A Contribution to the Mechanism of the Diels–Alder Reaction

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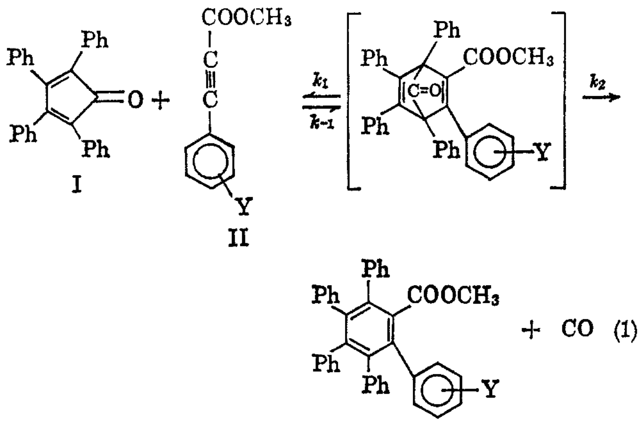
The second-order reaction of tetracyclone and methyl arylpropiolates has as the rate-determining step the formation of the complex rather than its breakdown. In the Hammett plot in which log k is plotted against log K_t/K_t° for the arylpropiolic acids, a curvature is observed, which can be eliminated if σ^- values are used. The curvature can thus be ascribed to extraresonance interaction between the substituent and the reaction site, which is construed to speak for a lopsided transition state in the Diels–Alder reaction.

The Diels–Alder reaction of tetracyclone (tetraphenylcyclopentadienone, I) with methyl arylpropiolates (II) has been previously studied by Benghiat and Becker. It has been shown[4] to be a good system for the study of the Diels–Alder reaction since the reverse Diels–Alder reaction cannot occur (eq 1). It also allows the kinetic data to be obtained at convenient times and temperatures. The investigation of the Diels–Alder kinetics was continued in an attempt to extend some of the results obtained in the previous study by Benghiat and Becker.



I II III

Experimental Section

Solvents.—Phenylcyclohexane was obtained as practical or purified solvent grades and purified by the procedure of Corson and Ipatieff.[5] Xylene reagent (Fisher) was purified by distillation, the cut between 139 and 140° being used.

Reactants.—Tetracyclone melted at 221–222°, lit.[6] mp 219–220°.

Preparation of Methyl Arylpropiolates.—The substituted phenylpropiolic acids were prepared by dehydrobromination of the corresponding cinnamic acid or ester dibromides with alcoholic potassium hydroxide according to literature procedures (see Table I). The preparation of the methyl arylpropiolates was accomplished by the reaction of the appropriate acid with 1 N HCl in methanol at room temperature according to the method of Pfeiffer[7] (see Table II).

Apparent Dissociation Constant for the *o*-Arylpropiolic Acids.—The determination of the dissociation constants for the arylpropiolic acids in 50 vol % ethanol was carried out exactly as described by Benghiat and Becker.[4] The maximum deviation between pairs of determinations was ±0.02 pK_a units. Table I lists the results.

Kinetic Measurements.—The method employed has been previously described by Benghiat and Becker.[4] The evolution of carbon monoxide as a function of time was used in the determination of the rate constants. The second-order rate constants are expressed in terms of molal^{-1} sec^{-1} in contrast to the usual molar^{-1} sec^{-1}. The results are recorded in Table III. Determination of the rates at different temperatures allowed the calculation of energies of activation and frequency factors for the Diels–Alder reaction of some of the arylpropiolic acid esters and tetracyclone. The results are also recorded in Table III.

Isolation of the Products.—Methyl 2-(*o*-tolyl)tetraphenylbenzoate was filtered from the reaction mixture after cooling. Evaporation of most of the solvent gave more pentaarylbenzoate. The yield of product was 86% and the extent of reaction as indicated by carbon monoxide evolution was 88%. The aryltetraphenylbenzoates not reported by Benghiat were isolated and recrystallized twice from either acetic acid or xylene, and the results are recorded in Table IV.

Absorption Spectra of Methyl Arylpropiolates.—The infrared spectra of 13 methyl arylpropiolates were taken in chloroform solution on a Perkin-Elmer Model 21 infrared spectrophotometer. A fixed cell (0.056 mm) was used together with sodium chloride optics. The position of the carbonyl and acetylenic vibrational absorptions were recorded and listed in Table V.

The ultraviolet spectra were taken in methanol solution on a Beckman Model DU quartz spectrophotometer with a Process and Instruments automatic recording attachment. The wavelengths and ϵ_{max} values for the methyl arylpropiolates are also listed in Table V.

