from the chair by a narrowly defined barrier form. These restrictions on the barrier form probably arise from the angle strain associated with the presence of the oxygen atoms as well as effects of the oxygen lone-pair electrons.

An assignment of the observed chemical shift values in I is made possible if the method discussed by Jackman[12] is followed. Jackman has presented arguments relating the long-range shielding effect to the diamagnetic anisotropy of the carbon–carbon single bond in the cyclohexane system. According to these arguments the 2,3 and 5,6 bonds (where the protons under discussion are at position 1) have the greatest effect on shielding differences between axial and equatorial protons and lead to a deshielding of the equatorial proton at 1 and a shielding of the axial proton. If these same arguments are applied to I where the 2,3 and 5,6 bonds are now oxygen–oxygen bonds, that is, if it is assumed that the electrons in these bonds are axially symmetrical, then the equatorial methyl group protons are more deshielded and absorb at 7.62 and the axial protons occur at 8.05. The center of the two absorptions occurs at 7.83 compared to 8.65 for tetramethyldioxane[7] where there is only one peroxy bond.

Experimental Section

The spectra were determined on a Varian A-60 high-resolution n.m.r. spectrometer equipped with a Varian V-6057 variable-temperature accessory. Temperatures were determined by measuring the peak separation in a methanol sample both before and after measurements on the acetone diperoxide sample at each temperature. Temperature could be controlled to $\pm 0.1°$ at the low temperatures and to $\pm 0.5°$ at the high temperatures. The samples of acetone diperoxide used were 4.2% solutions in deuteriochloroform sealed in Varian n.m.r. tubes. Chemical-shift values given are τ values relative to external tetramethylsilane.

The maximum errors in E_a and ν_0 were determined from the lines drawn on the log $1/\tau\delta\omega$ *vs.* $1/T$ plot using the maximum possible experimental errors at the temperature extremes. The maximum error in E_a was found to be ± 0.9 kcal. and the maximum range for ν_0 was calculated to be from 1.15×10^{10} to 2.05×10^{11} sec.$^{-1}$.

Preparation of 1,1,4,4-Tetramethyl-2,3,4,5-tetraoxacyclohexane. The Criegee[1] method was used. Tetramethylethylene was ozonized in pentane solution using a Welsbach Model T-23 ozonator. The white solid formed was filtered off and purified by gas chromatography using a 20-ft., 10% cyanosilicone column at 90°. The purified material had m.p. 133–134° (lit.[13] m.p. 132°). The infrared spectrum of this material was identical with the published spectrum for acetone diperoxide.[14]

Acknowledgment. The authors are grateful to Professor F. A. L. Anet, Dr. F. A. Bovey, and Dr. S. Meiboom for helpful discussions.

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[12] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, Section 7.2.

[13] R. Criegee and K. Metz, *Chem. Ber.*, **89**, 1714 (1956).

[14] R. Criegee and G. Paulig, *ibid.*, **88**, 712 (1955).

Substituent Effects in Unimolecular Ion Decompositions. II. A Linear Free Energy Relationship between Acyl Ion Intensities in the Mass Spectra of Substituted Acylbenzenes[1,2]

Maurice M. Bursey and F. W. McLafferty

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. *Received August 23, 1965*

Abstract: A linear relationship between the intensities of the fragments corresponding to the benzoyl ion and the acetyl ion in the mass spectra of substituted benzophenones and acetophenones has been found and explained on the basis of a kinetic argument. Much of the data can be correlated by the common relationhips of solution chemistry. Both the extent of this correlation and individual failures of relationship may be used to establish features of the structures of the ions involved. The new technique appears to have some generality for the prediction of spectra and the elucidation of mechanisms and structures of unimolecular ion decompositions.

Investigation of organic ion reactions in the gas phase, as observed in mass spectra, has been hampered by a scarcity of applicable techniques. The few available include the determination of elemental compositions by high-resolution spectroscopy,[3] the elucidation of decomposition pathways with metastable ions,[4] determination of structural detail by specific labeling with stable isotopes,[5] and assignment of structure on the agreement of appearance potentials with calculated internal energies of ions.[6]

In solution organic chemistry, correlation of data by linear free-energy relationships, particularly the Hammett equation, has been widely applied in the study of

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[1] F. W. McLafferty, *Anal. Chem.*, **31**, 477 (1959), should be considered paper I of this series.

