2	245	13 900	256	311	0.004
3	246	13 300	235	309	0.003
4	252	16 100	266	310	0.010
5	249	13 100	232	311	0.008
6	252	16 700	233	310	0.012
7	249	13 000	234	311	0.010
8	250	17 600	235	327	0.017
9	249	11 500	239	340	0.005
10	235	17 600	222	299	0.051
11	234	14 100	247	296	0.042
12	233	18 900	222	296	0.028
13	240	20 200	223	300	0.063
14	236	14 300	229	299	0.054
15	240	19 100	271	305	0.064
16	—	—	222	298	—
17	250	20 600	262	310	0.038
18	237	11 700	229	319	0.015

^aAll values determined in H_2O at pH 7.

^bProbably corresponds to $S_0 \rightarrow S_2$ or $S_0 \rightarrow S_3$ transition, since weaker, longer wavelength bands are observed, especially for phenylacetylenes 10–18.

^cMaximum in fluorescence excitation spectrum.

^dMaximum in fluorescence emission spectrum.

^eAverage of Φ_{L} and Φ_{pdt} (see text).

reaction. Quantum yields based on loss of substrate (Φ_{L}) were also determined for most substrates. These were found to be equal to, or in some cases greater than, Φ_{pdt}^0 , indicating that not all carbocation intermediates formed by protonation are successfully trapped by H_2O to give photohydration products, or that some reaction other than photoprotonation was occurring. Both types of quantum yield were determined at more than one wavelength for most substrates, and their values were found to be independent of wavelength. Table 1 lists values of Φ_0 , which is the average of Φ_{pdt}^0 and Φ_{L} , both determined at pH 7.

Fluorescence quenching studies

All substrates were fluorescent, and both excitation and emission spectra were recorded. Values of $\lambda_{\max}^{\text{excit}}$ and $\lambda_{\max}^{\text{F}}$ are listed in Table 1. Quenching studies were carried out by varying the sulphuric acid concentration and measuring the fluorescence intensity in each solution. Defining the fluorescence intensity (or quantum yield) at pH 7 as ϕ_{F}^0 , we have

$$\phi_{\text{F}}^0 = \frac{k_{\text{F}}^0}{k_{\text{F}}^0 + \Sigma k_{\text{d}}}$$

where Σk_{d} includes all deactivational processes other

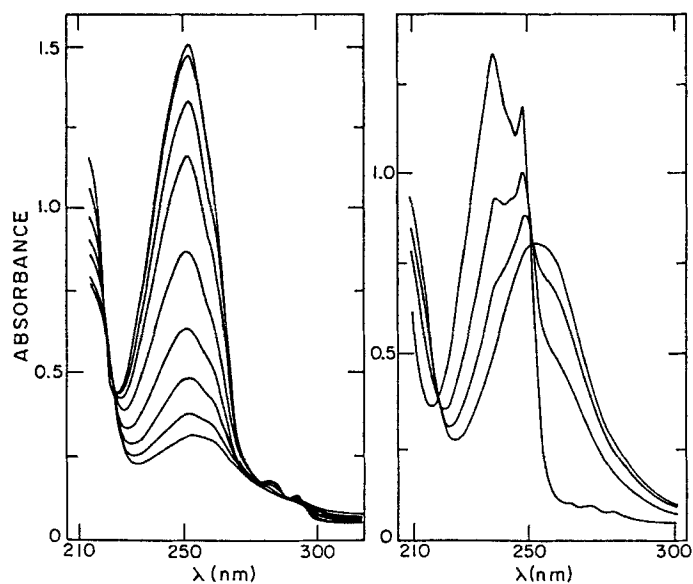


Figure 1. Decrease in UV absorbance with time for irradiation at 254 nm of *p*-ethylstyrene (6) in aqueous solution at pH 7 (left) and for *p*-methylphenylacetylene (13) at pH 2 (right)

than emission [this means that any constant quenching by solvent (H_2O) is included in Σk_d . At any given acid concentration, with quencher concentration $[\text{H}_3\text{O}^+]$,

$$\phi_F = \frac{k_F^0}{k_F^0 + \Sigma k_d + k_{H^+} [\text{H}_3\text{O}^+]}$$

Hence

$$\phi_F^0 / \phi_F = 1 + k_{H^+} \tau_F^0 [\text{H}_3\text{O}^+]$$

where τ_F^0 is the substrate's fluorescence lifetime at pH 7. Plots of ϕ_F^0 / ϕ_F versus $[\text{H}_3\text{O}^+]$ (values of $[\text{H}^+]$ as a function of wt% sulphuric acid were taken from Ref. 14 are linear from pH 7 up to approximately 3–4 M acid, where they start to curve upward. This is illustrated in Figure 2 for a typical styrene (8) and phenylacetylene (13). This type of curvature in Stern–Volmer plots has been noted previously,¹⁵ and implies that H_3O^+ can be a more efficient quencher

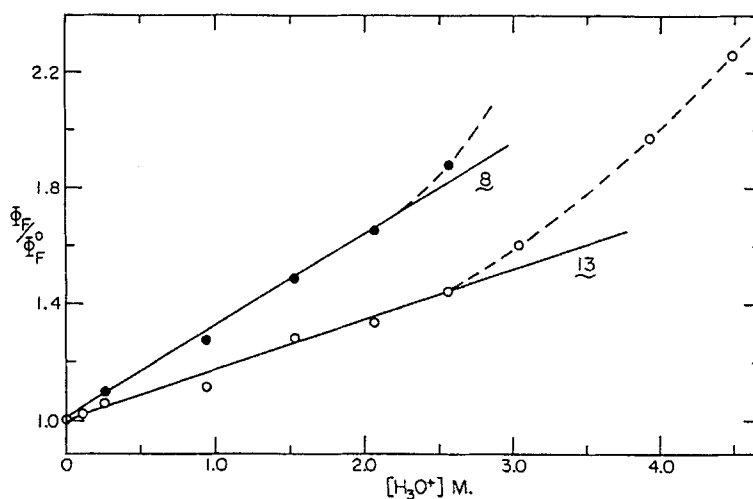


Figure 2. Stern–Volmer plots of Φ_F / Φ_F^0 versus $[\text{H}_3\text{O}^+]$ for *p*-methoxystyrene (8) and *p*-methylphenylacetylene (13)