Results

It has been observed that tetracyclone can react with oxygen at about 150° on long heating to give a colorless product or products.[8] This also occurs in phenylcyclohexane as solvent.[9] However, at 142.3° under identical conditions used in the present kinetic experiment, except for the absence of propiolic acid ester, the tetracyclone was recovered essentially unchanged.

The methyl *o*-nitrophenylpropiolate decomposed spontaneously at temperatures above 130°. At 130° the system could not be equilibrated for more than 5 min or again the material would decompose. The analysis of the gas evolved in this decomposition showed it to be carbon dioxide. The liquid remaining was a straw-colored oil which was not examined further. The rate of the *o*-nitro ester was fast enough to need temperatures only from 87 to 130° for the energy of activation and the log A term to be calculated. The linearity of the log k *vs.* $1/T$ plot supports the opinion that only one reaction is occurring.

Two experiments were tried to test the effect of large inert surfaces on the rate (wall effect). Powdered

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[1] Taken from the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1961.

[2] E. I. du Pont de Nemours and Co., Inc., Teaching Assistantship, 1957–1959.

[3] To whom inquiries should be directed: University of Massachusetts, Boston, Mass. 02116.

[4] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958).

[5] B. B. Corson and V. N. Ipatieff, *J. Am. Chem. Soc.*, **59**, 645 (1937).

[6] J. R. Johnson and O. Grummitt, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 806.

[7] P. Pfeiffer, *Ann.*, **411**, 148 (1916).

[8] W. Dilthey, S. Henkels, and M. Leonhard, *J. Prakt. Chem.*, **151**, 97 (1938).

[9] L. Rothman, unpublished results. However, this may be due to prior oxidation of phenylcyclohexane followed by reaction with tetracyclone.

TABLE I

PROPERTIES OF *ortho*-SUBSTITUTED PHENYLPROPIOLIC ACIDS AND SPECIFIC RATE CONSTANTS OF THE ESTERS IN DIELS–ALDER REACTION WITH CYCLONE

Substituent	Method of preparation	Mp, °C		Apparent pK_a[a]	σ			Specific rate constants of esters[e]
		Found	Lit.		Log K/K_0[b]	Newman[c]	Taft[d]	
H	[f]	135.5–137	135–136	3.43	0.00	0.00	0.00	0.170[g]
o-NO$_2$	[h]	158.5–159.5 dec	161–163 dec	3.13	0.30	0.41	0.80	(1.154)[i]
o-CH$_3$O	[j], [k]	125.5–127.5	128–128.5	3.51	−0.08	−0.13	−0.39	(0.168)[i]
o-CH$_3$	[l], [m]	93–94.5	94–95	3.55	−0.12	...	−0.17	(0.118)[i]
o-Cl	[m]	133–134.5	134–135	3.26[g]	0.14	0.16	0.20	0.473[g]

[a] At 24°. [b] Log K/K_0 for the arylpropiolic acids in 50 vol % ethanol at 24°. [c] Log K/K_0 for the arylpropiolic acids in 35 wt % dioxane. [d] σ^* values corrected to read zero for H. See D. A. D. Jones and G. G. Smith, *J. Org. Chem.*, **29**, 3531 (1964). [e] At 175.6°. [f] T. W. Abbott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 515. [g] Values determined by I. Benghiat in previous work. [h] K. Schofield and J. C. E. Simpson, *J. Chem. Soc.*, 512 (1945). [i] Values obtained from plots of log k *vs.* $1/T$. [j] F. G. Baddar, *J. Chem. Soc.*, 224 (1947). [k] W. Schlenk and E. Bergmann, *Ann.*, **463**, 82 (1928). [l] M. Reimer, *J. Am. Chem. Soc.*, **64**, 2510 (1942). [m] F. G. Baddar, L. S. El-Assal, and N. A. Doss, *J. Chem. Soc.*, 461 (1955).