[2] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[3] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 302.

[4] Reference 3, p 251.

[5] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectrometry," Vol. I, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter II.

[6] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p. 105.

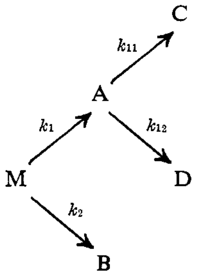
structures and mechanisms.[7,8] A preliminary communication reported that ion abundances in the mass spectra of substituted benzoyl compounds correlate with Hammett σ values,[1] and recent work has shown a similar relation for several fragment ions in the spectra of substituted acetophenones.[9] The ionization potentials of substituted benzyl radicals,[10] substituted acetophenones,[9] substituted benzenes,[11-13] and substituted pyridines[14] and the appearance potentials of substituted phenoxy ions[15] can be related by the σ^+ values of Brown.[16] In cases of extreme electron demand (the formation of substituted methyl ions from substituted methanes and the ionization of substituted benzenes) correlation with Taft's σ_I values has been observed.[17] The refinement and expansion of the earlier data for substituted acylbenzenes reported here suggests a broad applicability of substituent constants as a tool for the elucidation of organic ion decomposition mechanisms in the gas phase and the prediction of mass spectra.

Application of the Kinetic Approach to Mass Spectra. The statistical foundation of the kinetic approach to mass spectra is embodied in the "*quasi*-equilibrium" theory.[18] Mass spectral processes are considered as a set of competing consecutive unimolecular decompositions; the recorded spectrum corresponds to the product distribution of these processes.

A kinetic argument can be made to provide a basis for the applicability of free-energy relationships to ion abundances in mass spectra. For the decomposition of a molecular ion M, yielding among other products A, an ion formed only by a single process from the molecular ion, the rate of change in the concentration of A in the ion source is given by eq 1, where the

$$\frac{d[A]}{dt} = k_1[M] - \Sigma k_{1n}[A] - \Sigma k'_{inst}[A] \qquad (1)$$

second term on the right side includes the terms for all decomposition modes of A, and the third includes terms for real or apparent loss of A because of instrumental parameters.



If the steady-state approximation is applied to the concentrations of all the ions in the source, Z, the concentration of A, relative to the molecular ion, is described by eq 2. Provided that the recorded intensities are

$$\frac{[A]}{[M]} = \frac{k_1}{\Sigma k_{1n} + \Sigma k'_{inst}} = Z \qquad (2)$$

proportional to the concentrations of ions in the source, Z is the ratio of the rate of formation of A to the sum of its rates of removal. Mass spectra in which the common fragment ion A may be formed from different molecular ions can be related; for if A is formed with the same energy distribution from each molecular ion, the denominator of the term on the right is not dependent on the mode of formation of A. If this assumption is true, the magnitudes of Z in a series of spectra will parallel the different rates of formation of A from each molecular ion, and may therefore be related to a base rate constant for a standard compound, as in eq 3. If the effect of a substituent Y on the rate

$$\frac{Z}{Z_0} = \frac{\dfrac{[A]}{[M]}}{\dfrac{[A]_0}{[M_0]}} = \frac{k_1}{k_1^0} \qquad (3)$$

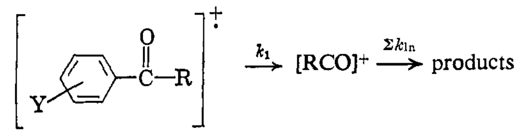
of formation of A from M is related to its effect on the rate of formation of some other A′ from some other M′ by eq 4, then this free-energy relationship must be reflected in the relative intensities Z and Z' as well, as in eq 5. The utility of this relationship in interpretation

$$\log \frac{k_1^Y}{k_1^0} = C \log \frac{k_1'^Y}{k_1'^0} \qquad (4)$$

$$\log \frac{Z}{Z_0} = C \log \frac{Z'}{Z_0'} \qquad (5)$$

of data occurs when C, the proportionality factor, is constant for a wide variation in Y; in this case, the substituent Y exerts a similar effect in the two series of reactions being compared, and the free-energy relationship is linear.

