25°.[6] In this case hydrogen is being transferred from silicon to another hydrogen atom from the solvent to produce H—H or D—H as product. For SiH and SiD bonds the stretching frequencies were taken as[6] 2135 and 1547 cm.$^{-1}$, respectively. The bending frequencies were taken as $\nu_H = 978$, 910,[7] and $\nu_H/\nu_D = 2135/1547 = 1.38$ was assumed for the bending frequencies. Frequencies of 4159 and 3627 were taken for HH and DH.[8] The translations and moments of inertia were neglected for SiH *vs.* SiD but included for HH *vs.* DH. K_H/K_D was calculated to be 1.7 at 25°. The transition state of this reaction must have the hydrogen atom which is being transferred closer to the reactants than to the products, since k_H/k_D is considerably less than K_H/K_D.

In reactions such as enolization or E2 elimination (the transfer of hydrogen from C to the O of HO$^-$), K_H/K_D was calculated to be about 0.9, using the previous values for the CH and CD frequencies and the known partition functions for water.[9] For CH being changed to $\overset{\diagdown}{\underset{\diagup}{\mathrm{O}}}{}^{+}$—H by attack of water (*e.g.* in enolization), K_H/K_D was calculated to be about 1.3.

For the reaction of bromine atoms with toluene, K_D/K_H was calculated to be 1.83 but $k_H/k_D = 4.9 \pm 0.3^2$ so no information is obtained. The vibration of HBr was used[10] together with the theoretical reduced mass to calculate the frequency of DBr, and translations and rotations were allowed for. However, it has already been concluded that the transition state for the abstraction of a hydrogen atom from toluene by a chlorine atom is closer to reactants than to products. The fairly large isotope effect for abstraction by bromine means that the transition state is *closer to products* than for chlorine. This is in accord with a recently proposed rule[11] for predicting effects of structural changes in reactants on the structure of transition states, since chlorine is predicted to lengthen the Cl---H bond and shorten the H---C bond relative to bromine. It is the first time the rule has been checked for a free radical reaction.

The results presented here are somewhat qualitative because the numbers used in calculating K_H/K_D were guessed at. Quantitative information can be obtained, however, by examining the spectra of deuterated and nondeuterated reactants and products. *All* isotopic frequency shifts can then be accounted for. Therefore, this approach offers a way of *analyzing the structure of some transition states by means of observable quantities.*

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[6] L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **77**, 1300 (1955).

[7] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945, p. 167 (SiH$_4$).

[8] Ref. 5, p. 532.

[9] C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, **10**, 200 (1960). The square root of the ratio for H$_2$O *vs.* D$_2$O was used.

[10] Ref. 5, p. 534.

[11] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

Extension of the Hammett Equation to Photochemical Quantum Yields

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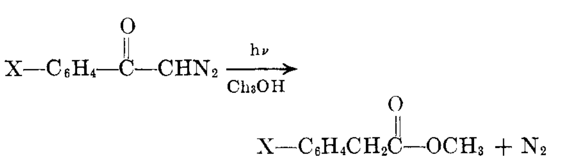
The quantum yields of a series of substituted diazoacetophenones have been correlated with the effects of substituents by means of the Hammett equation. A possible rationalé for this is discussed in terms of the excited state from which reaction occurs.

Recent interest in organic photochemistry has resulted in detailed studies of the mechanisms and quantum yields (molecules reacted per quantum absorbed) of many reactions,[1] although there seems to have been only one systematic study[2] of the effect of substituents on an aromatic ring on quantum yields in a photochemical reaction. In this study Kirmse and Horner[2] irradiated a series of substituted diazoacetophenones at their principal absorption maxima (approx. 290 mμ) and determined the quantum yields of the reaction. Since these quantum yields vary over a rather wide range, they permit *a test of the hypothesis that these variations are dependent on the resonance and inductive effects of the substituents.*



$$X\text{—}C_6H_4\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CHN_2 \xrightarrow[CH_3OH]{h\nu} X\text{—}C_6H_4CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OCH_3 + N_2 \quad (1)$$

The electronic effects of substituents in aromatic rings have been correlated with the nature of the substituents by means of the Hammett equation:

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[1] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., 1941, Appendices.

[2] W. Kirmse and L. Horner, *Ann.*, **625**, 34 (1959).

