19770-93-5; **17,** 19770-94-6; **18,** 19770-95-7; **19,** 19770-80-0; **21,** 19770-97-9; **22,** 19770-98-0; **23,** 19770-99-1; **24,** 19771-00-7; **24** (N-ethyl homolog), 19771-01-8; **25,** 19771-02-9.

**Acknowledgment.**—The authors are especially indebted to Dr. L. K. J. Tong for his interest in this work and for many helpful discussions. The assistance of Dr. T. H. Regan and Mr. R. L. Young (nmr), Mr. D. P. Maier (mass spectra), Miss T. J. Davis (ir), and Mr. D. F. Ketchum (microanalysis) is very much appreciated. Professor E. C. Taylor, of Princeton University, offered several helpful suggestions during the course of this work.

# Linear Free-Energy Relationship Involving *ortho* Substituents in Gas-Phase Reactions. XVII[1]

G. G. Smith, Kin K. Lum, J. A. Kirby, and J. Posposil

*Department of Chemistry, Utah State University, Logan, Utah 84321*

*Received November 12, 1968*

Rate constants, and in most cases Arrhenius parameters ($E_a$ and $\Delta S^{\ddagger}$ values), have been determined in the gas-phase pyrolysis of sixteen 1-arylethyl benzoates, sixteen 1-arylethyl acetates, and sixteen 1-arylethyl methyl carbonates. In each case the rates for the pyrolysis of the *meta* and *para* isomers were correlated in a Hammett plot using $\sigma^+$ constants. Furthermore, linear free-energy relationships involving *ortho* substituents were obtained in these gas-phase reactions when the log $(k/k_0)$ for the pyrolysis of 1-arylethyl methyl carbonate was plotted as a function of log $(k/k_0)$ for the pyrolysis of 1-arylethyl acetate or 1-arylethyl benzoate, each including *ortho* substituents. This demonstrates that proximity effects are minimal or nonexistent in these reactions. From this study the following $\sigma_o^+$ substituent constants have been obtained: *o*-MeO, −0.411; *o*-Me, −0.233; *o*-Br, +0.551; *o*-Cl, +0.452; *o*-NO$_2$, +0.749.

Equations of the Hammett type have been very successful in correlating equilibrium and rate data for reactions of *meta-* and *para*-substituted benzene derivatives. These equations, however, do not apply for similar reactions of *ortho*-substituted benzene derivatives in the condensed phase because of "proximity effects." Evaluation of *ortho*-substituent constants is extremely difficult since proximity effects for a given *ortho* substituent vary with the nature of the adjacent reaction center, the particular reaction, and especially with the reaction conditions (*e.g.*, solvent). It has been demonstrated, however, that proximity effects are not evident in a study of steric effects in the gas-phase pyrolysis of isopropyl benzoates.[2] From a vapor-phase kinetic study of the pyrolysis of *ortho*-substituted isopropyl benzoates, $\sigma_o^0$ constants have been obtained which correlate very well with Taft's calculated values[3] and with other data obtained from reactions thought to be free of the major contributing factor to the proximity effects.[4]

In the present investigation the objective was to evaluate $\sigma^+$ values for *ortho* substituents. Previous pyrolysis studies[5,6] have established that the unimolecular vapor-phase pyrolysis of *meta-* and *para*-substituted 1-arylethyl acetates and their methyl carbonates are correlated with the equation log $(k/k_0) = \rho\sigma^+$ using the standard $\sigma^+$ values. Assuming that proximity effects for *ortho* substituents in these gas-phase reactions are either negligible or equal, a linear free-energy relationship would result if log $(k/k_0)$ for *ortho*-substituted 1-arylethyl acetates were plotted as a function of log $(k/k_0)$ for *ortho*-substituted 1-arylethyl methyl carbonates. A preliminary report of the data on some of these compounds has been given.[6] In the present study, kinetic data of the gas-phase pyrolysis of sixteen *ortho-*, *meta-*, and *para*-substituted 1-arylethyl benzoates are presented along with some revised data from the gas-phase pyrolysis of the corresponding acetates and methyl carbonates. Linear free-energy relationships for *ortho* as well as *meta* and *para* substituents in these three reactions in the gas phase are reported. From these plots Hammett $\sigma^+$ constants are presented for the *ortho* substituents in reactions essentially free of proximity effects.

## Experimental Section

**Preparation of 1-Arylethyl Alcohols.**—All the alcohols, except 1-phenylethyl alcohol, which was purchased from Aldrich Chemical Co., were prepared by sodium borohydride reduction of the substituted acetophenone in 70% aqueous methanol.

**Preparation of 1-Arylethyl Benzoates.**—The benzoates were prepared by benzoylation of the appropriate alcohols with benzoyl chloride in chloroform in the presence of pyridine. The alcohol (0.1 mole) was mixed with a slight excess of pyridine (0.11 mole) in a three-necked flask fitted with a water condenser and a thermometer. The mixture was cooled externally by an ice-water bath and was stirred by a magnetic bar driven by a motor. Redistilled benzoyl chloride (0.11 mole) in chloroform (80 ml) was added a drop at a time through a dropping funnel, while the temperature of the mixture was kept below 15°. After all the benzoyl chloride was added, the mixture was stirred overnight at room temperature. The reaction mixture was diluted with ether and washed with dilute NH$_4$OH solution, water, dilute HCl solution, and then again with water. It was dried over magnesium sulfate prior to solvent removal. The desired benzoates were obtained either by fractional distillation at reduced pressure or by recrystallization from pentane. A shorter fractionation column was used in distilling high-boiling benzoates, *e.g.*, 1-*p*-methoxyphenylethyl benzoate [bp 140° (0.09 mm)], to avoid decomposition at the high temperature. Benzoates thus obtained were characterized by infrared and nmr spectra and refractive indices, and where practical the purity was checked by vpc or thin layer chromatography. The physical constants are listed in Table I.