The formation of acyl ions from substituted acylbenzenes affords a good illustration of the case leading to eq 3.



In this example, if the acyl ion is formed from the molecular ion in a single process, cleavage of the phenylacyl C–C bond, and if the acyl ion is formed with the same energy distribution from every acylbenzene in the series, so that it decomposes in the same manner in every case, then the hypothetical case is reproduced.

A Free-Energy Relationship in Ion Intensities. Table I collects data for two series of aromatic ketones, substituted benzophenones and substituted acetophenones. For the substituted benzophenones, Z equals the ratio

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(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(8) For recent reviews see (a) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964); (b) S. Ehrenson, *ibid.*, **2**, 195 (1964).

(9) A. Buchs, G. P. Rossetti, and B. P. Susz, *Helv. Chim. Acta*, **47**, 1563 (1964).

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

(11) H. Baba, I. Omura, and K. Higasi, *Bull. Chem. Soc. Japan*, **29**, 521 (1956).

(12) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963).

(13) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

(14) M. R. Basila and D. J. Clancy, *ibid.*, **67**, 1551 (1963).

(15) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Am. Chem. Soc.*, 84, 4 (1962).

(16) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(17) R. W. Taft, R. H. Martin, and F. W. Lampe, *ibid.*, **87**, 2490 (1965).

(18) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

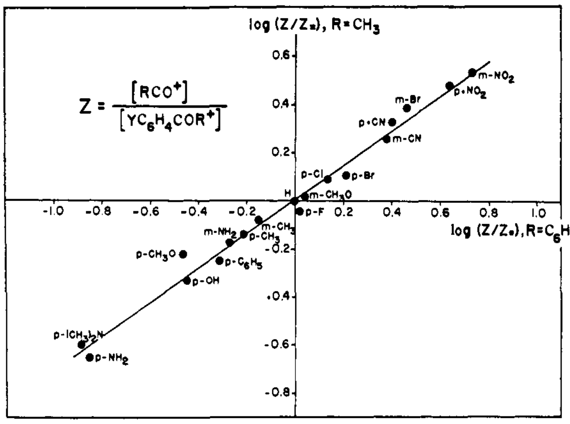

Figure 1. The linear free-energy relationship between the benzoyl ion intensity in substituted benzophenones and the acetyl ion intensity in substituted acetophenones. Linear correlation coefficient, r, = 0.992; standard deviation = 0.037 log unit.

of the intensity of the m/e 105 ion $(C_7H_5O)^+$ to that of the molecular ion; and for the acetophenones, Z is the ratio of the intensity of the m/e 43 ion $(C_2H_3O)^+$ to that of the molecular ion. A correlation of high precision exists between the two sets of data. This is illustrated in Figure 1 and is represented by eq 6.

$$\log \frac{Z}{Z_{0(R=CH_3)}} = 0.782 \log \frac{Z}{Z_{0(R=CH_3)}} + 0.007 \quad (6)$$

The utility of a correlation of such high precision in the quantitative prediction of mass spectra has been pointed out before.[1]

Table I

Substituent	Log Z/Z_0 for benzophenones	Log Z/Z_0 for acetophenones
p-NO_2[a]	0.64	0.48
m-NO_2[a]	0.72	0.54
p-CN	0.40	0.23
m-CN	0.38	0.26
m-CF_3	. . .	0.51
p-COOH	0.37	. . .
m-Br	0.45	0.39
m-COOH	0.43	. . .
m-Cl	0.31	. . .
m-F	0.22	. . .
p-Br	0.21	0.11
p-Cl	0.14	0.09
p-I	0.11	. . .
m-OCH_3	0.04	0.01
m-OH	. . .	−0.05
p-F	0.02	−0.04
H	0.00	0.00
p-C_6H_5	−0.31	−0.25
m-$(CH_3)_3C$	. . .	0.72
m-CH_3	−0.05	−0.08
p-CH_3	−0.21	−0.13
p-$(CH_3)_3C$	. . .	0.69
m-NH_2	−0.27	−0.17
p-OCH_3	−0.46	−0.22
p-OC_6H_5	. . .	−0.24
p-OH	−0.45	−0.33
p-NH_2	−0.85	−0.65
p-$(CH_3)_2N$	−0.88	−0.60

