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).

TABLE I

KINETIC DATA FOR THE PYROLYSIS OF 1-ARYLETHYL ACETATES

Compd.	Run	Temp., °C.	10^3k, sec.$^{-1}$	Av. 10^3k	Std. dev.	Calcd.[a] 10^3k, sec.$^{-1}$
I[b]		343.3	1.88			
II[c]	95	343.5	5.78			
	96	343.4	5.66	5.69	0.08	6.15
	97	343.3	5.62			
III	98	343.2	6.67			
	99	343.1	6.71	6.67	0.08	6.79
	100	343.2	6.33			
IV	101	343.2	5.08			
	102	343.4	4.70	4.89	0.19	7.50
	103	343.4	4.88			
V	104	343.3	2.76			
	105	343.4	2.46	2.57	0.16	2.30
	106					

[a] Value calculated from Hammett equation using σ^+-constants. [b] This value was obtained from ref. 3. [c] The value obtained in ref. 3, at 343.5°, was 5.78×10^{-3} sec.$^{-1}$.

TABLE III

ULTRAVIOLET SPECTRA OF 1-ARYLETHYL ACETATES

Compd.	λ_{max}, mμ	ϵ_{max}
II	273	4.6×10^3
III	274	4.05×10^3
IV	266	6.9×10^2

TABLE IV

τ-VALUE FOR THE METHOXY PEAK IN THE N.M.R. SPECTRA

Compd.	τ-value
II	6.39
III	6.37
IV	6.45

been determined several times by other workers.[3] The results of these pyrolyses are shown in Table I.

Experimental

Ester Preparation.—The esters were prepared by standard procedures. The yields, physical constants, and elemental analyses obtained are reported in Table II.

Method of Pyrolyses.—The pyrolyses of the acetate esters were carried out in a stainless steel static reactor (200 ml.) whose design and operation have been described.[6] The kinetics were monitored by measuring the change in pressure with time automatically with a strip chart recorder and a pressure transducer. The temperature was maintained to within 0.02° with a large glass wool lagged aluminum thermostatic block electrically heated. The reactor surface was deactivated with 3-butenoic acid, and by pyrolysing esters many times before esters II–IV were studied. A standard was used to ensure that accurate reproducible results were obtainable. The standard used was 1-(4'-methoxyphenyl)ethyl acetate which has a standard value of 5.78×10^{-3} sec.$^{-1}$ at 343.5°.[3] The average experimental value obtained was 5.69×10^{-3} sec.$^{-1}$ at 343.25 ± 0.15°. When the reactor was standardized, all of the substituted ethyl acetate esters were run in triplicate, at a constant temperature of 343.25 ± 0.15°, and without stopping until the pyrolysis of all the compounds were complete. Precautions were taken to exclude air from the reactor since air causes the reactor to be active. Table I lists the data obtained from the pyrolyses.

The pyrolysis data obtained were plotted using the Guggenheim method.[5] This method eliminates errors due to an inaccurate P_∞. By plotting log ΔP *vs.* time, a straight line was obtained over 85% completion of the reaction. The time interval for Δ was taken in the order of two to three half-lives for best result.

TABLE II

ARYLETHYL ACETATES AND SYNTHETIC INTERMEDIATES

Ester	Yield, %	M.p.[a] or b.p., °C. (mm.)	$n^{20}D$	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]
I	41.0	64–64.5 (0.2)[c]	1.5028[c]				
II	45.0	77–82 (0.62)	1.5040	69.21	69.27	7.74	7.66
III	49.8	75–78 (0.35)	1.5004	70.24	70.11	8.16	8.10
IV	54.3	67–67.5 (0.13)	1.4971	74.97	75.01	8.39	8.25
4-Methoxy-3-methylacetophenone[d]	21.5	24.5–25.0[e]					
3,5-Dimethyl-4-methoxyacetophenone[f]	77.6	39.5–40.5[g]					
3,5-Dimethylphenylmethylcarbinol[h]	77.3	48–56 (0.2)[i]	1.5293[i]				