---

[1] Paper number XVI: B. L. Yates and G. G. Smith, *J. Chem. Soc.*, 7242 (1965). Abstract, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 5100. Presented in part at the Second Conference on Linear Free Energy Relationships, University of California, Irving, March 27–29, 1968.

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

[3] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[4] (a) M. Charton, *J. Amer. Chem. Soc.*, **86**, 2033 (1964). (b) K. K. Lum and G. G. Smith, *Chem. Commun.*, 1208 (1968).

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

[6] G. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 434 (1965).

TABLE I
PHYSICAL CONSTANTS OF 1-ARYLETHYL BENZOATES

| Substituent[a] | Mp or bp, °C (mm) | $n^{20.5}D$ | Yield, % |
|---|---|---|---|
| H | 115–116 (0.19)[b] | 1.5568 | 66 |
| *p*-MeO | 140 (0.09) | 1.5575 | 64 |
| *o*-MeO | 34.0–34.4 | | 70 |
| *p*-Me | 117–118 (0.05) | 1.5516 | 66 |
| *o*-Me | 128–132 (0.5) | 1.5562 | 78 |
| *m*-Me | 126–127 (0.23) | 1.5524 | 84 |
| *p*-Br | 142–144 (0.07) | 1.5785 | 83 |
| *m*-Br | 139–141 (0.13) | 1.5793 | 50 |
| *p*-Cl | 152–156 (0.7) | 1.5642 | 72 |
| *o*-Cl | 131–132 (0.07) | 1.5669 | 70 |
| *m*-Cl | 141–143 (0.25) | 1.5651 | 76 |
| *p*-$NO_2$ | 94.8–95.5 | | 82 |
| *m*-$NO_2$ | 65.0–65.5 | | 64 |

[a] Satisfactory analytical data have been obtained for all compounds except those with H and *p*-Me substitutes. [b] A. Klages and P. Allendorff [*Ber.*, **31**, 1003 (1898)] reported bp 189° (21 mm).

**Preparation of 1-Arylethyl Acetates.**—The acetates were prepared by either of the following methods. (A) Equal molar quantities of the appropriate alcohol and pyridine were diluted with anhydrous ether (60 ml/0.1 mole of alcohol). The mixture was put into the same apparatus used in benzoylation and was cooled externally with an ice–water bath. A slight excess of acetyl chloride in ether (50 ml/0.1 mole of chloride) was added a drop at a time while the mixture was stirred magnetically. After the addition was complete, the reaction mixture was stirred overnight at room temperature. From then on the treatment was the same as in the preparation of benzoates. (B) Ketene, generated by pyrolyzing acetone over a glowing platinum wire, was bubbled directly into the appropriate alcohol either with or without a solvent (petroleum ether, bp 60–90°). The reaction was catalyzed by adding trace amounts of *p*-toluenesulfonic acid to the alcohol. The approximate duration of bubbling was 1.5–2 hr/0.1 mole of alcohol. The reaction mixture was diluted with ether and was washed with dilute $NH_4OH$ solution and water. It was then treated as in the preparation of benzoates. The acetates were characterized by their infrared and nmr spectra. Their physical constants are given in Table II.

**Preparation of 1-Arylethyl Methyl Carbonates.**—The carbonates were prepared by either of the following methods. (A) A large excess of methyl chloroformate was added to the alcohol and the mixture was refluxed for 10–12 hr. The reaction was initiated by adding a few drops of pyridine before refluxing the mixture. After the reaction was stopped and cooled to room temperature, it was treated in a manner similar to that employed in the preparation of acetates by ketenization. This method was used in the preparation of nitro- and halo-substituted 1-phenylethyl alcohols. (B) The methyl carbonates of unsubstituted or methyl- and methoxy-substituted 1-phenylethyl alcohols were prepared in a way similar to method A in the preparation of 1-arylethyl acetates. Yields were relatively low compared with those from the next method. (C) A large excess of methyl chloroformate was added a drop at a time to a solution of the alcohol in excess pyridine while it was stirred vigorously and cooled externally with an ice–water bath. A finger condenser with Dry Ice–alcohol as coolant was connected to the reaction flask. After the addition was completed, the mixture was refluxed for 1.5-2 hr. The reaction mixture separated as in method B. This method proved applicable to all the alcohols. The physical constants of 1-arylethyl methyl carbonates are given in Table III.

**Method of Pyrolysis.**—All esters were pyrolyzed in a stainless steel, constant-volume reactor possessing an automatic pressure monitoring system previously described.[7] The reactor, in this study, was used empty and also packed with enough stainless steel gauze to increase the reactor surface by a factor of ten to check for any surface reactions. None was observed in a seasoned reactor. The temperature of the reactor was measured to a precision of ±0.05°. About 200–300 μl of a liquid sample or equivalent amounts of a solid sample in purified chlorobenzene was used. Each ester was pyrolyzed at least three times at one temperature and repeated at several temperatures over a range of 30°. The temperatures used in the calculations for Arrhenius parameters are given in Table IV.