[a] A day-to-day variation between +0.40 and +0.68 for Z/Z_0 for p-nitrobenzophenone and between +0.46 and +0.80 for m-nitrobenzophenone has been observed. This phenomenon is not yet understood and is being explored.

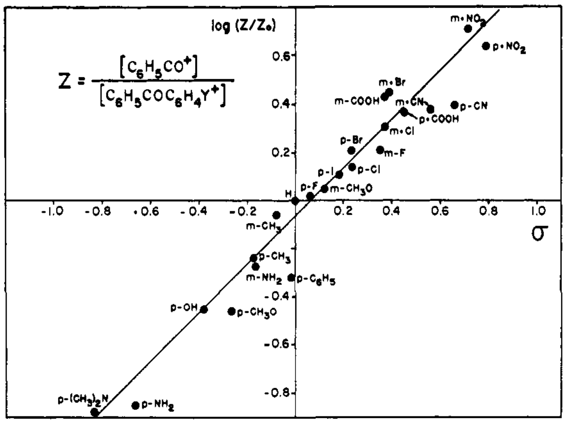

Figure 2. Correlation of the benzoyl ion intensity in the mass spectra of substituted benzophenones with Hammett σ constants. $\rho = 1.01$; linear correlation coefficient = 0.976; standard deviation = 0.094 log unit.

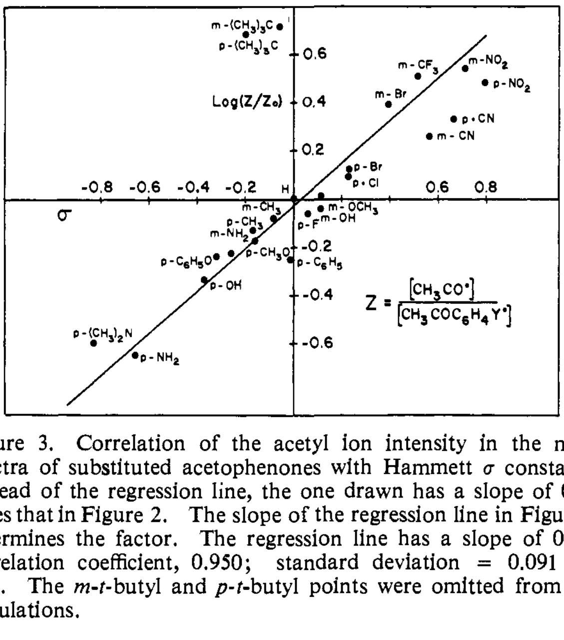

Figure 3. Correlation of the acetyl ion intensity in the mass spectra of substituted acetophenones with Hammett σ constants. Instead of the regression line, the one drawn has a slope of 0.78 times that in Figure 2. The slope of the regression line in Figure 1 determines the factor. The regression line has a slope of 0.73; correlation coefficient, 0.950; standard deviation = 0.091 log unit. The m-t-butyl and p-t-butyl points were omitted from the calculations.

Correlation with Solution Phenomena. Many of the arguments used to rationalize and to predict the course of organic reactions in solution have been applied to the study of unimolecular decompositions of ions in the gas phase.[19] The linear free-energy relationships for *meta* and *para* substituents are so general that it was advantageous to choose a standard reaction series to define $\log (K_Y/K_0)$ as a set of substituent constants. The earliest choice for such a set was the set of ionization equilibrium constants of substituted benzoic acids; these defined the σ values of the Hammett equation (7).

$$\log \frac{k}{k_0} = \rho\sigma \quad (7)$$

The present data are applicable to a quantitative extension of the parallelism noted previously, since the effect of ring substituents on the phenylacyl C–C bond is fairly adequately described by Hammett σ constants,[20] as Figures 2 and 3 indicate.