[a] Melting points were determined by a capillary method. [b] Analyses were by A. Bernhardt, Mikroanalytisches Laboratorium in Max-Plank Institute, Mülheim (Ruhr), Germany. [c] Lit.[3] b.p. 153–154° (27 mm.) and $n^{25}D$ 1.5039. [d] 4-Methoxy-3-methylacetophenone was prepared by Friedel–Crafts acetylation on *o*-methoxytoluene. [e] C. R. Noller and R. Adams [*J. Am. Chem. Soc.*, **46,** 1889 (1924)] reported m.p. 26–26.5°. [f] 3,5-Dimethyl-4-methoxyacetophenone was prepared by the method of F. Benington, R. D. Morin, L. C. Clark, and R. P. Fox, *J. Org. Chem.*, **23,** 1979 (1958). [g] Ref. *f;* however, after three recrystallizations, substituted acetophenone melted constantly at 39.5–40.5°; an infrared spectrum showed no OH present; hence, the compound was considered pure. [h] The carbinol was prepared by reducing the 3,5-dimethylacetophenone with sodium borohydride. The acetophenone was prepared by treating 3,5-dimethylbenzoyl chloride with diethyl malonate by the method of A. K. Kiang, F. G. Mann, A. F. Prior, and A. Tophan, *J. Chem. Soc.*, 1323 (1956). [i] K. Matsui [*J. Soc. Chem. Ind. Japan*, **45,** 300 (1942); *Chem. Abstr.*, **44,** 9186*d* (1950)] reported b.p. 123–125° (9 mm.), $n^{20}D$ 1.5309.

Ultraviolet Spectra.—The ultraviolet spectra of compounds II, III, and IV were taken in 95% ethanol solutions on a Cary Model 15 recording spectrophotometer and are reported in Table III.

N.m.r. Spectra.—The n.m.r. spectra of compounds II–IV were taken on a Varian 60 n.m.r. spectrophotometer. The τ-values for the methoxy peak are reported in Table IV.

Discussion

Among the many factors which influence reaction rates and equilibria are polar substituent effects which are often referred to as direct field, inductive, and resonance effects. Besides these electronic effects, steric factors often play a prominent role. The influence of steric factors on the resonance contribution is called steric inhibition of resonance or secondary steric effects. Substituent constants may also depend on the medium.[7] Solvents may change the resonance of the substituent.

Most of the studies on S.I.R. have dealt with a nitro group attached to an aromatic ring. For maximum delocalization of electrons, the ring and the nitro group must be in a coplanar configuration.

Since a methoxy group on a benzene ring may also exhibit delocalization of electrons if the two are co-

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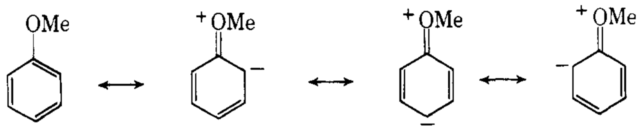
(6) G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28,** 3496 (1963).

(7) H. H. Jaffe, *Chem. Rev.*, **53,** 191 (1953).



planar, the vapor phase pyrolysis of esters containing a crowded methoxy substituent was chosen for the study of S.I.R. for the following reasons.

(1) The pyrolysis of 1-arylethyl acetates follows a homogeneous first-order reaction path, and the kinetics can be followed almost to completion of the reaction.[3] (2) The reaction is particularly susceptible to resonance contributions from the substituent, and its rate can be suitably correlated with a σ^+-modification of the Hammett equation. (3) The esters containing a *p*-methoxy substituent are comparatively less difficult to synthesize than nitro derivatives. (4) The reaction takes place in the vapor state where all solvent interactions are precluded.

