TABLE II

POSITIONS AND INTENSITIES OF RESOLVED PEAKS IN THE SPECTRA OF DIENES IN CYCLOHEXANE SOLUTION

	ν_{max}, cm.$^{-1}$ × 10^{-3} (ϵ)						Difference, cm.$^{-1}$ × 10^{-3}		Intensity ratios		
Compd.	B^-		B		B^+		$B^- - B$	$B - B^+$	$B^- - B$	$B^- - B^+$	$B - B^+$
Butadiene	46.7	(23,000)	45.4	(9700)	44.0	(7500)	1.3	1.4	2.4	3.1	1.3
Isoprene	45.6	(20,000)	44.5	(7000)	43.0	(7900)	1.1	1.5	1.9	2.7	1.4
2,3-Dimethyl-1,3-butadiene	45.0	(15,800)	43.7	(5900)	42.5	(5500)	1.2	1.1	2.9	3.8	1.3
2,5-Dimethyl-2,4-hexadiene	42.1	(22,700)	40.8	(7700)	39.5	(4900)	1.6	1.5	3.3	4.0	1.2
1,3-Pentadiene	46.2	(24,300)	44.5	(9900)	43.0	(8800)	1.7	1.5	2.5	3.0	1.2

the dienes[26-28] in as much as the energy differences, expressed in wave numbers, are of the same order. The fine structure has generally been attributed to vibrational sub-levels. Carr, Pickett, and Stücklen[29] and Dale[30] have examined the vapor phase spectra of a number of dienes and have quoted a figure of 1130–1450 cm.$^{-1}$ for the vibrational spacings, using unresolved bands. Our data (see Table II) are in agreement with this.

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(29) E. P. Carr, L. W. Pickett, and H. Stücklen, *Rev. Mod. Phys.*, **14**, 260 (1942).

(30) J. Dale, *Acta Chem. Scand.*, **11**, 265 (1957).

Pyrolysis Studies. XI.[1,2] Polar Effects of *ortho* Substituents

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Polar σ^0 substituent constants for several substituents have been determined from rate data for vapor phase elimination reactions in which resonance effects are eliminated and proximity effects are minimal. These σ_o^0-values agree fairly well with Taft's σ^*-values, and with σ_o^0-values obtained from other literature data. A table of values is given.

In reactions of simple benzene derivatives the substituents influence the reaction center by a combination of *polar* and *resonance* effects.[4] Additional *proximity* effects may occur in systems involving *ortho*-substituents.[5] These proximity effects are likely to be variable for a given *ortho* substituent, being dependent on the nature of the adjacent reaction center, on the particular reaction, and on the reaction conditions (*e.g.*, solvent). This seems to be the main reason why equations of the Hammett type, which have been very successful in correlating rate and equilibrium data for reactions of *meta*- and *para*-substituted benzene derivatives, do not generally apply for similar reactions of *ortho*-substituted compounds.[6,7]

Before the magnitude of the various proximity effects can be assessed quantitatively, it is necessary to know whether the polar effects and resonance effects are constant from system to system, and, if not, by how much they vary.

Previous studies[8] have shown that the unimolecular vapor phase pyrolysis of *meta*- and *para*-substituted isopropyl benzoates to propene and the corresponding benzoic acids is an ideal series in which to study polar effects, as the relative rate data correlate accurately with the Taft polar equation log $k/k_0 = \rho\sigma^0$.[9,4c] All solvent effects are precluded, and proximity effects are reduced to small secondary steric effects as the eliminations are intramolecular,[1] so that σ^0-values for the *ortho* substituents, obtained by substitution in the above equation, should give a good quantitative measure of their polar effects.

Experimental

Materials.—The *ortho*-substituted isopropyl benzoates were prepared and purified by the same methods as were used for the corresponding *meta* and *para* compounds.[8] Th physical properties and analytical data are given in Table I.

Method of Pyrolysis.—The absolute rates of pyrolysis were measured using the apparatus and methods described in full detail previously.[8,10,11] Each compound was pyrolyzed several

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(1) Part X: G. G. Smith and D. F. Brown, *Can. J. Chem.*, **42**, 294 (1964).