TABLE II

METHYL ARYLPROPIOLATES[a]

Substituent	Yield, %	Mp or bp (mm), °C		% C[b]		% H[b]	
		Found	Lit.	Calcd	Found	Calcd	Found
None	70	120–121 (16)[c]	132–133 (16)				
o-Cl	73.6	37.8–38.5	39.5–40.0[d]				
o-NO$_2$[e]	43.5	85.3–86.2	87.88[a]				
o-CH$_3$O	80	39.4–40.2		69.46	69.66	5.30	4.93
o-CH$_3$	44.5	90 (5)[f]		75.84	76.16	5.79	6.11

[a] Method of P. Pfeiffer, *Ann.*, **411**, 149 (1916). [b] Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. [c] $n^{26}\text{D}$ 1.5604 [$n^{22}\text{D}$ 1.5628: C. Moureu, P. T. Muller, and J. Varin, *Ann. Chim.*, (Paris), [9] **2**, 269 (1914)]. [d] Reference 4. [e] Decomposes slowly on standing over long periods. [f] $d^{20.5}{}_4$ 1.0728, $n^{20.5}\text{D}$ 1.5620, $n^{25}\text{D}$ 1.5600. Calcd for $C_{10}H_{11}O_2$: M$_R$, 49.05. Found: M$_R$, 52.64 (exhaltation 3.59). Similarly the exaltation calculated for methyl phenylpropiolate is 3.66.

TABLE III

KINETIC DATA FOR THE REACTION OF METHYL-SUBSTITUTED PHENYLPROPIOLATES WITH TETRACYCLONE

Substituent	Temp, °C	k (molal^{-1} sec^{-1}) × 1000	ΔE_a, kcal/mole	Log A
H	141.8	0.25		
	170.7	1.20	20.0	6.8
	175.6	1.48		
	187.8	2.52		
o-Cl	170.7	2.37	18.2[a]	6.3[a]
o-CH$_3$	146.2	0.282		
	157.4	0.485		
	170.8	1.05	19.0	6.3
	186.8	2.12		
	188.1	2.18		
o-CH$_3$O	146.2	0.612		
	170.8	1.80	16.3	5.3
	187.8	3.62		
o-NO$_2$	86.9	0.129		
	121.4	1.32	19.0	7.6
	130.1	2.17		
p-NO$_2$	142.2	1.52		
	146.2	1.92	18.4	6.9
	175.6	7.75		
p-CH$_3$	142.2	0.198		
	175.6	1.26	20.2	6.9
	189.5	2.37		
p-CH$_3$O	146.2	0.248		
	175.6	1.19	20.0	6.8
	188.1	2.26		
p-Cl			18.9[a]	6.6[a]

[a] See ref 4.

TABLE IV

METHYL 2-ARYLTETRAPHENYLBENZOATES

Substituent	Mp, °C	Carbon, %		Hydrogen, %	
		Calcd	Found	Calcd	Found
o-NO$_2$	297.7–299.7	81.26	81.34	4.85	4.75
o-CH$_3$O	275–276	85.69	85.85	5.53	5.55
o-CH$_3$	319–321	88.27	87.86	5.70	5.76
			88.04		5.62
			88.12		5.68

[a] Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

TABLE V

PHYSICAL ABSORPTION DATA ON THE METHYL ARYLPROPIOLATES[a]

Methyl-substituted phenylpropiolates	Infrared absorptions, cm^{-1}		Ultraviolet λ_{max}, mμ (ϵ × 10^5)	
	$\nu_{C=O}$	$\nu_{C\equiv C}$		
H	1724	2233	258 (16.0)	
o-Cl	1727	2238	260 (14.0)	
m-Cl	1726	2238	253 (16.0)	
p-Cl	1723	2230	264 (19.5)	
o-NO$_2$	1722	2235	262 (7.5)	234 (16.3) 306 (3.4)
m-NO$_2$	1728	2240	246 (23.9)	
p-NO$_2$	1727	2242	284 (19.5)	
o-CH$_3$	1710	2220, 2235	263 (13.6)	
m-CH$_3$	1721	2218, 2235	253 (15.0)	
p-CH$_3$	1722	2233	266 (8.8)	
o-CH$_3$O	1710	2220, 2230	263 (10.8)	308 (7.0)
m-CH$_3$O	1723	2220, 2240	263 (12.8)	300 (4.2)
p-CH$_3$O	1722	2230	284 (19.5)	

[a] All the methyl arylpropiolates not included in Table II were either obtained from I. Benghiat and E. I. Becker or else synthesized by methods already reported in their papers.

glass did not affect the rate of reaction of methyl *p*-nitrophenylpropiolate and tetracyclone; the blank and the run with the glass present both gave k values of 0.115. Neutral silica gave a value of 0.105, slightly lower, which might be rationalized, but which in any case, rules out an appreciable wall effect in this reaction in agreement with the earlier conclusion.[4]

A plot of log K/K_0 for the ionization constants of *meta*- and *para*-substituted phenylpropiolic acids in 50% ethanol *vs.* Hammett's σ constants has been shown to be linear. The plot of log K/K_0 for the *ortho* acids *vs.* Taft's *o*-benzoic acid values, reduced to hydrogen equal to zero, also appears to be linear. However, the slopes of the two plots do not coincide. The meaning of this disparity in slopes is not clear. It may be due to an "*ortho* effect"[10,11] or it may be that Taft[12]

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(10) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955).