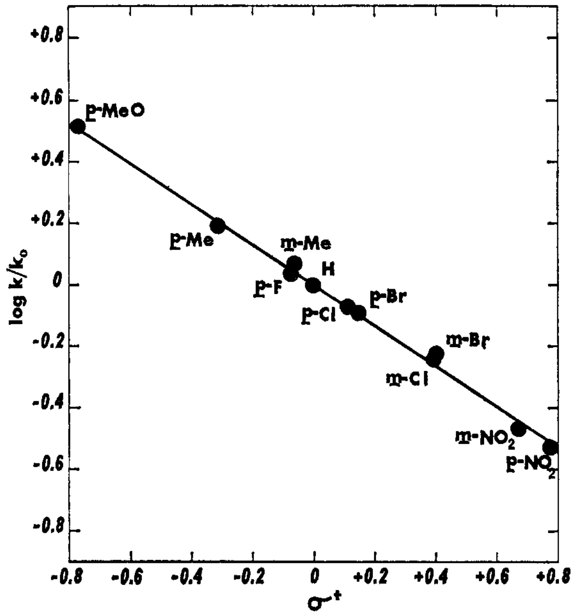


Figure 1.—Linear free-energy correlation, Hammett $\rho\sigma^+$ plot, for pyrolysis of 1-arylethyl acetates. $\rho = -0.663$, correlation coefficient = −0.998.

**Kinetics.**—Since the reaction was followed by measuring pressure change *vs.* time by means of a pressure transducer, the output, $E$, varied linearly with the absolute pressure, $P$. First-order rate constants were calculated directly from the slope of plots of log $(E_\infty - E_t)$ against time for four to six half-lives. Values of $E$ and the elapsed time, $t$, were obtained directly from the recorder chart, usually at 1-min intervals. The reproducibility of rate constants thus obtained was within ±2%, except for those of nitro-substituted esters, which were within ±10% due to secondary decomposition. The Arrhenius plots were linear (correlation coefficients >0.996) for all the esters pyrolyzed.

The Arrhenius parameters were calculated by combining the experimental rate equation with Eyring's rate expression assuming that $E_a = \Delta H^\ddagger$ and that the transmission coefficient is equal to one. Hence, $k_{expt} = (\mathbf{k}T/\mathbf{h})e^{\Delta S^\ddagger/R}e^{-E_a/RT}$. $E_a$ was evaluated from a plot of log $k_{expt}$ *vs.* $1/T$.

## Results

The pyrolyses of all the esters followed first-order kinetics up to six half-lives except for the nitro esters; in these, secondary decomposition occurred later in the reaction. For nitro esters the initial slope of the first-order plot (for 50–75% reaction) was used to estimate the rate constants. The relative rates of pyrolysis, energies, and entropies of activations are given in Table IV.

Figures 1–3 show the linear free-energy relationship in a Hammett $\sigma^+$ correlation in the pyrolysis of 1-arylethyl acetates, 1-arylethyl methyl carbonates, and 1-arylethyl benzoates, respectively. The linear correlation coefficient for these three plots are 0.998, 0.996, and 0.990, respectively. It has already been reported that the pyrolysis of acetates follows a $\sigma^+$ correlation.[5,8] The mechanism for ester pyrolysis has been studied extensively in the last 20 years and the available data has been reviewed recently.[9] There seems little doubt that charge separation occurs in the transition state in

---

(7) (a) G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32**, 703 (1961); (b) J. A. Kirby, Ph.D. Thesis, Utah State University, Logan, Utah, June 1967; (c) G. G. Smith and J. A. Kirby, *Analyst*, **94**, 242 (1969).

(8) A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965).

(9) K. K. Lum and G. G. Smith, *J. Chem. Kinetics*, in press.

TABLE II

PHYSICAL CONSTANTS OF 1-ARYLETHYL ACETATE

| Substituent | Mp or bp, °C (mm) | $n^{20.5}_D$ | Yield, % (method) | Lit. bp, °C (mm) | Lit. $n_D$ (°C) |
|---|---|---|---|---|---|
| H | 49 (0.04) | 1.4940 | Purchased | | |
| *o*-Me | 59.0–59.5 (0.08) | 1.4981 | 67 (A) | 80 (2)[a] | 1.4991 (25)[a] |
| *m*-Me | 80–80.5 (0.76) | 1.4943 | 84 (B)[b] | | |
| *p*-Br | 84–85 (0.16) | 1.5297 | 60 (B) | 108 (2)[a] | 1.5351 (25)[a] |
| *m*-Br | 75.0–75.5 (0.14) | 1.5294 | 79 (B) | 96 (1.1)[a] | 1.5295 (25)[a] |
| *o*-Cl | 70.0–70.5 (0.08) | 1.5100 | 66 (A) | 64–65 (0.05)[c] | 1.5011 (20)[c] |
| *m*-Cl | 67.5–68.0 (0.18) | 1.5091 | 82 (B) | 65–66 (0.5)[a] | 1.5116 (25)[a] |
| *p*-$NO_2$ | 55.5–56 | | 81 (B)[d] | | |
| *m*-$NO_2$ | 105–106 (0.16) | 1.5227 | 65 (A) | 131 (1.6)[a] | 1.5225 (25)[a] |

[a] Reference 5. [b] *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.91. Found: C, 74.38; H, 8.07. [c] Reference 6. [d] *Anal.* Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.69. Found: C, 57.41; H, 5.31; N, 6.62.

TABLE III

PHYSICAL CONSTANTS OF 1-ARYLETHYL METHYL CARBONATES

| Substituent | Bp, °C (mm) | $n^{20.5}_D$ | Yield, % (method) | Lit. bp, °C (mm) | Lit. $n^{20}_D$ |
|---|---|---|---|---|---|
| H | 64.0–64.5 (0.25) | 1.4912 | 64 (C) | 85 (0.4)[a] | 1.4930[a] |
| *p*-MeO | 99.5–100 (0.23) | 1.5011 | 59 (C) | 88 (0.2)[a] | 1.5021[a] |
| *o*-MeO | 87–88 (0.2) | 1.5012 | 25 (B) | 76–77 (0.1)[a] | 1.5078[a] |
| *p*-Me | 67.5–68.5 (0.08) | 1.4910 | 24 (B) | 62–64 (0.3)[a] | 1.4920[a] |
| *m*-Me | 74.5–76.0 (0.22) | 1.4914 | 70 (C)[b] | | |
| *m*-Br | 90–91 (0.19) | 1.5257 | 46 (C)[c] | | |
| *o*-Cl | 81.0–81.5 (0.17) | 1.5055 | 90 (A) | 74–75 (0.5)[a] | 1.5068[a] |
| *m*-Cl | 82–83 (0.24) | 1.5059 | 62 (C) | 80–82 (0.1)[a] | 1.5074[a] |
| *o*-$NO_2$ | 123 (0.4) | 1.5175 (22) | 81 (A)[d] | | |