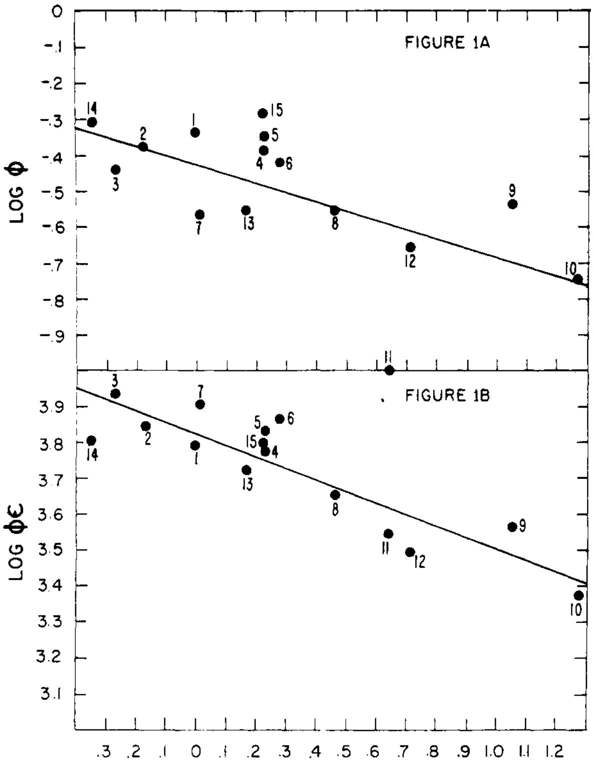

Figure 1

$$\log k - \log k_0 = \sigma\rho$$

where k is either a rate or equilibrium constant; k_0 is the rate or equilibrium constant for the corresponding unsubstituted compound; ρ, the reaction constant, is specific for the reaction under consideration; while σ, the substituent constant, measures the electronic influence of the various substituents on the aromatic ring. As far as the authors are aware, there has been no report of an attempt to correlate the effect of substituents on quantum yield with the Hammett equation. In fact, the recent work of both Havinga[3] and Zimmerman[4] suggests that a relation of this sort does not exist.

When the logarithm of the quantum yield (ϕ) for reaction 1 was plotted as a function of Hammett's σ constant, a satisfactory correlation between log ϕ and σ was obtained (Fig. 1).[5] The probability that the relationship is accidental is less than 0.05.[7]

TABLE I

Compound number	Substituent X	ϵ	λ_{max} mμ	ϕ	σ^a
1	H	13,500	294	0.46	0.000
2	p-CH_3	16,800	297	.42	− .170
3	p-CH_3O	24,100	304	.36	− .268
4	p-Cl	14,500	299	.41	+ .227
5	p-Br	15,100	299	.45	+ .232
6	p-I	19,300	301	.38	+ .276
7	p-C_6H_5	29,500	309	.27	+ .009
8	p-C_6H_5CO	16,000	299	.28	+ .459
9	p-CH_3SO_2	12,700	304	.29	+1.049
10	p-NO_2	13,300	307	.18	+1.270
11	p-$C_6H_5N{=}N$	35,300	334	.10	+0.640
12	m-NO_2	14,200	297	.22	+ .710
13	β-naphthyl	18,900	317	.28	+ .170
14	o-CH_3O	13,000	288	.49	− .34
15	o-Cl	12,100	287	.52	+ .22

[a] σ values for compounds 1–13 from H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); compounds 14 and 15, A. T. Shulgin, and A. W. Baker, *Nature*, **182**, 1299 (1958).

In correlating quantum yields with the Hammett equation, we have used σ, which is a reflection of the electronic distribution in the *ground* state, to predict reactivities of the *excited* state. The recent work by Jackson and Porter[8,9] has shown that the electronic distribution of excited *triplet* states in naphthylamines, naphthols, naphthoic acids, and acridine differs very little from that of the ground state. This is *not true*, however, in the case of the excited *singlet*, which appears to have an electronic distribution differing from that of the ground state. In the case of the photochemically catalyzed hydrolysis of p-, m-, and o-nitrophenyl dihydrogen phosphate esters described by Havinga,[3] the reactive species is probably the first excited singlet and consequently the electronic distribution (σ) of the ground state cannot be used to predict the reactivity of the excited states.[4] There is reason to believe, however, that the excited state of the diazoacetophenones *from which reaction occurs* may be a triplet; hence the electronic distribution of the ground state could be used to predict the reactivity of the excited state. It has been shown that the reactive species of acetophenone and benzophenone

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(3) E. Havinga, R. O. De Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(4) H. E. Zimmerman, Abstracts of the Seventh National Organic Chemistry Symposium of the American Chemical Society, Bloomington, Ind., June, 1961.

(5) The marked deviation of compound 11 (X = p-azophenyl-) in the correlation of log ϕ with σ can be rationalized in either of two ways. The substituent, p-azophenyl-, in this compound may be acting as an "inner filter"[2,6] by absorbing light without undergoing any photochemical reaction. Or, since these irradiations were conducted at the absorption maximum which occurs at the longest wave length (see Table I) for compound 11, there may be insufficient excess energy for reaction. A detailed investigation of the dependence of ϕ on wave length would therefore be desirable. One might obtain a better correlation of ϕ with structure by a comparison of log ϕ with σ.

(6) Ref. 1, p. 152.