(11) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(12) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 590–594.

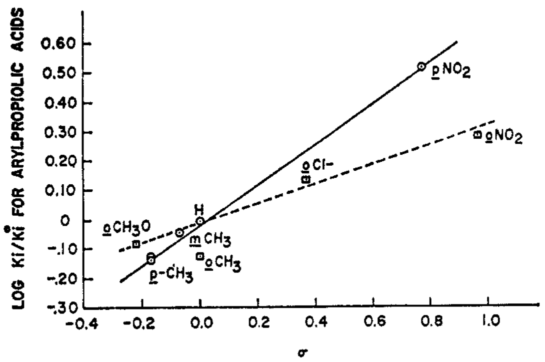

Figure 1.—Plot of log $K_i/K_i°$ for arylpropiolic acids *vs.* σ values of Hammett and Taft.

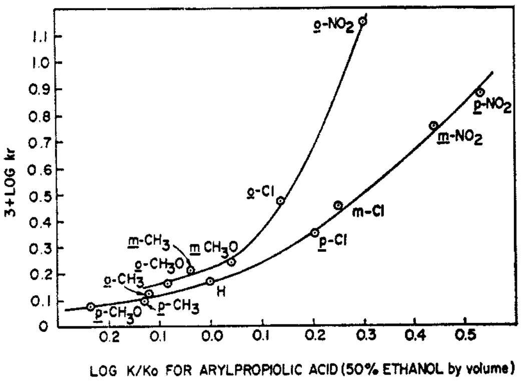

Figure 2.—Plot of log k_r for methyl arylpropiolate–cyclone reaction *vs.* log K/K_0 for arylpropiolic acids.

has not succeeded in relating his values directly to Hammett's (see Figure 1).

The logarithms of the rate constants for the methyl *o*-arylpropiolates reacting with tetracyclone have been plotted against the log K/K_0 values of the *o*-arylpropiolic acids. This plot, together with the previous one,[4] is shown in Figure 2. It is evident that the rates of reaction of the *ortho* esters are much more rapid than one would predict from their σ values (log K/K_0 rates).

The plot of the activation energies *vs.* the log of the frequency factors for the Diels–Alder reaction does not include enough widely spaced points to show a clear-cut linear relationship. However, if such a relationship is assumed, the correlation is adequate, save for the *o*- and *p*-nitro-substituted esters (slope = +2.43, r = 0.966, and S = 0.343) (see Figure 3). These effects are paralleled in the behavior of substituted cinnamic acids.[13]

Discussion

The kinetics show that the reaction is second order even when carried to over 90% completion. The results are consistent with either a rate-determining formation of complex followed by a rapid elimination of carbon monoxide or a second-order formation of complex followed by a consecutive breakdown of the complex at comparable rates. Kinetics cannot show unequivocally whether the formation or breakdown of complex is rate-determining. However, there are strong indications that the rate-determining step is the Diels–Alder step.

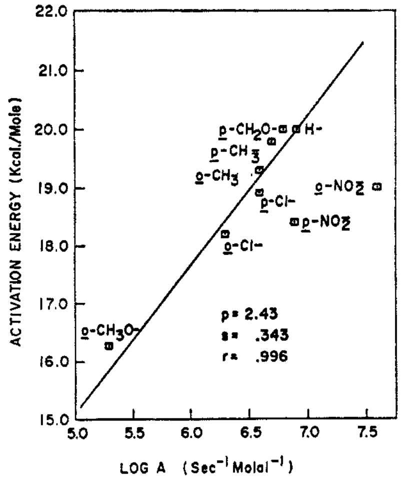

Figure 3.—Reaction of methyl arylpropiolates with tetracyclone.

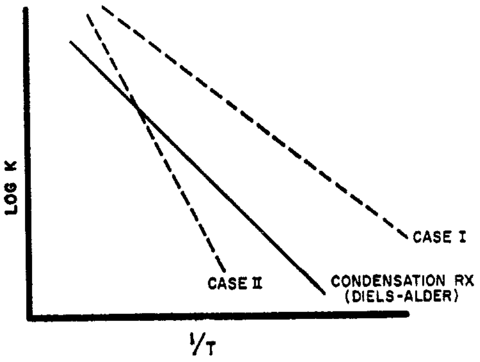

Figure 4.