Table 2. Stern–Volmer slopes, singlet lifetimes and hydronium ion quenching rate constants

Compound	K_{SV} (l mol ⁻¹) ^a	τ_F^0 (ns) ^b	k_{H^+} (l mol ⁻¹)	Estimated error (%) ^c
1 ^d	0.061	7.5	8.1×10^6	
2	0.030 ∓ 0.005^e	4.9	6.1×10^6	16.8
3	0.058 ∓ 0.003	4.3	1.35×10^7	5.9
4	0.154 ∓ 0.001	4.5	3.42×10^7	2.3
5	0.333 ∓ 0.008	7.9	4.22×10^7	2.6
6	0.220 ∓ 0.007	4.2	5.24×10^7	4.0
7	0.390 ∓ 0.003	7.8	5.00×10^7	2.2
8	0.310 ∓ 0.006	1.2	2.6×10^8	8.5
9	6.0 ∓ 0.10	8.3	7.23×10^8	2.1
10 ^d	0.037	4.5	8.3×10^6	
11	0.018 ∓ 0.002	4.0	4.5×10^6	11.3
12	0.175 ∓ 0.008	5.6	3.13×10^7	4.8
13	0.091 ∓ 0.02	2.9	3.14×10^7	4.1
14	0.353 ∓ 0.001	3.9	2.05×10^7	2.5
15	0.084 ∓ 0.001	2.9 ^f	2.90×10^7	3.8
16	0.42 ∓ 0.01	3.7	1.14×10^8	3.5
17	0.11 ∓ 0.01	0.84	1.31×10^8	15.3
18	0.23 ∓ 0.01	0.9 ^f	2.6×10^8	12.1

^aSlope of plot of Φ_F^0/Φ_F versus $[H_3O^+]$, where Φ_F^0 is fluorescence intensity at pH 7).

^bMeasured at pH 7 by single photon counting.

^cBased on standard deviations of K_{SV} and τ_F^0 (see text).

^dData taken from Ref. 12.

^eStandard deviation of slope of Stern–Volmer plot.

^fEstimated value (see Experimental).

than its molarity suggests. Similar observations using cyanonaphthalene quenching by H_3O^+ have been used to derive¹⁵ an excited-state acidity function $[H^+]^{h\nu}$. However, at lower acidities (<3 M) where the Stern–Volmer plots are linear, the values of $[H^+]^{h\nu}$ are almost identical with $[H_3O^+]$. Values of the Stern–Volmer constant K_{SV} ($= k_{H^+} \tau_F^0$) were therefore determined from the initial linear portion of each plot (from pH 7 to 2 M acid) and are given for each substrate in Table 2 (the standard deviations of the slopes of the Stern–Volmer plots are also listed).

The fluorescence lifetimes τ_F^0 were determined in water at pH 7 by the standard flash fluorimetry method based on single photon counting.¹⁶ These are also listed in Table 2. It can be seen that these singlet lifetimes are mainly in the 3–8-ns range. In all cases but three, the fluorescence showed a clean single exponential decay and there was no problem in obtaining accurate τ_F^0 values. In the case of **8** and **9**, double exponential decay was observed. In both cases there was a minor component (9% and 35%, respectively) whose lifetime corresponded closely with that of the expected alcohol product. Since **8** and **9** are the two most reactive substrates investigated, it is believed that during the time the samples were repeatedly flashed (0.5–1 h) some photohydration had occurred. In these two cases the τ value of the major component was taken to be τ_F^0 . In only one case (**18**) the fluorescence was too weak to give a reliable decay curve and a τ_F^0 value had to be estimated.

From the K_{SV} values obtained from the quenching plots and the measured τ_F^0 values, values of k_{H^+} , the hydronium ion-catalysed rate constant, were calculated for each substrate. These are listed in Table 2, and are generally in the range 10^7 – 10^8 l mol⁻¹ s⁻¹ for both the styrenes and phenylacetylenes, although the former substrates are more reactive.

It should be possible in principle to measure these same rate constants k_{H^+} via the Stern–Volmer approach based on relative quantum yields for reaction, as well as by fluorescence quenching. However, the situation is more complicated owing to the competing water-catalysed reaction. Nonetheless, it should be possible to check the k_{H^+} values obtained from fluorescence quenching by measuring Φ_{pdt} or Φ_L values based on Φ_{pdt} at pH 7 and k_{H^+} at various acidities.