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(19) F. W. McLafferty, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 309.

(20) The values tabulated in ref 8a were used.

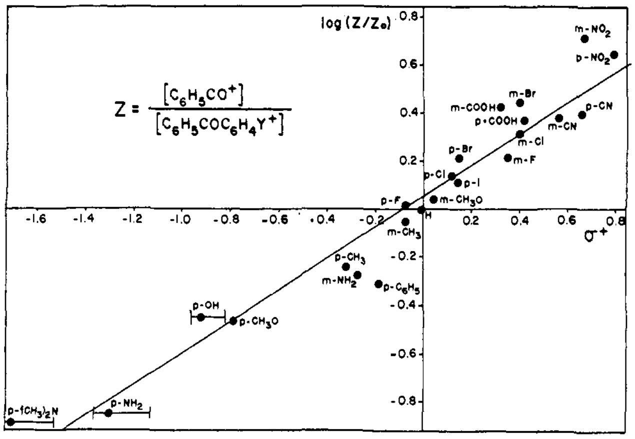

Figure 4. Correlation of the benzoyl ion intensity in the mass spectra of substituted benzophenones with σ^+ constants. ρ = 0.66; linear correlation coefficient = 0.963; standard deviation = 0.106 log unit.

Because of the observation that the ionization and appearance potentials of certain aromatic ions showed better correlation with σ^+ constants, the data for benzophenones were similarly graphed. Figure 4 represents the least-squares correlation. If one uses both the coefficient and the standard deviation from the line of regression as criteria, the fit of the present data with σ values is better than that with σ^+ values. This stands in contrast to the better correlation of ionization potential and appearance potential data with σ^+ values in previous work. However, the preference of one set of constants over the other is not based on an obvious improvement in the value of either criterion. A choice between the two sets of values is further complicated by the lack of well-defined σ^+ values for the amino, hydroxy, and dimethylamino substituents in the *para* position. Only approximate values for these substituents were suggested originally[16] because of the difficulty in studying the base reaction which defines σ^+ constants in these three cases. The variation of observed substituent constants in the auxiliary reactions used to approximate σ^+ values for these substituents is indicated in Figure 4 by the horizontal extensions of these points. Choice of the extreme value nearest the regression line for each of the three cases reduces the standard deviation to 0.093. This value is nearly the same as that for σ values, so that the criterion fails. The standard deviation for the acetophenone data is 0.091 in a plot *vs.* σ values and is 0.111 *vs.* σ^+. Variance in σ^+ values again allows a reduction of this value, but only to 0.103. This indicates once again a slight preference for correlation with σ values.

Finally, it should be noted that loss of a positive charge in the decomposition of a positive ion does not produce substituent effect capable of interpretation with σ^- values. Such an attempt produces a markedly curved line, and the best correlation remains the one discussed earlier.

The method of Taft and Lewis[21] appears to be the most useful general tool for the detection of deviations in substituent behavior, especially in cases like the present one, in which choice between σ values and σ^+ values is almost arbitrary. Application of their technique to the benzophenone data gives a result illustrated in Figure 5. Benzophenone and six *meta*-substituted benzophenones fit eq 8 nearly to within the

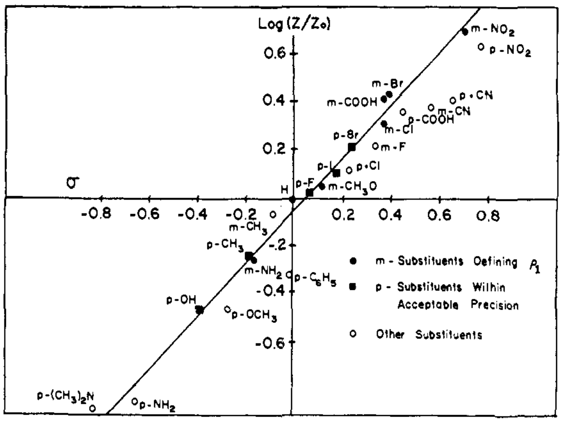

Figure 5. Correlation of the benzoyl ion intensity in the mass spectra of substituted benzophenones with Hammett σ constants according to the procedure of Taft and Lewis.[21] Substituents used to define ρ_I have a linear correlation coefficient of 0.989; standard deviation = 0.04 log unit.