(1) The energies and entropies of activation for the above reaction are what one would expect for the Diels–Alder reaction. For example, in typical Diels–Alder reactions the logarithm of the frequency factor is between 6 and 10 while the breakdown of the adduct has a frequency factor of about 13.[14] Jarvie and Janz[15] had already used these kinetic parameters to establish a typical Diels–Alder association reaction between a diene and a nitrile. However, it should be pointed out that in nonhydrocarbon solvents, Diels–Alder reactions can have abnormally high or low activation energies and frequency factors.[16] The mechanism is assumed to be the same in the above cases since a plot of ΔE_a *vs.* log A gives a linear correlation.[17] In hydrocarbon solvents, the "normal" values prevail and tend to substantiate the Diels–Alder mechanism for the reaction of tetracyclone and methyl arylpropiolates.

(2) Newman and Caflisch,[18] in their study of the McFadyen–Stevens reaction, had observed that the reaction could not take place unless some solid surface was present. In fact, the authors found that as a rule, solid surfaces catalyze reactions in which a gas is evolved. The statement that solid surfaces catalyze reactions in which a gas is evolved should undoubtedly include the stipulation that the formation of gas has

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[13] C. R. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 4878 (1955).

[14] A. Wassermann, *Trans. Faraday Soc.*, **34**, 128 (1938).

[15] J. M. S. Jarvie and G. J. Janz, *J. Phys. Chem.*, **60**, 1430 (1956).

[16] M. Gillois and P. Rumpf, *Bull. Soc. Chim. France*, 1823 (1959).

[17] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

[18] M. S. Newman and E. Caflisch, Jr., *J. Am. Chem. Soc.*, **80**, 862 (1958).

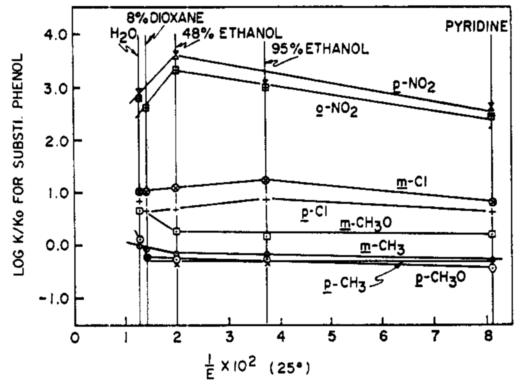

Figure 5.—Log K/K_0 of apparent ionization constants of phenols in various solvents and their relation to E.

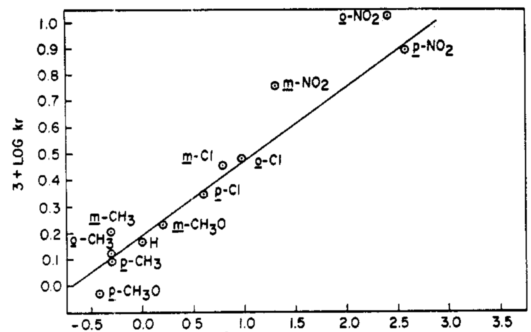

Figure 6.—Correlation of reaction rates of Diels–Alder reaction with substituent constants obtained from phenols (pyridine).

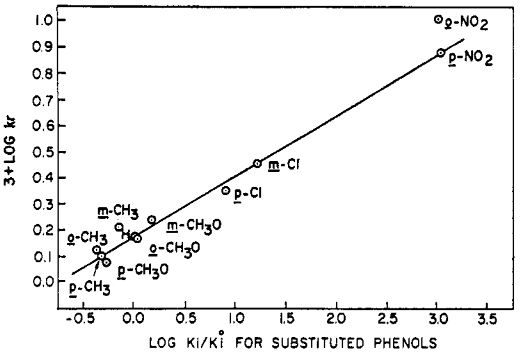

Figure 7.—Correlation of reaction rates of Diels–Alder reaction with substituent constants obtained from phenols (95% alcohol).

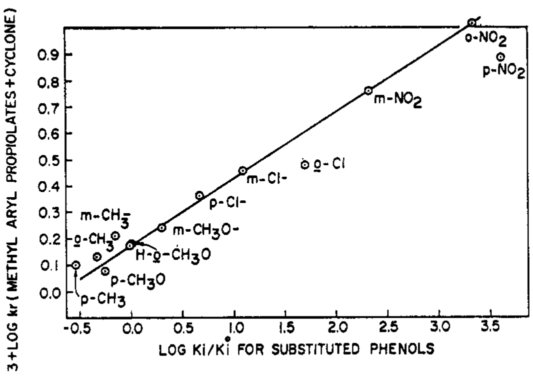

Figure 8.—Correlation of reaction rates of Diels–Alder reaction with substituent constants obtained from phenols (48.9% alcohol).

to be the rate-determining step. In the present work no wall effect was found, suggesting that the elimination of carbon monoxide was not involved in the rate-determining step.