At pH 7 we have

$$\Phi_R^0 = \frac{k_{H_2O}[H_2O]}{k_{H_2O}[H_2O] + k_F^0 + \Sigma k_d} = k_{H_2O}[H_2O] \tau_F^0$$

where Σk_d now includes all non-productive modes of decay except fluorescence. At some acidity where $[H_3O^+]$ catalysis is significant,

$$\Phi_R = \frac{k_{H^+}[H_3O^+] + k_{H_2O}[H_2O]}{k_{H^+}[H_3O^+] + k_{H_2O}[H_2O] + k_F^0 + \Sigma k_d}$$

Hence

$$\Phi_R/\Phi_R^0 = \frac{k_{H^+} [H_3O^+] + k_{H_2O} [H_2O]}{k_{H^+} [H_3O^+] + k_{H_2O} [H_2O] + k_F^0 + \Sigma k_d} \cdot \frac{1}{k_{H_2O} [H_2O] \tau_F^0}$$

Unfortunately, no simple cancellation occurs as in the previous ϕ_F^0/ϕ_F expression, and the standard Stern–Volmer approach cannot be used over the whole acidity range. However, there are two limiting cases. At high pH, where $[H_3O^+]$ is very low, $k_{H_2O} [H_2O] \gg k_{H^+} [H_3O^+]$ and we have simply

$$\Phi_R^0 = k_{H_2O} [H_2O] \tau_F^0$$

This expression can be used to obtain k_{H_2O} values for each substrate, which are listed in Table 3. It can be seen that in general the k_{H_2O} values (10^4 – 10^6 l mol⁻¹ s⁻¹ range) are much lower than the k_{H^+} values in Table 2.

At higher acidities, where $k_{H^+} [H_3O^+] \gg k_{H_2O} [H_2O]$, we have

$$\frac{\Phi_R}{\Phi_R^0} = \frac{k_{H^+} [H_3O^+]}{k_{H^+} [H_3O^+] + k_F^0 + \Sigma k_d} \cdot \frac{1}{k_{H_2O} [H_2O] \tau_F^0}$$

This expression can be used, together with the previously determined k_{H^+} and k_{H_2O} values, to calculate values of Φ_R/Φ_R^0 at higher acidities than pH 7, where $k_{H^+} [H_3O^+] \gg k_{H_2O} [H_2O]$, and these are compared with calculated values in Table 4. The agreement between the calculated and observed values is reasonable, when the approximations are considered. In the majority of cases $(\Phi_R/\Phi_R^0)_{\text{calc}}$ is larger than the observed values, which again supports the idea that not all cationic intermediates produced are successfully trapped. The discrepancies between $\Phi_{P(\text{calc})}$ and $\Phi_{R(\text{obs})}$ become particularly noticeable at even higher acidities. For example, at $[H_3O^+] = 3.56$ M (where the Stern–Volmer plots show upward curvature), calculated Φ_R values are several times higher than those observed.

Overall, the standard Stern–Volmer quenching

Table 3. Water-catalysed rate constants^a for styrene and phenylacetylene photohydrations

Substituent	$k_{H_2O}(\text{styrene})$ (l mol ⁻¹ s ⁻¹)	$k_{H_2O}(\text{phenylacetylene})$ (l mol ⁻¹ s ⁻¹)
H	1.86×10^4	2.29×10^5
<i>p</i> -F	1.48×10^4	1.66×10^5
<i>m</i> F	1.41×10^4	1.26×10^5
<i>p</i> -Me	3.80×10^4	3.89×10^5
<i>m</i> -Me	1.91×10^4	3.55×10^5
<i>p</i> -Et	5.01×10^4	7.41×10^5
<i>m</i> -Et	2.24×10^4	—
<i>p</i> -OMe	2.45×10^5	8.91×10^5
<i>m</i> -OMe	1.10×10^4	4.57×10^5

^aCalculated from expression $\Phi_R^0 = k_{H_2O} [H_2O] \tau_F^0$ where $[H_2O] = 55.5$ M, where Φ_R^0 is the value based on Φ_0 at pH 7 from Table 1.

approach is much simpler to apply, and the general agreement shown in Table 4 illustrates that the k_{H^+} values obtained are reliable and consistent with the mechanistic scheme previously proposed¹³ for photohydration. Estimates of the error involved in determining k_{H^+} are also given in Table 2. These are based on the sum of the variances (S) in both the K_{SV} and τ_F^0 values, according to the expression¹⁷

$$S_x = \sqrt{\frac{S_u^2}{u^2} + \frac{S_v^2}{v^2}}$$

where x , u and v refer to k_{H^+} , K_{SV} and τ_F^0 , respectively. In most cases the estimated error in the rate constant is in the range 2–5%, except for the shorter lived singlet states where it is the 8–15% range. In terms of log k_{H^+} values and any derived σ values, this corresponds to an error of approximately 0.05 log unit.

DISCUSSION

Excited-state σ values

The log k_{H^+} values were first correlated against

Table 4. Comparison of calculated and experimental quantum yields for product formation

Substrate	$[H_3O^+]$	$k_{H^+} [H_3O^+]$	k_{H_2O}	$\frac{k_{H^+} [H_3O^+]}{k_{H_2O} [H_2O]}$	$(\phi/\phi_0)_{\text{calc.}}$	$(\phi/\phi_0)_{\text{obs.}}^a$
3	0.29	3.92×10^6	1.48×10^4	5.0	4.9	3.9
	0.95	1.28×10^7		16.2	15.4	9.7
5	0.12	5.06×10^6	1.97×10^4	4.9	4.7	5.7
	0.29	1.22×10^7		11.8	10.7	10.5
6	0.29	1.87×10^6	5.01×10^4	5.3	6.7	3.8
7	0.12	6.0×10^6	2.24×10^4	4.9	4.7	4.2
	0.29	1.45×10^7		11.8	10.7	7.5
9	0.12	8.68×10^7	2.45×10^5	6.3	3.9	5.2

^aBased on absolute quantum yield Φ_1 , at pH 7, and relative Φ_1 at acidity defined by $[H_3O^+]$ column.