$$\log \frac{Z}{Z_0} = 1.11\sigma - 0.045 \qquad (8)$$

precision suggested by Taft and Lewis, 0.03 log unit. Of the *meta*-substituted benzophenones, the *m*-cyano compound deviates seriously (by 0.19 log unit) from the expected value. Likewise, while only five *para* substituents fit eq 8 to within the suggested precision, extremely serious deviations are found only for the *p*-phenyl (0.25 unit), *p*-cyano (0.29 unit), and *p*-nitro (0.19 unit) substituents. In every case of a serious deviation, the observed value falls below the regression line. Such deviations are to be distinguished from those where the observed value falls above the regression line, as will be shown later.

Consider first the deviation of the phenyl substituent. The greatly increased resonance stabilization of the phenylacyl C–C bond can be a reflection of the change in the angle which the plane of the substituent phenyl ring makes with the plane of the substituted ring. The surprisingly small σ value (−0.01) of the phenyl substituent has been ascribed to this angle, which results from an energy barrier caused by steric interference of the orthohydrogens of the two rings.[22] The magnitude of the angle is itself a function of the electron demand of the reaction site, as has been concluded by the failure of the phenyl substituent to conform to the extended selectivity relationship. In solution chemistry a resonance effect which varies with the electron demand of the reaction, increasing markedly with increasing demand, has been observed. In the present case the charge is present in an unsolvated reactant ion; an approach to coplanarity in the reactant itself is favored by the lack of solvation. The charge decreases in the transition state, but the electronic demand is still great. In addition, any excess vibrational energy produced by electron impact would aid in overcoming the barrier to internal rotation between the rings. The magnitude of the substituent effect is comparable only to that in the extreme case in solution chemistry, bromination of the aromatic ring.[22]

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(21) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

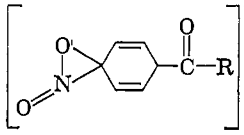
(22) (a) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1242 (1962); (b) H. C. Brown and L. M. Stock, *ibid.*, **84**, 3298 (1962).

Otherwise, in general, the resonance effects of substituents are approximately the same as those found in solution chemistry. The resonance effect parameters for substituents in the *meta* and *para* positions may be obtained by subtraction of the inductive contribution, σ_I,[23] from the observed substituent constant, and are designated σ_R values. The correlation of σ_R values for the available substituents in both *meta* and *para* positions is shown in Figure 6. The correlation is not so good as that observed for the σ_0 scale,[23] but six substituents and hydrogen still follow the mesomeric order of Ingold.[24] Thus the resonance effects of these substituents, which are all $-$R substituents, are approximately the same as those found in solution chemistry.

The two substituents which show the most serious deviations in Figures 5 and 6 are the +R substituents, nitro and cyano. The cause of their deviation is not necessarily due to an alteration of their usual electronic effect; it may very well be an alteration of the structures of the substituents. The loss of nitric oxide from aromatic nitro compounds is a well-known mass spectral process.[25a] This demands a rearrangement in the

$$C_6H_5NO_2^+ \longrightarrow C_6H_5O^+ + NO$$

molecular ion, in which the oxygen atom becomes attached to the same carbon atom as the nitrogen had been,[25,26] as in I. If part of the molecular ions from nitrobenzophenone have this structure, they should cause an appreciable change in the magnitude of the substituent effect.



I

Likewise the cyano substituents may show decreased reactivity because of an isomerization of some of the molecular ions. The spectra of benzonitriles show a

$$C_6H_5CN^+ \longrightarrow C_6H_4^+ + HCN$$

remarkable loss of HCN from the molecular ion; this reaction is not well understood, but again the formation of a certain amount of an isomer of the molecular ion as the intermediate for this competing reaction must almost certainly affect the substituent properties compared with that of the normal structure.