(2) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, and at the I.U.P.A.C. Conference, London, July, 1963 (paper A1-125).

(3) (a) Postdoctoral Research Associate, 1961–1962; (b) to whom inquiries should be addressed.

(4) (a) Taft's terminology is used. *Cf.* R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13. (b) It should be noted that in this treatment, which focuses attention on the Ar–Y bond rather than the X–Ar bond, it is more correct to refer to the effects of the *meta*- and *para*-substituted phenyl groups as a whole. (c) See R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960), section C (2).

(5) Proximity effects may include primary steric effects between the *ortho* substituent and approaching or leaving species, and secondary steric effects such as steric inhibition of resonance, steric interference with internal rotations, and hydrogen bonding.

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1963, Chapter VII.

(7) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(8) G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963).

(9) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(10) G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32**, 703 (1961).

(11) G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, **83**, 3647 (1961).

TABLE I

PHYSICAL CONSTANTS AND RATES OF PYROLYSIS OF *ortho*-SUBSTITUTED ISOPROPYL BENZOATES

Substituent	Yield, %	B.p., °C., (mm.)	n^{20}D	Formula	Calcd., % C	Calcd., % H	Calcd., % N or Hal	Found, %[a] C	Found, %[a] H	Found, %[a] N or Hal	10^3k sec.$^{-1}$
o-Me	38	129–133 (13)	1.5097	$C_{11}H_{14}O_3$	68.02	7.27	...	68.29	7.26	...	0.83
o-Me	43	67–68 (0.5)	1.4978	$C_{11}H_{14}O_2$	74.13	7.92	...	74.00	7.89	...	1.10[b]
H[c]	...	...	...	...	...	...	...	...	...	...	1.24
o-F	65	113–113.5 (18)	1.4811	$C_{10}H_{11}FO_2$	65.92	6.08	10.42[d]	65.93	6.00	10.28[d]	1.4
o-Cl	17	132–134 (22)[e]	1.5103[e]	...	...	...	...	...	...	...	1.56[b]
2,3-C_4H_4[f]	23	110–112 (0.9)	1.5765	$C_{14}H_{14}O_2$	78.48	6.59	...	78.45	6.75	...	1.69
o-NO_2	36	106–108 (0.5)	1.5129	$C_{10}H_{11}NO_4$	57.42	5.30	6.69	57.54	5.31	6.87	2.50[b]

[a] Analyses were by A. Bernhardt, Mülheim (Ruhr), Germany. [b] Some secondary decomposition was evident in these cases; values of *k* were obtained from plots of d*E*/d*t* against *E* as explained previously [G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963)]. [c] Physical constants recorded by Smith and Jones.[b] [d] % F. [e] Lit. b.p. 118° (12 mm.), n^{25}D 1.5085° [T. D. Dorris and F. J. Sowa, *J. Am. Chem. Soc.*, **60**, 358 (1938)]. [f] α-Naphthyl.

TABLE II

POLAR $\sigma_o{}^0$-VALUES CALCULATED FOR VARIOUS REACTIONS AND EQUILIBRIA[a]

Substituent	A	B	C	D	E	F
OMe	−0.53	−0.39	−0.67		−0.30	
OEt		−0.35				
Me	−0.16	−0.17	−0.14		−0.02	
H	0.00	0.00	0.00	0.00	0.00	0.00
2,3-C_4H_4	0.41					
F	0.16	0.24	0.23			
Cl	0.31	0.20	0.37	0.53	0.34	0.12
Br		0.21	0.41			0.29
I		0.21	0.43			
NO_2	0.94	0.80	0.97	0.67	0.66	

[a] A: Pyrolysis of isopropyl benzoates (this work). B: Taft's σ^*-values.[13] C: Ion-pair formation between benzoic acids and 1,3-biphenylguanidine, in benzene [M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, **60**, 569 (1958)], using ρ = 2.24 Taft.[4c] D: Ionization of phenylacetic acids in water [J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938)], using ρ = 0.46 Taft.[4c] E: Ionization of β-phenylpropionic acids in water (Dippy and Page) using ρ = 0.24 Taft.[4c] F: Ionization of $ArPO_2OH^-$ in water [H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953); **76**, 1548 (1954)] using ρ = 1.19 Taft.[4c]

times and the mean values of the first-order rate constants are given in Table I. Average deviations from the mean were within ±1% with the exception of isopropyl *o*-fluorobenzoate (±2.3%). The reaction temperature was 337.4–0.2°.