[a] Reference 6. [b] *Anal.* Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.07; H, 7.16. [c] *Anal.* Calcd for $C_{10}H_{11}BrO_3$: C, 46.31; H, 4.28; Br, 30.81. Found: C, 46.09; H, 4.51; Br, 30.56. [d] *Anal.* Calcd for $C_{10}H_{11}NO_5$: C, 53.33; H, 4.92; N, 6.22. Found: C, 53.03; H, 5.19; N, 6.15.

TABLE IV

LOG OF THE RELATIVE RATES AND ENERGIES AND ENTROPIES OF ACTIVATION OF PYROLYSES OF 1-ARYLETHYL BENZOATES, ACETATES, AND METHYL CARBONATES

| | Acetates (374.1°) | | | | | Benzoates (374.1°) | | | | | Carbonates (346.0°) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substituent | Registry no. | Log ($k/k_0$) | $E_a$ | $\Delta S^{\ddagger}$ | *r* | Registry no. | Log ($k/k_0$) | $E_a$ | $\Delta S^{\ddagger}$ | *r* | Registry no. | Log ($k/k_0$) | $E_a$ | $\Delta S^{\ddagger}$ | *r* |
| H | 93-92-5 | 0.00 | 43.1 | −2.9 | 0.999 | 13358-49-1 | 0.00 | 42.6 | −2.5 | 0.998 | 1796-59-4 | 0.00 | 41.2 | −1.8 | 0.999 |
| *p*-MeO | 945-89-1 | 0.52 | 38.9 | −7.4 | 0.998 | 19771-09-6 | 0.77 | 43.9 | 3.4 | 0.999 | 1678-47-3 | 0.61 | 41.1 | 0.56 | 0.999 |
| *o*-MeO | 19759-39-8 | 0.26 | | | | 19771-03-0 | 0.38 | 46.6 | 5.7 | 0.998 | 2016-97-9 | 0.33 | 37.9 | −5.7 | 0.998 |
| *p*-Me | 19759-40-1 | 0.19 | 43.2 | −1.32 | | 19771-04-1 | 0.25 | 47.2 | 6.0 | 0.997 | 1796-67-4 | 0.23 | 41.0 | −1.1 | 0.999 |
| *o*-Me | 19759-21-8 | 0.17 | 44.4 | −0.3 | 0.999 | 19771-05-2 | 0.21 | | | | 1678-48-4 | 0.20 | 42.7 | 1.6 | 0.998 |
| *m*-Me | 19759-22-9 | 0.07 | 43.6 | −1.9 | 0.997 | 19771-06-3 | 0.08 | 44.1 | 0.65 | 0.999 | 19759-33-2 | 0.09 | 44.2 | 3.3 | 0.999 |
| *p*-F | 2928-12-3 | 0.035 | | | | | | | | | 1796-57-2 | 0.02 | | | |
| *p*-Br | 19759-23-0 | −0.09 | 46.2 | 1.2 | 0.999 | 19771-07-4 | −0.105 | 44.8 | 7.4 | 0.999 | 1796-69-6 | −0.14 | | | |
| *o*-Br | 1796-61-8 | −0.33 | | | | | | | | | 1796-70-9 | −0.40 | | | |
| *m*-Br | 6948-02-3 | −0.23 | 45.7 | −7.1 | 0.999 | 19771-10-9 | −0.25 | 44.7 | −0.10 | | 19759-34-3 | −0.25 | 44.0 | 1.3 | 0.999 |
| *p*-Cl | 19759-43-4 | −0.07 | | | | 19771-11-0 | −0.09 | | | | 1796-71-0 | −0.085 | | | |
| *o*-Cl | 1996-62-9 | −0.28 | 46.1 | 0.32 | 0.999 | 19771-12-1 | −0.30 | 43.1 | −2.8 | 0.996 | 1796-56-1 | −0.32 | 42.9 | −0.55 | 0.999 |
| *m*-Cl | 19759-26-3 | −0.24 | 44.9 | −1.3 | 0.999 | 19771-13-2 | −0.27 | 45.9 | 1.6 | 0.999 | 1796-72-1 | −0.26 | 44.0 | 1.3 | 0.999 |
| *p*-$NO_2$ | 19759-27-4 | −0.53 | 40.5 | −9.8 | 0.999 | 19771-14-3 | −0.50 | 43.5 | −3.5 | 0.999 | 19759-49-0 | −0.50 | 42.4 | −2.3 | 0.998 |
| *o*-$NO_2$ | | | | | | | | | | | 19759-37-6 | −0.51 | 41.2 | −4.2 | 0.999 |
| *m*-$NO_2$ | 19759-28-5 | −0.47 | 41.3 | −8.3 | 0.999 | 19771-15-4 | −0.48 | 44.7 | −1.6 | 0.999 | 1796-68-5 | −0.46 | 41.7 | −3.5 | 0.998 |