An explanation of the very large positive deviation for the *t*-butyl substituent in both the *meta* and *para* positions is required in a discussion of Figure 3. These deviations must be distinguished from the others discussed, which were all negative. The data are corrected for 5% of the total intensity of the *m*/*e* 43 ion caused by $C_3H_7^+$ in each case.

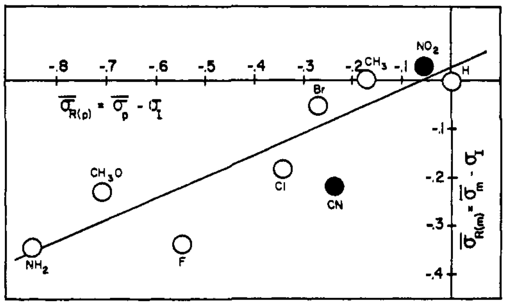
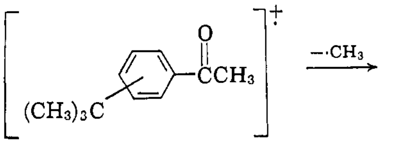
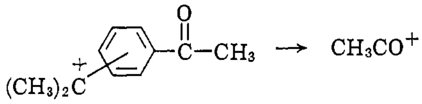


Figure 6. Relation of the resonance parameters for substituents in *meta* and *para* positions for the formation of benzoyl ions from benzophenone ions. The ρ_1 values are aliphatic ρ_I values.[23] Slope = 0.44; standard deviation = 0.06 log unit. Substituents represented by solid circles were omitted from calculations.

The original assumption was that the cleavage of the phenylacyl C–C bond represents the kinetic example; that is, the cleavage occurs entirely in the molecular ion, and no contribution to the intensity of the acyl ion results through its formation from another fragment ion. Ion III has 3.8 times the relative abundance of the molecular ion in the *meta*-substituted compound and 3.7 times in the *para*. Metastable peaks for both steps support formulation of this additional route of formation of acetyl ion. Interpolation of substituent effect data on the intensity of the (M $-$ 15) ion in the acetophenones suggests that ion III has 1.8 times the relative abundance of the molecular ion in the *meta*-substituted compound and 1.7 in the *para*. With the assumption that normal σ values for the *t*-butyl group govern the formation of acetyl directly from II, 17 and 15% of the intensity of the [CH_3CO^+] ion are formed from the molecular ions of the *t*-butyl groups, respectively. If one assumes further that the same ρ value applies to the decomposition of the intermediate ion III, and that no other ions contribute to the formation of the acetyl ion, a value of +0.39 may be calculated for this new dimethylcarbinyl substituent in either the *meta* or the *para* position. This value is positive, as expected, but apparently resonance effects contribute to bond strengthening so that the absolute value is lowered. The substituent effect of a formally charged resonating group has not been estimated from solution chemical data; no comparison with existing data is therefore possible.



II



III

Implications of the Degree of Correlation with σ Values. The fact that a correlation of fairly high precision exists at all implies first that the assumptions (formation of the acyl ion from the molecular ion in one step and formation of the acyl ion with similar energy distribution from all types of molecular ions) are justifiable; the intervention of other processes would cause deviations from the line of regression,

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(23) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VI.

(25) (a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, 4, 311 (1964); (b) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 180 (1965); (c) J. H. Beynon, personal communication, July 1965.

(26) M. M. Bursey and F. W. McLafferty, unpublished results.

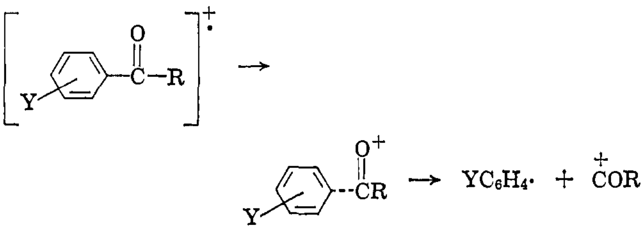
because of contributions from alternate pathways. Further, the existence of a precise correlation implies that with respect to the effect of the substituent the transition state for the gas phase reaction is similar to those for solution chemistry. Therefore, up to the transition state for the loss of the acyl ion, the geometry of the substituted aromatic ring remains intact; it has not been rearranged or ruptured.