Discussion

The rate data (Table I) were used to calculate values of σ^0 for *ortho* substituents ($\sigma_o{}^0$) by substitution in the equation $\log k/k_o = \rho\sigma^0$, using the ρ-value found previously.[8] These values are listed in column A of Table II.

Taft has attempted to draw up a table of polar substituent constants using an alternate approach. Following Ingold,[12] Taft assumed that the steric (proximity) effects in acidic and basic hydrolyses of any given benzoate ester were the same. To this he added the assumption that the resonance effects were correspondingly similar and that a certain modified Hammett equation applied. From the rate data available in the literature he was able to calculate "σ^*"-values for various substituents.[13] These are referred to as σ^0 rather than σ^* when H is the standard substituent for which σ by definition is zero.[4c,9]

Table II lists these Taft values (column B) together with some other $\sigma_o{}^0$-values which we have calculated from literature data for other series of equilibria which are considered to be free from resonance complications. The $\sigma_o{}^0$-values were calculated in the usual way by substitution in the equation $K/K_0 = \rho\sigma^0$ using the appropriate polar ρ-values.[4c] The $\sigma_o{}^0$-values from the pyrolysis data (column A) agree reasonably well with those from the other reactions. Reactions B, D, E and F were studied in aqueous or mixed aqueous solvents so that the calculated $\sigma_o{}^0$-value may be complicated by solvent effects.[4c] Also in the acid ionization series C, D, E and F there may be hydrogen bonding.[14] It is of great significance that the Taft values agree fairly well with the others as this seems to confirm the validity of his two main assumptions. However, because of the complications mentioned above, we believe that the $\sigma_o{}^0$-values from the pyrolysis data in column A give the most accurate measure of the polar effects of *ortho* substituents.

The work of Roberts[15] and Dewar[16,17] suggests that the direct field contribution to the polar effect is the most important, at least for substituents which are more than one or two bonds away from the reaction center. Although there is some difference of opinion as to the best forms of equations to use,[16] simple theory predicts that the interaction is proportional to $1/r^n$, where r is the distance between the reaction center and the substituent.[18] It is clear, therefore, that a given substituent would be expected to show a somewhat wider range of polar effect in the *ortho* position than in the *meta* or *para* position. Unfortunately it is not possible at present to predict how much this would

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(12) C. K. Ingold, *J. Chem. Soc.*, 1032 (1930).

(13) Full details are given in ref. 4a, a list of values being given on p. 619.

(14) C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 106 (1961).

(15) (a) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953); (b) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(16) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539 (1962).

(17) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3548 (1962).

(18) The magnitude of the interaction may also be dependent on their mutual orientations: J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. H. Kirkwood, *ibid.*, **6**, 513 (1938).

affect σ_o^0-values, but vapor phase studies in other systems may allow a decision to be reached.

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Pyrolysis Studies. XII.[1] Steric Inhibition of Resonance in the Vapor Phase

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A careful determination of the absolute reaction rate constants for the vapor phase thermal decomposition of 1-(4′-methoxyphenyl)ethyl acetate and its 3′-methyl and 3′,5′-dimethyl derivatives provides convincing evidence that π-orbital overlap of the methoxy substituent with the π-electrons of the ring is markedly reduced by steric hindrance of methyl groups *ortho* to the methoxy substituent. Therefore, steric inhibition of resonance is a property of the molecule and does not require solvation of the substituents.