Table 5. Attempted correlations of photohydration reactivities versus reported ground- and excited-state σ values

Parameter	σ^a	$\sigma^+{}^a$	$\sigma_{ex}{}^b$	σ^{*c}
Log k_{H^+} (styrenes):				
Slope (ρ)	-1.08	-0.68	-3.59	-0.52
Intercept (log k_{H^+})	7.60	7.55	7.19	7.52
r^d	0.292	0.276	0.627	0.217
σ_y^e	0.689	0.693	0.562	0.704
Log k_{H^+} (phenylacetylenes):				
Slope	-0.59	-0.13	-2.62	-0.46
Intercept	7.60	7.60	7.30	7.52
r^d	0.185	0.060	0.535	0.225
σ_y^e	0.605	0.615	0.520	0.600

^aTaken from Ref. 18.^bTaken from Ref. 3.^cTaken from Ref. 8.^dCorrelation coefficient.^eStandard deviation on log k_{H^+} axis.

existing σ values reported^{3,8,19} for both ground- and excited-state reactions, namely σ , σ^+ , σ_{ex} and σ^* . The results of these attempted correlations are summarized in Table 5. It is clear from the very low correlation coefficients ($r=0.185-0.627$) and large σ_y (0.520-0.704) values obtained that existing σ scales are not appropriate to either the styrene or phenylacetylene photoreactions. It was therefore decided to examine whether the log k_{H^+} values for these two series could be used to set up a viable σ scale from these data which might be applicable to other photochemical reactions. A plot of log k_{H^+} (PA) versus log k_{H^+} (STY) gives only a fair linear correlation ($r=0.891$) with a slope of 0.76 and $\sigma_y=0.280$. However a multiple non-linear regression treatment showed that this was not due to systematic differences between the two series, since the initial (linear) value of the F -statistic (26.9) actually decreased on the addition of further polynomial terms. It therefore appears that the two series of log k_{H^+} values are linear related, although the quality of fit is not high. It was therefore decided to define a σ^{hv} scale in the following way, to achieve best fit to the experimental data. Using the phenylacetylene series as reference (with $\rho^{hv} = -1.0$, since more electron-donating groups accelerate the reaction), initial estimates were set at

$$\sigma^{hv} = \log k_{H^+}^{H^+}(\text{PA}) - \log k_{H^+}^X(\text{PA})$$

and

$$\sigma^{hv} = 0.76[\log k_{H^+}^{H^+}(\text{STY}) - \log k_{H^+}^X(\text{STY})]$$

Naturally the correlation of these two sets of σ^{hv} values is no better than the initial one, therefore weighted values were calculated based on the inverse of the standard deviation of each point (we are grateful to Dr

R. A. Cox for the statistics programs used in this data analysis). This improved the correlation coefficient to 0.994 and gave a σ_y of 0.019. The average of these slope and standard deviation weighted values was then taken as σ^{hv} . Values of these constants are listed in Table 6. As a check on the goodness of fit of these σ^{hv} values to the original experimental data, a plot of log k_{H^+} (PA) versus σ^{hv} is shown in Figure 3. This shows that as typical linear free energy relationships, these are acceptable. The correlation coefficients are 0.975 (PA) and 0.969 (STY), with standard deviations (σ_y) on the log k_{H^+} axis of 0.136 (PA) and 0.178 (STY). The latter would correspond to deviations in predicted rate constants of 30-50%.

Before attempting correlations of these σ^{hv} values with other photochemical reaction series, it is worth noting that in each case (F, Me, Et, OMe) the σ_{meta}^{hv} value suggests that not only are direct conjugative effects of the meta substituents greater than they are in ground states, but also that they are more electron-donating than the corresponding *para*- substituents.

Table 6. Log k_{H^+} values and derived σ^{hv} parameters

Substituent	Log k_{H^+} (STY)	log k_{H^+} (PA)	σ^{hv} ^a
H	6.91	6.92	0
<i>p</i> -F	6.78	6.65	+0.18
<i>m</i> -F	7.13	7.49	-0.37
<i>p</i> -Me	7.53	7.50	-0.53
<i>m</i> -Me	7.62	7.96	-0.79
<i>p</i> -Et	7.72	7.46	-0.58
<i>m</i> -Et	7.70	8.06	-0.87
<i>p</i> -OMe	8.41	8.12	-1.17
<i>m</i> -OMe	8.86	8.40	-1.48

^aWeighted average of σ (PA) and 0.76 σ (STY) (see text).

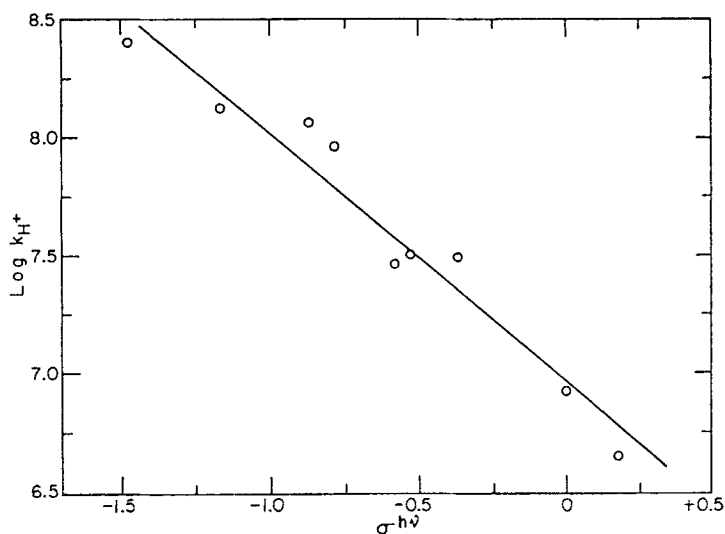


Figure 3. Plot of $\log k_{H^+}$ for phenylacetylene photohydrations versus $\sigma^{h\nu}$