TABLE V

$\sigma_0^+$ SUBSTITUENT CONSTANTS FROM GAS-PHASE PYROLYSIS OF ESTERS

| | $\sigma_0^+$ | | | | | |
|---|---|---|---|---|---|---|
| Substituent | A[a] | B[b] | C[c] | Av | $\sigma_p^+$ | $\sigma_m^+$ |
| MeO | −0.382 | −0.46 | −0.435 | −0.426 | −0.78 | −0.047 |
| Me | −0.246 | −0.24 | −0.251 | −0.246 | −0.31 | −0.066 |
| Br | +0.508 | | +0.594 | +0.551 | +0.15 | +0.405 |
| Cl | +0.433 | +0.45 | +0.482 | +0.455 | +0.11 | +0.399 |
| $NO_2$ | | | +0.749 | +0.749 | +0.778 | +0.674 |

[a] (A) Pyrolysis of acetates, $\rho = -0.663$, correlation coefficient = −0.999. [b] (B) Pyrolysis of benzoates, $\rho = -0.795$, correlation coefficient = −0.990. [c] (C) Pyrolysis of carbonates, $\rho = -0.709$, correlation coefficient = −0.996.

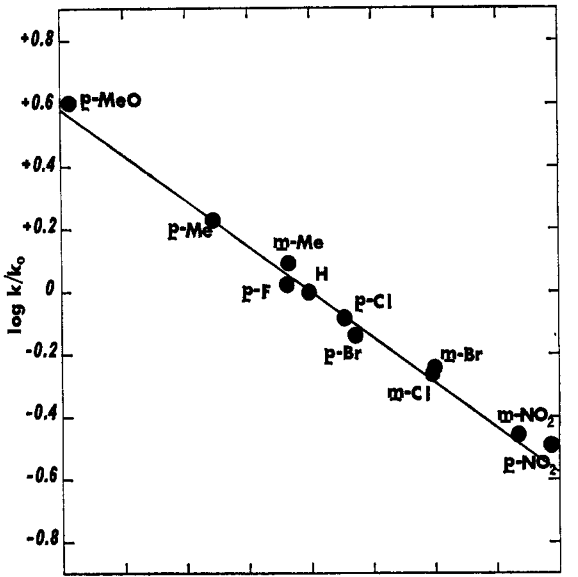


Figure 2.—Linear free-energy correlation, Hammett $\rho\sigma^+$ plot, for the pyrolysis of 1-arylethyl carbonates. $\rho = -0.709$, correlation coefficient $= -0.996$.

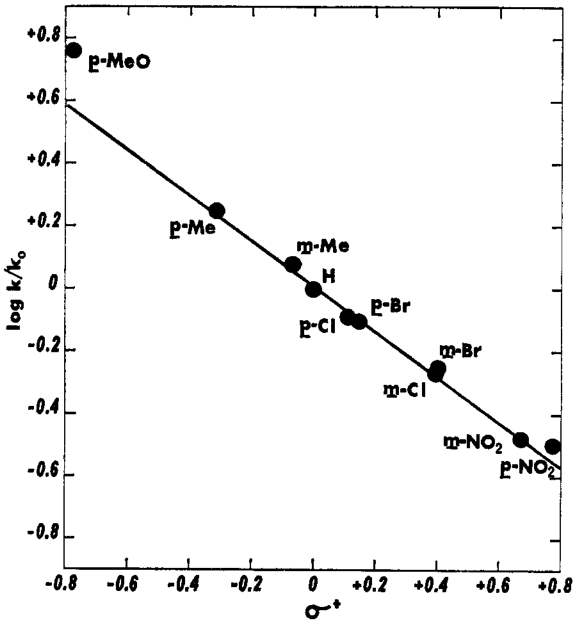


Figure 3.—Linear free-energy correlation, Hammett $\rho\sigma^+$ plot, for the pyrolysis of 1-arylethyl benzoates. $\rho = -0.795$, correlation coefficient $= =0.990$.

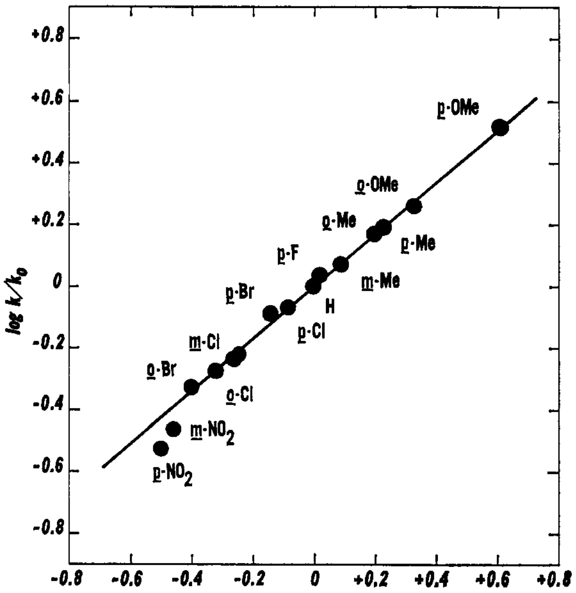


Figure 4.—Linear free-energy correlation, log $(k/k_0)$ for the pyrolysis of 1-arylethyl acetates *vs.* log $(k/k_0)$ for the pyrolysis of 1-arylethyl carbonates, including *ortho* substituents. $\rho = 0.833$, correlation coefficient $= 0.994$.