(3) The third indication that the formation of adduct is rate-determining is a consideration of the plots of log k *vs.* $1/T$ for the reaction of the propiolate esters with tetracyclone (Figure 4). The log A terms must be such that the value of the gas elimination step is larger than that of the condensation step. If the activation energy of the gas elimination step is smaller than that of the condensation step, then the gas elimination reaction cannot be rate determining. If the activation energy is larger, it is possible for the two log k *vs.* $1/T$ plots to cross each other and therefore allow the elimination reaction to be rate determining at some lower temperature, one might expect at some higher temperature the Diels–Alder reaction with its more negative entropy term would now become rate determining, leading to a break in the present plot. In all cases the plots of the log k *vs.* $1/T$ were linear, showing that no change in mechanism had occurred.

The Hammett plot of log K/K_0 for the ionization of the arylpropiolic acids *vs.* the log of the rate constants for the Diels–Alder reaction of methyl arylpropiolates and tetracyclone does not give a linear correlation, as pointed out by Benghiat and Becker for rates of the *meta-* and *para*-substituted propiolates. DeWitt, *et al.*,[19] had found a curvature in the Hammett plot of the Diels–Alder reaction between substituted 1-phenylbutadienes and maleic anhydride. The curvature was attributed to the polarizability of the p-methoxy group. Brown and Okamoto[20] showed that DeWitt's data were better correlated by using σ^+ values as a measure of the polar contribution of substituents. Here, it will be remembered that σ^+ values are useful in correlating reactions involving direct resonance interaction between the electron-deficient center and the substituent groups.[21] If one is dealing with a direct resonance interaction between an electron-rich center and the substituents, "σ^-" values should be used.[22,23] The ionization of phenols, an equilibrium reaction, allows direct interaction of anion produced and the substituents. This allows calculation of "σ^-" values. An added advantage in using this reaction to calculate "σ^-" values is that the apparent ionization constants of a great number of substituted phenols have been reported in the literature. The agreement among different workers is quite good. The σ^- values calculated in this way have already been used to correlate reaction rates.[24] However, from the pK_a values in various solvents it becomes apparent that log K/K_0 varies according to the solvent chosen. For the electron-donating substituents the variations are not serious. The electron-attracting substituents, on the other hand, show wide variation in log K/K_0 (see Table V, Figure 5).

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[19] E. J. DeWitt, C. T. Lester, and G. A. Ropp, *J. Am. Chem. Soc.*, **78**, 2101 (1956).

[20] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[21] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

[22] J. F. Bunnett, F. Draper, Jr., P. R. Ryason, P. Noble, Jr., R. G. Tonkyn, and R. E. Zahler, *ibid.*, **75**, 642 (1953).

[23] J. Miller, *Australian J. Chem.*, **9**, 61 (1956).

[24] *Cf.* E. Gaetjens, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, June 1961; E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.*, **82**, 5328 (1960).

The increase in values of log K/K_0 terms for the more electronegative substituents on going from solvents of low dielectric constant to those of higher dielectric constant may be due to proportionally larger interactions of the anions with solvent as compared to phenol anion itself. At some point, however, a leveling effect would become evident for the substituted phenol while the interaction of the phenol anion would continue to increase until it, too, reached a plateau. The net effect is an increase of log K/K_0 followed by a decrease so that a maximum is observed.[25] The carboxylic acids also appear to behave in this manner.

Since the solvent for the Diels–Alder reaction under investigation in this work was nonpolar in character, the values for the lower dielectric solvent systems were used. The three plots, Figures 6, 7, and 8, using σ^- values obtained from the ionization of phenols in pyridine, 95% ethanol, and 48.9% ethanol together with the rate constants for the methyl arylpropiolates and tetracyclone reaction at 175.6° show that no one plot can correlate all the log k values (see Table VI for actual values).