(7) The regression equation of log ϕ and σ is given by:

$$\log \phi = -0.423 - [0.2625 \text{ [illegible] } 0.0900]\,\sigma$$

with a standard error of estimate of 0.155 log units. This is calculated from the equation:

$$SE = \sqrt{\Sigma d^2/(n - 2)}$$

and represents the root mean square deviation of the points from the regression equation. The variance ratio, F (8.51) is a measure of the significance of the relationship between the variables. The higher this value, the more significant the relationship; from F one can estimate P, the probability that the relationship observed is accidental. In this case $P < 0.05$. A remarkable improvement in the correlation of log ϕ *vs.* σ was noted when (log ϕ + log ϵ) was plotted against σ (see Fig. 1B). The regression equation was:

$$\log \phi = 3.579 - [0.3138 \pm 0.0473]\sigma - [0.9425 \pm 0.1558]\log \epsilon$$

The statistical criteria in this case are $SE = 0.080$ log units, $F = 36.59$ and $P << 0.001$. We are unable at the present time to account theoretically for this improvement.

(8) G. Porter in "Symposium in Light and Life," Johns Hopkins University Press. Baltimore, Md., 1960.

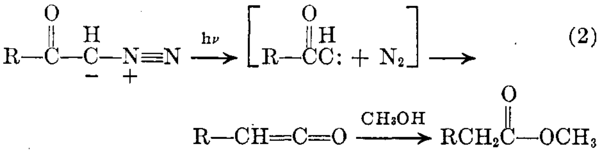
(9) G. Jackson, *Disc. Farad. Soc.*, **27**, 103 (1959).

TABLE II

	Regression variables	Regression equation	F	P	Standard error of estimate, log units
1.	$\log \phi$ on σ	$\log \phi = -0.423 - [0.2625 \pm 0.0900]\sigma$	8.51	<0.05	0.155
2.	$\log \phi$ on σ and $\log \epsilon$	$\log \phi = 3.579 - [0.3138 \pm 0.0473]\sigma - [0.9425 \pm 0.1558] \log \epsilon$	36.59	$\ll 0.001$	.080

when irradiated at 3130 Å. and 3660 Å. are triplets[10]; by analogy the reactive species of diazoacetophenone is probably a triplet. It would be desirable to verify this point, which, if true, provides a reasonable explanation for the correlation of the quantum yield with the Hammett sigma function.

The photochemical decomposition of diazo ketones, like the Wolff rearrangement, proceeds *via* a ketene[11] and may be formulated by the following probable mechanism[12]:



$$R\!-\!\overset{\overset{O}{\|}}{C}\!-\!\overset{H}{C}\!-\!\underset{-\ \ +}{N}\!\equiv\!N \xrightarrow{h\nu} \left[R\!-\!\overset{\overset{O}{\|}}{C}\overset{H}{C}\!: + N_2\right] \longrightarrow R\!-\!CH\!=\!C\!=\!O \xrightarrow{CH_3OH} RCH_2\overset{\overset{O}{\|}}{C}\!-\!OCH_3 \qquad (2)$$

Examination of the possible physical significance of this relationship between log ϕ and σ suggests that the slope of the curve (ρ) should be consistent with a reasonable mechanism for the reaction. Previous investigations have demonstrated that a positive value of ρ indicates that the reaction is facilitated by a low electron density at the reaction site, while a negative value implies that the reaction is favored by high electron availability.[11]

Since the group R is required to migrate with its electron pair, a high electron density at the reaction site R should favor the reaction. The negative slope shown in Fig. 1 is consistent with this interpretation. This electronic influence is also consistent with the results of Briggs and Lyttleton[15] in their study of the Schmidt reaction:

$$xArCOOH + HN_3 \longrightarrow xArNH_2 + N_2 + CO_2 \qquad (3)$$

which proceeds by a mechanism similar to that of the Wolff rearrangement. The slope (ρ) of -1.4 found for this nonphotochemical reaction is similar to that obtained in the photochemical decomposition (-0.26) of diazoacetophenones, but indicates a somewhat higher sensitivity to substituent effects. It therefore appears that the Hammett relationship may be used to describe the influence of substituents on an aromatic ring upon quantum yields of a photochemical reaction provided the reactive species is a triplet.

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[10] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961); H. L. J. Backstrom and K. Sardros, *Acta Chem. Scand.*, **14**, 48 (1960).

[11] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, 1949, p. 47.

[12] Horner[13] first suggested a carbene intermediate and recent work by Skell, *et al.*[14] has shown that carbenes are generated by the photolysis of various diazo compounds. Carbenes so generated are triplets.[14a,14b] The suggestion that the excited state of the diazoacetophenones is a triplet, is therefore compatible with the available information.

[13] L. Horner, E. Spieschka, and A. Gross, *Ann.*, **573**, 17 (1951).

[14] (a) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2398 (1961); (b) R. M. Etter, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959).

[15] L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943)