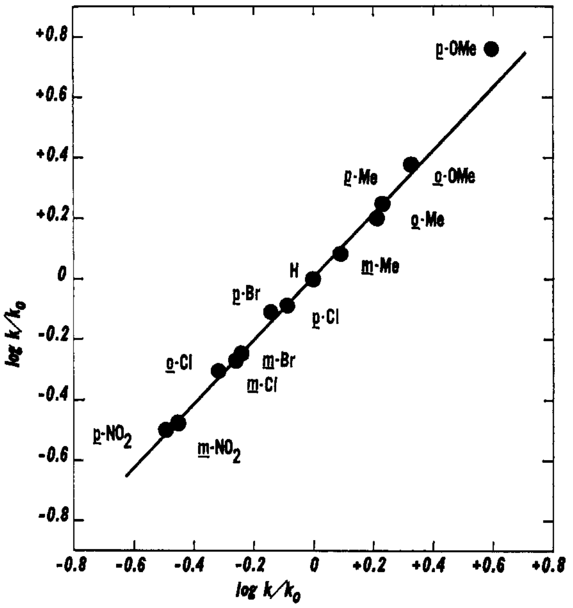


Figure 5.—Linear free-energy correlation, log $(k/k_0)$ for the pyrolysis of 1-arylethyl benzoates *vs.* log $(k/k_0)$ for the pyrolysis of 1-arylethyl carbonates, including *ortho* substituents. $\rho = 1.00$, correlation coefficient $= 0.996$.

this unimolecular gas-phase reaction, but a serious question has been raised about the formation of an ion-pair intermediate, which has been proposed for reactions of this type.[10]

Figures 4 and 5 are linear free-energy plots for the pyrolysis of acetates *vs.* carbonates and benzoates *vs.* carbonates with linear correlation coefficients of 0.994 and 0.996, respectively. The *ortho* substituents, as well as the *para* and *meta* substituents, are all correlated with a degree precision. These plots demonstrate that substituent effects in all three gas-phase pyrolysis reactions are directly comparable, and any proximity effects by the *ortho* substituents are constant or perhaps even negligible.

In such a situation, $\sigma^+$ constants could be determined for *ortho* substituents from the rate data of each individual reaction using the $\rho$ value for the equation log $(k/k_0 = \rho\sigma^+$ for the *para* and *meta* substituents). The $\sigma^+$ values for *ortho* substituents thus calculated are listed in Table V. The $\sigma_o{}^+$ values obtained from these different reactions agree reasonably well with each other. Included for comparison are $\sigma^+$ constants for the corresponding *meta* and *para* substituents.[11]

---

[10] (a) M. Hanack, H.-J. Schneider, and H. Schneider-Bernlohr, *Tetrahedron*, **23**, 2195 (1967); (b) J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. Chim.*, **82**, 1123 (1963); (c) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, **190**, 715 (1961).

[11] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

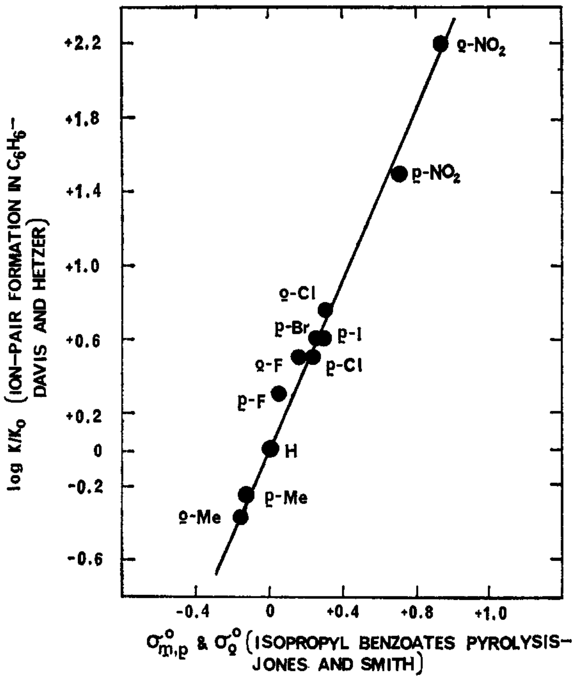


Figure 6.—Linear free-energy correlation, log $(k/k_0)$ for the ion-pair formation of benzoic acid with 1,3-diphenylguanidine in benzene (Davis and Hetzer[24]) against $\sigma_{m,p}{}^0$ and $\sigma_o{}^0$ (Jones and Smith[2]) determined from the pyrolysis of substituted isopropyl benzoates.

## Discussion

**Evidence for Proximity Effects.**—Relating structure to reactivity for rigid systems, where the substituent is located *meta* or *para* to the reactive site in benzene derivatives, has been remarkably well accomplished with linear free-energy relationships of the Hammett type.[12] Results in the less rigid aliphatic systems and in *ortho*-substituted benzene derivatives, where the problem is substantially more complex, have not been as fruitful. *Ortho* substituents are considered to involve a variety of effects in addition to the well-known inductive, field, and resonance effects generally acknowledge with *meta*- and *para*-substituted derivatives. These additional effects are frequently referred to as "proximity effects" and have been reported in measurements of half-wave potential in polarographic analysis;[13] ir,[14a] uv,[14b] and nmr[14c,d] spectra; diffraction patterns;[15a] and, of course, in many chemical reactions such as the ionization of acids, hydrolysis of esters and amides, and numerous addition reactions to carbonyl compounds.[15b]

**Explanations for Proximity Effects.**—In an attempt to explain these complicating proximity effects many hypotheses have been suggested such as primary[16] and secondary steric effects,[17] intramolecular hydrogen bonding,[18] field effects,[14d,19] and effects of substitution on solvation,[20] as well as several less understood concepts such as ponderal effects,[21] London forces,[22] and miserable effects.[23]

Brown, *et al.*,[16] have emphasized the importance of primary steric effects (compression between the reactant and the neighboring substituent in bimolecular reactions). In contrast and opposition to Brown, a long series of papers published by Chapman, Shorter, and coworkers deal with attempts to separate polar, resonance, and steric effects in systems involving *ortho* substituents. This group has stressed recently[20i] the importance of the solvent participation, including steric inhibition of solvation, in both the ground state and transition state, the polar facilitation of solvation, and the ring solvation effects. Solvation effects alter both the entropy and enthalpy of activation. Many other scientists have also spoken of the importance of steric interference with solvation of the transition state.[20] Hojo, *et al.*,[20d] have shown that the extent of solvent participation is dependent on the solvent as well as the reaction. For example, proximity effects are present but constant in various solvents in reactions such as the alkaline hydrolysis of *ortho*-substituted ethyl benzoates, whereas the solvent effect on the *ortho*-proximity effect (or *vice versa*) is marked and variable in the ionization of aryl acids.