In order to have maximum delocalization of electrons between a substituent on the aromatic nucleus and the ring, the two must be coplanar. In this conformation the π-orbitals are parallel. As groups are caused to assume other conformations, the overlap decreases, thus reducing delocalization or resonance. Where this decrease in resonance is caused by steric factors, the phenomenon is generally attributed to inhibition of resonance or secondary steric effects. There are many studies where steric inhibition of resonance (S.I.R.) has been proposed to explain the reduction in chemical reactivity, ultraviolet light absorption, changes in dipole moment, etc. These studies have been essentially carried out in the condensed phase, and the question may logically be raised: what, if anything, is the role of the solvent? In other words, is it necessary to have solvation of substituent groups, *e.g.*, NO_2, OMe, or $(CH_3)_2N$, before an *ortho* methyl or halogen substituent can effectively force them out of coplanarity with the ring? By studying this phenomen in the vapor state it should be possible to establish if steric inhibition of resonance can occur in a solvent-free system and therefore, if it is a property of the molecule or restricted to condition of solvation.

For this study it was necessary to study a reaction that is markedly influenced by the resonance contribution of a substituent and a substituent that makes its maximum contribution when it is coplanar with the ring.

From extensive studies, it is known that the thermal elimination of acetic acid from 1-arylethyl acetates is markedly influenced by electron delocalization from a substituent is indicated by the fact that the kinetics of this first-order, unimolecular, homogeneous pyrolytic elimination cannot be accurately predicted by the standard Hammett equation but can be when σ^+-substituent constants are used.[3] This has been interpreted to mean that there is appreciably more resonance delocalization in the transition state than in the ground state in contrast to a rather minor difference in reactions that follow a simple $\rho\sigma$-correlation.[4] The methoxy substituent is one of the substituents where σ- and σ^+-values are markedly different ($\sigma^+_{p\text{-MeO}} = -0.778$, $\sigma_{p\text{-MeO}} = -0.268$) and furthermore, since the methoxy substituent is nonlinear, it can be forced into a nonplanar conformation causing the π-orbitals to become out of parallel with those of the benzene ring.

A study of the kinetics of the vapor phase pyrolysis of 1-(4′-methoxyphenyl)ethyl acetate and its 3′- and 3′,5′-dimethyl derivations provides a suitable way to evaluate this phenomenon in a solvent-free system.

Results

Five 1-arylethyl acetates [1-phenylethyl acetate (I), 1-(4′-methoxyphenyl)ethyl acetate (II), 1-(3′-methyl-4′-methoxyphenyl)ethyl acetate (III), 1-(3′,5′-dimethyl-4′-methoxyphenyl)ethyl acetate (IV), and 1-(3′,5′-dimethylphenyl)ethyl acetate (V)] have been synthesized and pyrolyzed to acetic acid and a substituted styrene.

Each ester was pyrolyzed in a carefully aged reactor (homogeneous reaction conditions) free from heterogeneous radical reactions. The reaction proceeded by a first-order rate and was shown to be a unimolecular. First-order plots to greater than 85% of reaction were obtained by plotting the log ΔP *vs.* time according to the Guggenheim method.[5] All studies were made under identical conditions, in triplicate, with the exception of I, whose pyrolysis rate at 343.3° was calculated using data obtained from an Arrhenius plot.[3] Although consistent results are obtainable when the experiments are carried out over several periods of time, to ensure as much consistency as possible, all compounds were studied during one interval to ensure complete uniformity of reaction conditions. The pyrolysis of II served as the standard to check reaction conditions. Its rate has

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[1] Part XI: D. A. K. Jones and G. G. Smith, *J. Org. Chem.*, **29**, 3531 (1964).

[2] Taken from a dissertation of D. V. White presented to the Graduate School Faculty of Utah State University in partial fulfillment of the requirements for the M.S. degree, June, 1964. This work was presented at the Northwest Regional Meeting of the American Chemical Society, Spokane, Wash., June 16, 1964.

[3] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Am. Chem. Soc.*, **84**, 4817 (1962).

[4] (a) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958); (b) P. D. Bartlett and C. Ruchardt, *ibid.*, **82**, 1756 (1960); (c) A. G. Harrison, P. Kebarle, and F. P. Lossing, *ibid.*, **83**, 777 (1961).

[5] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).