This is generally consistent with many previous suggestions of a so-called *meta* effect in photochemical reactions, originally noted by Zimmerman and co-workers^{19,20} and Havinga *et al.*²¹ For example, Wehry and Rogers⁵ have attempted to estimate this effect semi-quantitatively by using the Taft equation:⁶

$$\alpha = \frac{\rho_1\sigma_1 - \log(k^*/k_0)_{meta}}{\rho_1\sigma_1 - \log(k^*/k_0)_{para}}$$

to assess the relative importance of conjugative effects at *meta* and *para* positions in ground and lowest-singlet excited states. The values of α they obtained (given in Table 7) led them to conclude that conjugative effects at the *meta* position are nearly as important as at the *para* position. We have similarly calculated α_0 and α^* values for the thermal and photochemical hydrations of styrenes and phenylacetylenes. The values listed in Table 7 support Wehry and Rogers' conclusion,⁵ and indeed suggest that *meta* conjugation in excited states is

perhaps more important than *para* conjugation. One reason for the differences in α values in Table 7 may be that Wehry and Rogers based their calculations on phenol ionizations, rather than on reaction rates.

Application of the $\sigma^{h\nu}$ scale to other photoreactions

The new $\sigma^{h\nu}$ scale was tested against all available kinetic data in the literature, based on photochemical reactions involving the same substituents as in the present study. Generally the correlations were fairly good, with r values in the range 0.957–0.996 (with one exception, which was based on reaction quantum yields rather than rate constants or reciprocal lifetimes). Examples are shown in Figure 4, which illustrates that the new substituent scale appears to be applicable to reactions of both S_1 and T_1 states, and those with both positive and negative ρ values. The overall results of these correlations are given in Table 8. Although the

Table 7. Relative importance of inductive and resonance effects in thermal and photochemical reactions

Substituent	α_0^a			α^{*b}		
	Phenols ^c	Styrenes	Phenylacetylenes	Phenols ^c	Styrenes	Phenylacetylenes
F	0.31			0.8	1.21	1.46
Cl	0.37		0.19	0.8		
Br	0.25	0.07		0.6		
Me	0.26	0.14	0.20	0.5	1.20	2.22
Et					0.97	2.77
OMe	0.28			0.6	1.32	1.12

^aBased on Taft equation, ground-state value.

^bBased on Taft equation, excited-state value.

^cTaken from Ref. 5.

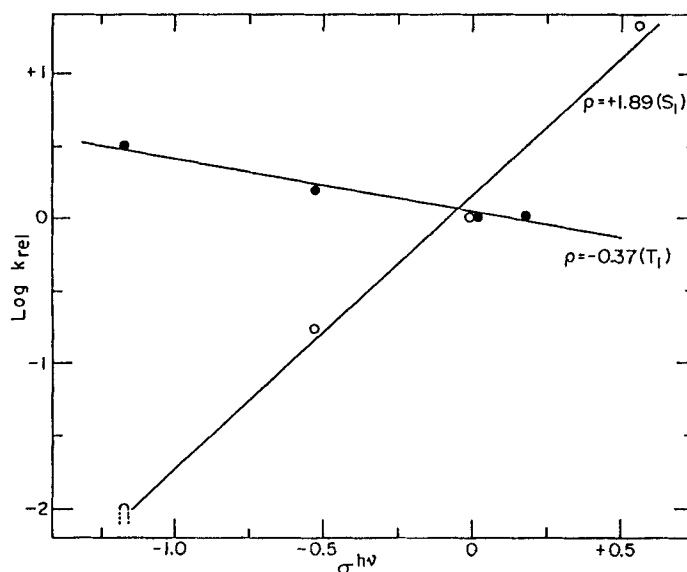


Figure 4. Plot of $\log k_{rel}$ versus $\sigma^{h\nu}$ for (○) S_1 reactions of substituted arylethylenes (from Ref. 28) and (●) T_1 reactions of disubstituted benzophenones (from Ref. 29)

data available to test the $\rho^{h\nu}$ values are unfortunately limited, the correlations are much better statistically than those in Jaffé and Jones' review,¹ where only 12 of 34 correlations based on pK^* values gave r values of 0.96 or better, and 13 gave correlations of less than 0.9. Similarly, the σ_y values in Table 8 are fairly low, representing deviations in calculated rate constants of the order of 50% on average, whereas in the earlier pK^* correlations¹ the mean σ_y value of 1.21 represents a factor 16 in a calculated equilibrium constant. Even if reported σ_{ex} or σ^* values^{3,8} were used to correlate the kinetic data in Table 2, it is clear that the correlations would be much worse than with $\sigma^{h\nu}$, since the pK^* (σ_{ex} , σ^*) and $\log k_{H^+}$ ($\sigma^{h\nu}$) values on which these scales were based correlate poorly with each other.

The serious problem with any σ scales based on pK^* values, alluded to earlier, is clearly illustrated by the data in Table 9. This is a collection of reported pK^* values for phenols with the same substituents as in the present study. Even setting aside the pK^* values derived by Sengupta and Lahiri,⁴ which do not agree at all with other reported values, the average values for the other five sets do not show very good internal agreement, with deviations from the average of up to 0.9 for a given phenol. All of these pK^* values are based on the Förster cycle approach,² except the limited set of Avigal *et al.*²³ It is interesting that if pK^* values are calculated from reported ρ^* values and the present $\sigma^{h\nu}$ scale, the deviations from the average of reported values as shown in Table 9 are in most cases within ± 0.5 log

Table 8. Rates of photoreactions as a function of $\sigma^{h\nu}$

System	Reactive state	ρ	r^a	σ_y^b	n^c	Ref.
X-arylethylenes	S_1	+1.89	0.996	0.152	4	28
X-benzophenones	T_1	-0.19	0.971	0.042	4	30
X-benzyl alcohols	S_1	-0.76	0.957	0.321	4	31
X ₂ -benzophenones	T_1	-0.37	0.977	0.060	4	29
X-arylbutadienes	S_1	+0.03	0.708 ^d	0.020	5	32
9-Arylxanthyl cations	S_1	-1.24	0.969	0.178	9	33
X-styrenes	S_1	-1.24	0.969	0.178	9	
X-phenylacetylenes ^e	S_1	-1.06	0.975	0.136	9	

^aCorrelation coefficient.