The pyrolysis data on the five esters, shown in Table I, illustrates that the experimental values and the calculated values using the modified Hammett equation, $\log k = \log k_0 + \Sigma\sigma^+$ are within a few per cent with the exception of 1-(3′,5′-dimethylphenyl-4′-methoxy)ethyl acetate (IV).

According to this equation the calculated rate at 343.15°. is 7.50×10^{-3} sec.$^{-1}$. In marked contrast, however, the determined rate was only $4.89 \pm 0.19 \times 10^{-3}$ sec.$^{-1}$, a difference of almost 50%. The most likely explanation for this discrepancy is that the two methyl substituents *ortho* to the methoxy force the methoxy out of coplanarity with the ring, thus sterically inhibiting the resonance of the methoxy with the ring and hence with the partially formed carbonium ion proposed as the reaction intermediate.[3]

The introduction of one *m*-methyl substituent, compound III, apparently does not cause the *p*-methoxy substituent to be forced out of copolanarity because the observed rate of 6.67×10^{-3} is essentially the same as the calculated value 6.79×10^{-3}. A *m*-methyl group normally enhances the rate of this reaction.[3] Therefore, it was predicted that the rate constant for 1-(3′-methyl-4′-methoxyphenyl)ethyl acetate (III) would be greater than the rate of thermal decomposition of 1-(4′-methoxy phenyl)ethyl acetate (II), which in fact it was. This is rather convincing evidence that the methoxy substituent in compounds II and III are in much the same configuration, essentially coplanar with the ring.

Compound V was shown to pyrolyze at this temperature at a rate constant of $2.57 \pm 0.16 \times 10^{-3}$ sec.$^{-1}$, which is in reasonably good agreement with that calculated from the σ^+-modification of the Hammett equation (2.30×10^{-3} sec.$^{-1}$). This result was, of course, anticipated since no proximity effects are expected.

These results, obtained from experiments carried out in the vapor phase, support the theory that two methyl groups *ortho* to the *p*-methoxy substituent force the methoxy substituent out of coplanarity with the ring and cause the rate to drop in the thermal decomposition 1-(3′,5′-dimethyl-4′-methoxyphenyl)ethyl acetate (IV) from the value calculated for this compound using the Hammett equation. Since this is vapor phase reaction, the S.I.R. is not caused by the added crowding resulting from solvation of the methoxy substituent but rather by intramolecular interaction.

This interpretation is given additional support by a study of the ultraviolet spectra. From Table III it can be readily observed that with compounds where there are no blocking groups *ortho* to the methoxy (II) or only one blocking group (III) the $\lambda_{\max}$ and $\epsilon_{\max}$ are essentially the same. However, the second blocking group *ortho* to the methoxy (IV) causes a marked change in both $\lambda_{\max}$ and $\epsilon_{\max}$. From the calculated $\epsilon_{\max}$ it is possible to estimate the angle by which the methoxy group is forced out of coplanarity with the ring.[8]

$$\cos^2\theta = \epsilon/\epsilon_0$$

ϵ = hindered molecule

ϵ_0 = unhindered molecule

$$\cos^2\theta = \frac{6.9 \times 10^2}{4.6 \times 10^3} = 0.150$$

$$\theta = 67°$$

In the ultraviolet study it is not known if the solvent participates in the S.I.R. It is possible that the methoxy substituent is solvated by the 95% ethanol which would bring about additional steric requirements and enhance the angle.

A likely explanation for chemical shift downfield in the n.m.r. is that the methoxy is forced out of the plane of the aromatic ring by the two methyl groups *ortho* to it, thus causing less delocalization to occur between the benzene ring and the methoxy oxygen. If the methoxy group does maintain its copolanar position, however, the shift could be due to shielding of the methoxy methyl by the methyl group by a direct field interaction. We, however, favor the first explanation.

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(8) E. A. Braude, F. Sondheimer, and W. F. Forbes, *Nature*, **173**, 117 (1954).