There is little doubt that the medium plays a very important role in reactivity in the condensed phase and that this role is dependent on the *ortho* substituent. Studies of *ortho*-substituent effects in the condensed phase are, therefore, very formidable, particularly when polar solvents are involved.

Whatever the explanation for proximity effects, the problem of evaluating *ortho*-substituent constants is appreciably eased in studies of unimolecular reactions where the primary steric effects have been excluded and the reacting molecules are sufficiently separated

---

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 184–199.

(13) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Amer. Chem. Soc.*, **86**, 987 (1964); W. H. Hussey and A. J. Diefenderfer, *ibid.*, **89**, 5359 (1967).

(14) (a) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957); 3465 (1958); M. L. Josein and C. Castinel, *Bull. Soc. Chim. France*, 801 (1958); I. R. Solomon and R. Filler, *J. Amer. Chem. Soc.*, **85**, 3492 (1963); G. Elington, G. Ferguson, K. M. Islam, and J. S. Glasley, *J. Chem. Soc., B*, 1141 (1967); (b) R. C. Cookson, *ibid.*, 282 (1954); I. R. Solomon and R. Filler in ref 14a; E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; H. Foster, *J. Amer. Chem. Soc.*, **82**, 3780 (1960); (c) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **37**, 1009 (1962); F. C. Stehling, *Anal. Chem.*, **35**, 773 (1963); (d) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964); M. T. Tribble and J. G. Traynham, 2nd Conference on Linear Free Energy Relationships, University of California, Irvine, March 27–29, 1968.

(15) (a) G. Ferguson and J. M. Robertson, *Advan. Phys. Org. Chem.*, **1**, 203 (1963), and references contained therein; G. Eglington, G. Ferguson, K. M. Islam, and J. S. Glasley, in ref 14a; (b) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp 192–194, 593; N. B. Chapman, M. G. Rodgers, and J. Shorter, *J. Chem. Soc., B*, 164 (1968), and earlier papers.

(16) H. C. Brown and B. Kanner, *J. Amer. Chem. Soc.*, **88**, 986 (1966).

(17) (a) G. G. Smith and D. V. White *J. Org. Chem.*, **29**, 3533 (1964); (b) J. F. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, 1470 (1954); (c) N. B. Chapman, J. Shorter, and J. H. P. Utley, *ibid.*, 1824 (1962).

(18) R. Stewart and M. R. Granger, *Can. J. Chem.*, **39**, 2508 (1961).

(19) The importance of the field effect between the reaction site and the substituent is gaining recognition and is dependent on the distance and direction between the reacting site and the substituent: (a) P. R. Wells and W. Adcock, *Australian J. Chem.*, **18**, 1365 (1965); (b) M. J. S. Dewar and T. G. Squires, *J. Amer. Chem. Soc.*, **90**, 210 (1968); (c) H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5183, 5188 (1964); **87**, 2404 (1965); R. Golden and L. M. Stock, *ibid.*, **88**, 5928 (1966); (d) M. J. S. Dewar, *Chem. Commun.*, 547 (1968); (e) K. Bowden, *Can. J. Chem.*, **44**, 661 (1966).

(20) (a) J. G. Watkinson, W. Watson, and B. L. Yates, *J. Chem. Soc.*, 5437 (1963); (b) C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.*, **73**, 5836 (1951); (c) J. B. Hyne and R. Wills, *ibid.*, **85**, 3650 (1963); (d) M. Hojo, M. Utaka, and Z. Yoshida, *Tetrahedron Letters*, 19 (1966); *Yuki Gosei Kagaku Kyokai Shi*, **23**, 1034 (1965); *Chem. Abstr.*, **64**, 4916 (1966); (e) K. Yates and R. Stewart, *Can. J. Chem.* **37**, 664 (1959); (f) C. H. Rochester and B. Rossall, *J. Chem. Soc., B*, 743 (1967); (g) F. E. Condon, *J. Amer. Chem. Soc.*, **87**, 4494 (1965); (h) C. L. De Ligny, *Rec. Trav. Chim.*, **85**, 1114 (1966); (i) N. B. Chapman, M. G. Rogers, and J. Shorter, ref 15b; (j) S. Ehrenson, 2nd Conference on Linear Free Energy Relationships, University of California, Irvine, March 27–29, 1968.

(21) C. K. Ingold, *Quart. Rev.* (London), **11**, 1 (1957).

(22) J. D. Reinheimer and J. F. Bunnett, *J. Amer. Chem. Soc.*, **81**, 315 (1959).

(23) J. F. Bunnett and J. Y. Bassett, Jr., *J. Org. Chem.*, **27**, 2354 (1962).

from one another to avoid interaction with the solvent or other reacting molecules. This has been accomplished in gas-phase reactions. $\sigma_o{}^0$ substituent constants obtained in the gas-phase pyrolysis of isopropyl benzoates[2] correlate very well with other polar *ortho*-substituent constants obtained from Davis and Hetzer's work on the reaction of benzoic acid with 1,3-diphenylguanidine in benzene.[24] This correlation is shown in Figure 6.