TABLE VI

RATES FOR THE DIELS–ALDER REACTION AND CALCULATED VALUES FOR VARIOUS SUBSTITUENTS IN SEVERAL SOLVENTS

		Log K/K_0 of phenols at 25°		
Substituent	3 + log k_r[a]	95% EtOH	48.9% EtOH	Pyridine
o-CH_3O	(0.168)[b]	(0.01)[c]	(0.00)[c]	
m-CH_3O	0.238	0.17	0.29	0.20
p-CH_3O	0.076	−0.27	−0.24	−0.41
o-CH_3	(0.118)[b]	(−0.36)[c]	(−0.35)[c]	−0.30
m-CH_3	0.207	−0.17	−0.15	−0.30
p-CH_3	0.100	−0.33	−0.33	−0.30
H	0.170	0	0	0
o-Cl	0.473	...	...	1.00
m-Cl	0.458	1.22	1.11	0.80
p-Cl	0.352	0.78	0.68	0.61
o-NO_2	(1.154)[b]	3.00	3.35	2.42
m-NO_2	0.758	...	...	1.33
p-NO_2	0.889	3.04	3.60	2.58

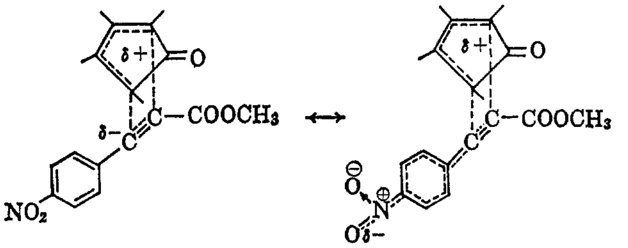
[a] Rates of Diels–Alder reaction of methyl arylpropiolates with tetracyclone at 175.6°. [b] Values obtained from the plots of log k vs. $1/T$. [c] Estimated values using proportion set up from values in other solvents. It is believed possible to do this since the electron-donating groups do not give radically different log K/K_0 terms as the dielectric is changed.

The above results can be interpreted on the basis of the transition state of the Diels–Alder reaction. The transition state must contain polar character and the amount of this character must vary according to the substituents. The value of log K/K_0 (σ^-) which allows the corresponding rate constant to be correlated linearly with the other log K/K_0 values is a measure of the amount of polar character induced on the transition state by the substituent. The idea of variable σ values is not new. Taft,[12] Jaffé,[26] Brown,[21] and others have been aware that the Hammett equation fails when there are resonance effects resulting from direct interaction between the substituent and the reaction site. A more recent paper[27] is even more explicit that resonance interactions lead to a general multiplicity of values. The decision as to whether a polar or a radical mechanism is involved is not greatly affected by the fact that extraresonance factors are involved. Bartlett,[28] in his investigation of the thermal decomposition of t-butyl arylperacetates, showed that the rates could be correlated by σ^+ rather than σ values even though the reaction was shown experimentally to be a radical reaction.

The reaction of the methyl arylpropiolates and tetracyclone could not very well be an ionic one since the ρ values are all small. For example, the ρ value for the plot of log k vs. log K/K_0 in pyridine is +0.28 (S = 0.22, r = 0.997), the ρ values using log K/K_0 values obtained in 95% ethanol is +0.24 (S = 0.019, r = 0.998); and finally the ρ value for log K/K_0 values in 48.9% is +0.29 (s = 0.28, r = 0.997). A purely cyclic mechanism would also be ruled out if one were to use Brown's definition; namely, that in a purely cyclic mechanism one cannot distinguish which electron came from diene and which came from the dienophile.[29] It appears, therefore, that the reaction is a synchronous one involving extraresonance factors to a greater or lesser degree depending on which methyl arylpropiolate was used.

The correlation of the rate with σ^- may be interpreted in the following way. From the data one can postulate that in the transition state the propiolic acid has a partial negative charge which has some direct resonance interaction with the substituent on the phenyl ring. Consistent with such an interpretation would be the formation of a C–C bond between the cyclone and the propiolate at the acetylenic carbon nearest the ester group of the propiolate prior to the complete formation of the other C–C bond at the acetylenic carbon nearest the phenyl ring. The latter carbon would thus have a partial negative charge which could then be stabilized by direct interaction with the electron-withdrawing substituent on the aromatic nucleus.

Such a reaction mechanism in which one bond forms slightly ahead of the other while the partners are held together by electrodynamic forces is formally consistent with the two-stage mechanism proposed by Woodward and Katz,[30] except that polar effects are not involved in their mechanism, but it does give experimental support for the concept of the lopsided transition state, one of the proposals of Berson and Remanick.[31] The lopsided transition state may be considered intermediate between the one-stage mechanism in which both bonds form simultaneously,[29,32]



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[25] J. H. Elliott, *J. Phys. Chem.*, **46**, 221 (1942).