^bStandard deviation on $\log k$ axis.

^cNumber of points.

^dIf widely deviating point is omitted.

^eDefining reaction for $\sigma^{h\nu}$ scale.

Table 9. Summary of reported pK_a^* values for substituted phenols

Substituent	Ref.						Average value ^d
	5 ^a	3 ^a	7 ^a	22 ^b	34 ^a	4 ^c	
H	4.0	3.8	3.8	3.7	3.62	5.41	3.8 ± 0.2
<i>p</i> -F	4.4	3.95	4.0		3.5	6.51	4.0 ± 0.5
<i>m</i> -F	3.8	3.8	3.8			5.73	3.8
<i>p</i> -Me	4.3	4.2	3.9	3.7	4.1		4.0 ± 0.3
<i>m</i> -Me	4.0	4.1	4.1		4.2	5.66	4.1 ± 0.1
<i>p</i> -Et	4.3	4.3		4.3		4.3	
<i>m</i> -Et	4.3	4.3		4.5			4.4 ± 0.1
<i>p</i> -OMe	5.6	5.03	4.8	4.1	4.7	5.52	4.8 ± 0.8
<i>m</i> -OMe	4.6	4.12	3.6	3.4	2.7	6.22	3.7 ± 0.9

^aExperimental values based on Förster cycle method.

^bExperimental values based on Stern-Volmer.

^cCalculated from benzoic acid pK_a^* values.

^dAverage of reported experimental values.

unit, which represents an error in locating the 0-0 transition energy of only 1-2 nm at 286 nm, and even in the worst cases the error would only represent 5-6 nm. Thus it is not clear whether the failure to correlate photochemical rate and equilibrium data with each other is due to the uncertainty in determining pK_a^* via the Förster cycle, or to different types of substituent dependence for photochemical rates and equilibria. (Although in principle this should not be any different from correlating rates with equilibria for thermal reactions, there is a possible complication when making such correlations for photoreactions. The rate constants only require knowledge of the reactant lifetime, but accurate photochemical equilibrium constants require determination of the lifetimes of both species involved

in the equilibrium, and a detailed kinetic treatment in cases where photoequilibrium is not established. Therefore, the possible substituent dependence of non-productive decay processes will be more complicated in the equilibrium case).

If the latter is the case, this implies that the ratio of resonance to inductive effects for *meta* substituents in excited states may not only be different from that in ground-state behaviour, but may vary depending on the type of photochemical process involved (i.e. rate versus equilibrium). The calculations of Wehry and Rogers⁵ in Table 7 support this idea, when compared with the present α^* and α_0 values. This may mean that more than one type of σ scale will be required for different types of photoreaction, as is the case for thermal

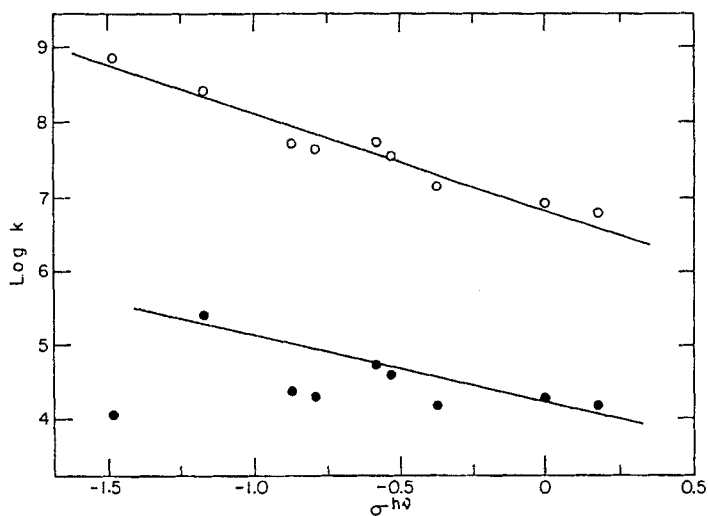


Figure 5. Comparison of (○) $\log k_{H^+}$ and (●) $\log k_{H_2O}$ (closed circles) versus σ^{hv} for styrene photohydrations

reactions (σ , σ^+ , σ^- , etc.). As an illustration of the problem, the $\log k_{H_2O}$ values for the water-catalysed photohydrations listed in Table 3 do not correlate very well against σ^{hv} , which was at first surprising. An example is shown in Figure 5, comparing both $\log k_{H_2O}$ and $\log k_H^+$ for the styrene photohydrations. It is evident that whereas σ^{hv} works fairly well for the $\log k_{H_2O}$ values of *para* substituents, it grossly overemphasizes the electron-donating ability of *meta* substituents. It is difficult to draw any firm conclusion about this for two reasons. One is that the $\log k_{H_2O}$ values are probably much less accurate than $\log k_H^+$, since they are necessarily based on single-point determinations, rather than on multi-point Stern–Volmer plots. Secondly, the overall range of $\log k_{H_2O}$ obtained is small, leading to very low overall ρ values (-0.2 to -0.3), which can often lead to low correlation coefficients. It is also significant that $\log k_H^+$ represents a cation-forming reaction where conjugative effects would be expected to be important, whereas $\log k_{H_2O}$ involves the reaction of a polarized S_1 state with a neutral molecule. It may be that charge development, and hence conjugative effects, are less important than in the analogous H_3O^+ -catalysed process.