As solvent molecules apparently play a major role in proximity effects, it is not surprising that *ortho*-substituent effects in one gas-phase reaction correlate with *ortho*-substituent effects in another, particularly if the reactions both utilize a similar pathway. Unimolecular gas phase reactions correlated by $\sigma^+$ substituent constants, therefore, afford an approach to establishing $\sigma^+$ substituent constants for *ortho* substituents free from solvent participation and, of course, primary steric effects. Apparently the secondary steric effects for such reactions are negligible or similar and cancel out. Earlier studies[17a] showed that two methyl groups, flanking a *p*-methoxy substituent, exhibited steric inhibition of resonance in the gas-phase pyrolysis of 1-arylethyl acetates.

The general applicability of these *ortho*-substituent constants will be shown as other similar systems are studied where different bonds are broken such as in the thermolysis of 1-arylethyl methyl xanthates, amine oxides, and $\beta$-hydroxy olefins ($CH_2{=}C(Ar)CH_2CH_2OH$, $ArCHOHCH_2CH{=}CH_2$).

Strong support has already been obtained for these *ortho*-substituent constants in an electron-impact study of substituted benzophenones. Mass spectral data for *ortho*-, *meta*-, and *para*-substituted benzophenones, log $(Z/Z_0)$ ($Z = [C_6H_5CO^+]/[XC_6H_4COC_6H_5{}^+]$, $Z_0 = [C_6H_5CO^+]/2X[C_6H_5COC_6H_5{}^+]$) were plotted *vs.* $\sigma^+$ constants for *meta* and *para* substituents, and for the *ortho* $\sigma^+$ constants reported from this study. The correlation coefficient in this study, which is reported elsewhere,[25] is 0.984.

**Acknowledgment.**—This work was supported in part by two National Science Foundation Grants, GP 2940 and GP 6006. Grateful acknowledgment is given for this support.

---

[24] M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, **60**, 569 (1958).

[25] K. K. Lum and G. G. Smith, *J. Org. Chem.*, **34**, 2095 (1969).

---

# Linear Free-Energy Relationship Involving *ortho* Substituents in Mass Spectrometry

KIN K. LUM AND GRANT GILL SMITH

*Department of Chemistry, Utah State University, Logan, Utah 84321*

*Received November 12, 1968*

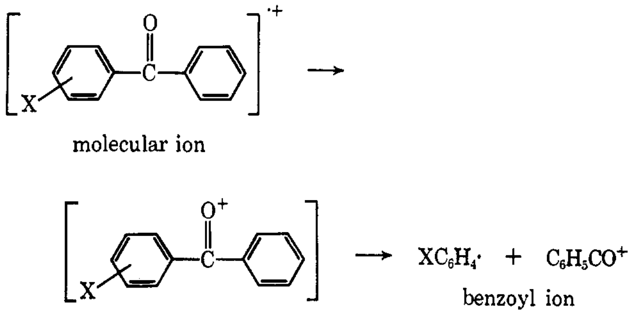
A linear free-energy relationship involving *ortho* substituents has been found between the benzoyl ion intensities in the mass spectra of substituted benzophenones and $\sigma^+$ substituent constants. This good correlation indicates that proximity effects are equivalent or negligible in gas-phase electron-impact reactions of benzophenones.

The evaluation of *ortho* $\sigma^0$ [1] and $\sigma^+$ constants[2] has been carried out in this laboratory by studying the gas-phase pyrolysis of esters which is a unimolecular, homogeneous reaction. The correlation of the $\sigma_o{}^0$ constants with the ion-pair formation of benzoic acid in benzene[3] is remarkable.[2] The present study was designed to test whether $\sigma_o{}^+$ constants previously obtained from kinetic data of pyrolysis of various esters[2] could be correlated in another gas-phase reaction which is unimolecular and homogeneous.

Mass spectrometry provides a system for this purpose. Lossing, *et al.*,[4] have shown that the ionization potentials of benzyl radicals, eq 1, can be correlated in a linear free-energy relationship involving $\sigma^+$ substituent

$$XC_6H_4CH_2I \xrightarrow{\Delta} XC_6H_4CH_2\cdot \xrightarrow{e^-} XC_6H_4CH_2{}^+ + 2e^- \qquad (1)$$

constants. They limited their study to *meta* and *para* substituents. McLafferty, *et al.*,[5] have investigated substituent effects in benzophenones and acetophenones by studying the ratio of ion intensities in mass spectrometry. They also limited their study to *meta* and *para* substituents. In the present investigation the method of McLafferty, *et al.*, of correlating relative ion intensities with $\sigma^+$ substituent constants was adopted. Mass spectral data for *ortho*-, *meta*-, and *para*-substituted benzophenones, log $(Z/Z_0)$, ($Z = [C_6H_5CO^+]/[XC_6H_4COC_6H_5{}^+]$, $Z_0 = [C_6H_5CO^+]/2[C_6H_5COC_6H_5{}^+]$) were plotted *vs.* $\sigma^+$ constants for *meta* and *para* substituents, and the recently reported *ortho* $\sigma^+$ constants were determined from pyrolysis of esters.[2]



## Experimental Section

**Preparation of Benzophenones.**—Substituted benzophenones commercially available were recrystallized two or three times from spectral grade methanol or fractionally redistilled at reduced pressure. *o*-Hydroxy, *m*-chloro-, and *m*- and *o*-bromobenzophenones were prepared by a Friedel–Craft reaction with the

---

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

[2] G. G. Smith, K. K. Lum, J. A. Kirby, and J. Pospisil, *ibid.*, **34**, 2090 (1969).

[3] M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, **60**, 569 (1958); G. G. Smith and K. K. Lum, *Chem. Commun.*, 1208 (1968).

[4] A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961).

[5] (a) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 529 (1966); (b) F. W. McLafferty, *Chem. Commun.*, 956 (1968), and references therein.