[26] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[27] See H. van Bekkum, P. E. Verkade, and B. M. Wepster [*Rec. Trav. Chim.*, **78**, 815 (1959)] for a general critique of the variability of σ values.

[28] P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

[29] R. D. Brown, *Quart. Rev.* (London), **6**, 63 (1952).

[30] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[31] J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

[32] S. Seltzer, *ibid.*, **87**, 1534 (1965).

and the two-step mechanism in which one bond forms directly before the other.[33,34]

For the retrodiene decarboxylation of the maleic anhydride-α-pyrone adduct,[34] it has been shown that the decomposition is probably two step. For decomposition of the adduct of 2-methylfuran and maleic hydride, the reaction has been shown to be one step.[32] Both of these mechanisms are consistent with the proposal of Woodward that a broad spectrum of partial ionic intermediates may be realized between the extreme cases for pure cyclic reactions (little or no polarity in the reactants) and for reactions in which the reaction partners give rise to highly unsymmetrical polar transition states.

The Leffler-type plot of activation energies *vs.* the logs of the frequency factors as mentioned before did not include enough widely spaced points to show a clear-cut relationship. However, when such a relationship is assumed, the *o*- and *p*-nitro esters are far enough removed so that Leffler's treatment[17] would predict a different reaction mechanism for these two esters. It has been shown, however, that the extra resonance stabilization of the transition state can well account for the deviation without having to postulate a change in mechanism. The isokinetic temperature calculated from the slope is 262.2°. This is 86.6° higher than the 175.6° temperature used in the Hammett-type plots. It will be remembered that near or at the isokinetic temperature all the rate constants will tend to be the same and the variations in rate constants will be due to random deviations rather than to kinetically significant results.[35]

From Figure 3 it is clear that the *ortho*-substituted phenylpropiolic esters react at a much faster rate than would be predicted by the corresponding log K/K_0 values for the substituted phenylpropiolic acids. The extrapolation is not entirely valid because of the difference in solvent. Nevertheless, this *ortho* effect has been encountered previously by both Newman[10] and Roberts[11] in reactions catalyzed by bases and by acids, respectively.

That acceleration is observed for *ortho* substituents rules out large steric effects. Furthermore, this is reinforced by the fact that correlation of the rates for the *ortho*-substituted esters is possible on the same plot as that used for *meta*- and *para*-substituted esters when σ^- values are used. We do not clearly understand the *ortho* effects; however, the fact that the σ^- values obtained from the ionization of phenols do correlate our data recognizes Robert's admonition that the correlation of the effect of an *ortho* substituent must be related to the position of the reacting site in the side chain.

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[33] M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961), and references cited therein.

[34] M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1925, 1933 (1965).

[35] However, see R. C. Petersen, *J. Org. Chem.*, **29**, 3133 (1964).

Organic Reactions and the Critical Energy Density of the Solvent. The Solubility Parameter, δ, as a New Solvent Parameter

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It is suggested that Hildebrand's solubility parameter, δ, provides a measure of the effect of solvent on organic reactions. Quantitative comparisons are made between the use of intrinsic properties of the solvent, such as δ or the dielectric constant, and parameters, such as Y, Ω, Z, S, and E_T, attributable to the interaction of a reference solute with the solvent.

A number of solvent parameters have been introduced recently with the intent of providing an empirical measure of the effect on an organic reaction of changing solvent.[2] Of those available for application at 25°, Y,[3a] Ω,[3b] Z,[3c] S,[3d] and E_T,[3e] S is most inclusive, covering values for 47 pure solvents and the gaseous state. These empirically determined constants relate, each in a different way, to the interaction of a reference solute with an array of solvents. Attempts to demonstrate a relationship between these constants and intrinsic properties of each solvent, such as functions of the dielectric constant like $1/D$,[3a] $(D - 1)/(2D + 1)$,[3a-c,e] or $\rho(D - 1)/M(2D + 1)$,[3b] with D the dielectric constant, ρ the density, and M the molecular weight of the solvent, have been only moderately successful. For example, eq 1 was found to reproduce the data for

$$\Omega_{20} = 0.0251\left[\frac{D - 1}{2D + 1}\,\frac{10^3\rho}{M}\right] + 0.472 \qquad (1)$$

eight solvents with a correlation coefficient of $r = 0.957$ if the hydroxylic solvents ethanol, methanol, and acetic acid were excluded.[3b]

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[2] For a recent review, see C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

[3] (a) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956); (b) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962); (c) E. M. Kosower, *ibid.*, **80**, 3253 (1958); (d) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960); (e) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).