It is important to emphasize that the present attempt to establish a σ^{hv} scale is exploratory. There are clearly still several potentially serious problems in trying to set up any useful σ scale for photochemical reactions, and these are not all obviated by using excited-state rate constants rather than equilibrium constants. One problem is that the data available to test the present scale are very limited, and the apparently good agreement obtained may be vitiated as more photochemical data sets are reported. Secondly, it is surprising that the present σ^{hv} values appear to correlate reactions which are completely different, with respect to both mechanisms and type of excited state involved. Thirdly, it is probably overoptimistic to expect that excited states will be simpler in their behaviour than analogous ground states, and that one set of σ^{hv} values will adequately describe the behaviour of given substituents in all cases. Finally, an aromatic substituent could affect both the rate and efficiency of production of the reactive excited state, in addition to its effect on the rate of the actual photoreaction from that state. This problem is associated with the way in which photochemical rate constants are generally determined, namely from quantum yields and fluorescence lifetimes. However, given that the rate processes which lead from the Frank–Condon state to the lowest (reactive) excited state are generally very fast in comparison with all subsequent photochemical and photophysical processes, and that it is virtually always this state which fluoresces, this should not be a serious problem. In other words, any possible substituent effect on how the reactive state was actually arrived at should be much less important than its effect on how the state subsequently behaves.

Despite the above caveats, it is believed that the present σ^{hv} scale will prove to be useful, either in the sense that it will need to be refined as more data become available, or that it will clearly show that more than one set of σ values is required for photochemical reactions. At present, it offers clear advantages over previous scales, and again focuses on the different behaviour of *meta* substituents in excited- versus ground-state reactions.

EXPERIMENTAL

General. Fluorescence spectra were measured on a Perkin-Elmer MPF-66 instrument, UV spectra on a Varian 2300 spectrophotometer and NMR spectra on a Varian T-60 instrument. Argon was used as provided (Canox, >99.9% pure). Reagent-grade acetonitrile (Aldrich) was used to prepare stock solutions of substrates. Volumes of 10–30 μ l of these solutions (*ca* 10^{-2} M in substrate) were injected into 3 ml of aqueous acid solution, sufficient to give suitable intensity or absorbance readings. Sulphuric acid solutions were prepared by diluting 98% acid (Caledon) with distilled water. Concentrations were determined by using an Anton Paar DMA 02C precision density meter and converting the measured densities to wt% sulphuric acid using available literature tables.²³

Substrates. Substrates **1–5**, **8** and **10** were available commercially (Fisher, ICN or Aldrich) and were distilled prior to use (except for **10**, which was sublimed). Substrates **6**, **7**, **9**, **11–15**, **17** and **18** are all known compounds, and were synthesized according to standard literature methods. These compounds were all distilled or sublimed prior to use. Purity was checked by gas chromatography and in all cases was >99.9%. Substrate **16** (*m*-ethylphenylacetylene) was synthesized by the method of Allen and Cook,²⁴ as used for the *para* isomer **15**, with the following modification. A mixture of *m*-ethylacetophenone and PCl_5 was heated at 60–70°C for 2 h. After the mixture had cooled, water was added dropwise and solution was extracted with diethyl ether. The ether extracts were washed twice ($NaHCO_3$, water) and dried ($MgSO_4$). The residue after evaporation was refluxed twice with fresh KOH in *t*-BuOH, each time for 6 h. The reaction mixture was poured into a large excess of distilled water and extracted with dichloromethane. Repeated washing (water) was used to remove *t*-BuOH, and the extract was dried ($MgSO_4$). Evaporation of solvent, followed by distillation, gave *m*-methylphenylacetylene (b.p. 62–63°C/15 mmHg).

All the product ketones (from the photohydration of **10–18**) were available commercially (Fisher, ICN or Aldrich). The alcohol products from the photohydration of **1–9** were synthesized from these ketones via $NaBH_4$ reduction in ethanol.

Absolute quantum yield determinations. Malachite green leucocyanide, used as actinometer, was prepared by the method of Calvert and Rechen.^{25,26} A standard optical bench set-up was used, consisting of a 200-W high-pressure mercury lamp, high-intensity monochromator, filters and lenses. Slits were adjusted for an effective bandpass of 10 nm. This gave light intensities of 10^{-9} – 10^{-8} einstein s^{-1} in the 240–252 and 285–295 nm regions. The UV cells used were cooled to offset both the effects of irradiation and heat from the magnetic stirrer plate. All quantum yields were determined at 23.0 ± 0.5 °C. Values of the product quantum yield were calculated from the expression

$$\Phi_{\text{pdt}} = \frac{\Sigma A}{10^3 \epsilon I \Delta t (1 - 10^{-OD})}$$

where I is the light beam intensity in einstein $s^{-1} \text{ cm}^{-2}$, Δt is the irradiation time in s, ϵ is the molar absorptivity in $\text{l mol}^{-1} \text{ cm}^{-1}$ and ΣA is the change in absorbance. The last term in the denominator corrects for the fraction of light actually absorbed by the sample, where OD is the average absorbance reading at the excitation wavelength. When both the substrate and product have significant absorption at the monitoring wavelength, the term ϵ must be corrected to $\Delta\epsilon$, which is the absolute value of the difference in ϵ between product and starting material. Matched UV cells were used to irradiate the actinometer and substrate solution, and blanks were run to subtract out any accompanying thermal hydration. The light intensity I was calculated from the expression

$$I = \frac{\Delta A}{10^3 (0.91) (1.063 \times 10^5) \Delta t}$$

where ΔA now refers to the change in absorbance of the malachite green solution at 622 nm, 0.91 is the reported^{25,26} quantum yield for malachite green cation formation and 1.063×10^5 is its molar absorptivity at 622 nm in 10^{-3} M HCl .

Relative quantum yield determinations. Irradiations were carried out in a Rayonet RPR-100 reactor using 8–16 254- or 300 nm mercury bulbs, as appropriate. The reaction solutions were placed in quartz UV cuvettes in a 'merry-go-round' apparatus to ensure that each cell received the same amount of light. Distilled water at pH 7 was used as the reference solution (Φ_0) in one cell and the appropriate sulphuric acid concentrations (Φ) in the remaining cells. Separate blanks in each solution (without irradiation) were checked before and after each experiment to correct for any small extent of thermal hydration, which was usually negligible over the time period involved (5–10 min). The absorbance of each solution was measured before and after irradiation to give ΔA , and the ratio $\Delta A/\Delta A_0$ was taken to be equal to Φ/Φ_0 , where ΔA_0 corresponds to

the absorbance change at pH 7, and ΔA corresponds to the acid solution of interest. It was determined that ϵ of the substrate was the same (within experimental error) at pH 7 and in all acid solutions used.

Problems were encountered in the higher acid solutions owing to the high efficiency of the photohydration reaction in this region. Where the ratio of the two absorbances ΔA and ΔA_0 becomes large, absolute errors in the measurement of the reference solution (Φ_0) are magnified. In addition, where the percentage reaction is high, the average absorbances of the acid solution and the reference are significantly different, also leading to errors in Φ/Φ_0 . Therefore to determine Φ/Φ_0 values at the higher acidities, a 'step-out' approach was used. The term ΔA_0 was redefined each time, at the lower acidity of two pairs of solutions being compared. In this way it was hoped to keep errors to a minimum. The pairs of acid solutions compared were usually pH 7/1.14% H_2SO_4 , 1.14%/2.86%, 2.86%/11.46% and 11.46%/23.74% H_2SO_4 , and Φ/Φ_0 was taken as the product of each successive pair of determinations. The reproducibility of the final values of Φ/Φ_0 obtained was very good, providing not too large a ratio of ΔA to ΔA_0 was measured in any one step (usually in the range 2–3).

Fluorescence quenching. Fluorescence quenching of the substrate was accomplished by varying the concentration of acid. The solutions were prepared by pipetting 3 ml of the appropriate acid solution or pH 7 reference into fluorescence cuvettes and then injecting 30 μl of the substrate stock solution with a microlitre syringe into each of the cuvettes. The error introduced by thermal reactions occurring at higher acidities was minimized by injecting the substrate immediately prior to fluorescence measurement.

Fluorescence intensity measurements (arbitrary units) were made in two ways: (1) the entire fluorescence spectrum was recorded using the excitation wavelength which gave the most intense emission and the area under the curve was then calculated using a standard program on the MPF-66; (2) the fluorescence intensity at the emission maximum ($\lambda_{\text{em max}}$) was measured (the MPF-66 allows the intensity at this wavelength to be calculated as an average over 1–99 s in order to smooth out noise). The two methods gave identical results. The second method has the advantage of being fast (typical averaging times employed were 2–5 s). This is important for compounds that are thermally reactive because running an entire spectrum can take 2–3 min. Results can be skewed when thermal reactions are significant. This is also a problem for the more photochemically reactive compounds. Therefore, monitoring the fluorescence intensity is the method of choice. The data were treated by dividing the intensity at pH 7 into the intensities in sulphuric acid. The resulting $(\phi/\phi_0)_B$ values were plotted against free hydrogen ion concentration

and the initial linear portions of the graphs were used to obtain the slopes ($= K_{SV} = k_H + \tau$). The slopes were evaluated by least-squares analysis.

Lifetime measurements. All lifetimes were obtained via single photon counting.¹⁶ The measurements were performed on a PRA System 3000 Fluorescence Lifetime Instrumentation machine. The decay curves were deconvoluted using the available software. Lifetime measurements were carried out at ambient temperatures (*ca* 23 °C) on solutions in fluorescence cuvettes. These were prepared in the same manner as for the fluorescence studies. Generally, data points were collected until 10 000 counts had been obtained. This took from 30 min to several hours depending on how strongly the sample fluoresced. For some of the more weakly fluorescent samples, only 5000 counts were collected owing to time constraints. The analysis of these data was still satisfactory owing to the high quality of the data (low scatter) and the fact that single exponential decay was observed in all but two cases. The double exponential decay observed for **8** and **9** has been discussed earlier. In one case, **18**, the fluorescence was too weak for the instrument to detect accurately. (Since the lifetimes for the *meta*-substituted phenylacetylenes are generally longer than for their *para* analogues, the value of τ_F^0 for **19** would be expected to be at least as large as that for **18**, which has $\tau_F^0 = 0.84$ ns. However, since the fluorescence of **19** was too weak for reliable single photon counting measurements over a reasonable time period, this indicated that its τ_F^0 was in the sub-nanosecond region. Therefore, an estimated value of 0.9 ns for **19** was used in the calculation of its k_H^+ value from the measured K_{SV} value.) A value of 0.9 ns was estimated by comparing the fluorescence intensities of **9** and **18** at λ_F^{\max} and by assuming that these two closely related compounds had the same intrinsic k_F^0 value.²⁷

The excitation and emission wavelengths used in determining the lifetimes were determined by fluorescence spectroscopy. A 280-nm cutoff filter was used on the emission side when measuring lifetimes, in order to eliminate scatter from the lamp, because $\lambda_{ex} < 280 \text{ nm} < \lambda_{em}$ for all compounds. In every case, a small rise time of approximately 100 ps was observed. This is probably not significant because the instrument is only able to measure lifetimes as short as 0.5 ns at best.

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