Formation of species with excess energy is not often found in mass spectra, in spite of the great energy of the bombarding electrons. Such species, when they do occur, may be detected by tailing of the peak for the product ion,[27] and by broadening of the metastable for the transition.[24b] The present data allow an extension of this observation: not only is the ring intact, but the data suggest that contributions to this pathway from molecular ions in electronically excited states are small. Data for the *excited* state pK values of *meta*-substituted aromatic compounds, from ultraviolet absorption and fluorescence studies, do not show good correlation with Hammett σ constants or with variations of these.[28] The effects of *meta* substituents in the excited state generally are altered by pronounced enhancement of the resonance parameter; this suggests direct interaction of the reaction site with a *meta* substituent.[29]

However, the high precision found in this work for the correlation of *meta* substituent effects with Hammett σ values (Figure 5) and the absence of special resonance effects (which would have been clear in Figure 6) militate strongly against the intervention of excited states of the molecular ion in the formation of the acyl ion.

This observation complements the recent observation of appearance potentials of benzoyl ions and phenyl ions from several compounds, from which it was concluded that benzoyl ions are formed in the ground state, but phenyl ions are not;[30] it excludes the possibility of formation of these species from an electronically excited molecular ion. Since our data indicate that the substituted ring is not part of an electronically excited system, the whole process of acyl ion formation may now be described with certainty in terms of ground-state structures for all of the species involved.

The values of ρ found in other studies involving ionization potentials and appearance potentials have been negative in sign and extremely large in magnitude.[9,10-14,16] In contrast, the reaction constant for the decomposition of benzophenones is a small, positive value, 1.01 (Figure 2). In the molecular ion, the positive charge is distributed over the carbonyl group and the aromatic ring; in the product, the substituted aromatic ring has no positive character. At the transition state, there has been a decrease in the positive character sensed by the substituent, and this loss is reflected in the positive sign of the ρ value.[31] The ρ value for the acetophenones is 0.78 times that for benzophenones; in the former, then, the substituent experiences less of a change in its interaction with the reaction site; more of the charge is retained by the aromatic ring. This indicates that the bond is less dissociated in the transition state for the formation of acetyl ion, and that the phenyl group is better able to support the positive charge in benzoyl ion than the methyl group in acetyl ion, since it assumes more of the charge in the transition state. The comparison of the relative abundance data in the parent compounds also supports this conclusion; Z_0 for benzoyl ion from benzophenone (taking into account a statistical correction of 2) is 1.44, and Z_0 for acetyl ion from acetophenone is 0.57. Comparison of these data is, of course, endangered by the failure to take decomposition pathways into account.



Both the reactant and the product containing the substituent in these reactions are radicals. Enhancement of resonance effects from the *meta* positions have been cited as characteristic of radical reactivities (formation of a radical from a molecule), particularly those in which there is a great deal of radical cation character in the transition state for the reaction.[32] No indication of special *meta* resonance enhancement is apparent from inspection of Figure 6; for comparison, the slope of the regression line for σ^0 values in the *meta* and *para* positions is 0.50. The value of 0.44 in Figure 6 is hardly distinguishable from this, and the resonance effect of the *m*-amino substituent, which exhibits a free-energy decrease of 3.0 kcal/mole in the polarographic oxidation of substituted anilines,[32] is enhanced in the present case by less than 0.1 kcal/mole. The dissociation of benzophenone ions into phenyl radicals and benzoyl ions constitutes the first case of formation of a radical from a radical ion studied in sufficient detail; it appears that special stabilization of radicals is essentially uniform in product and reactant for a given substituent, and further, that formation of a radical from a radical cation by loss of an even-electron fragment cannot be detected by special enhancement of *meta* resonance effects.

The success of the kinetic argument emphasizes an additional point. In using a mass spectrum to elucidate the structure of a molecule, the rate of the decomposition reaction producing a particular ion is an indication of the molecular environment near that reaction site. It does not seem to be generally appreciated that evaluation of the effect of this local molecular environment *on an absolute basis* must be done by comparison of the abundance of the product ion (A) to that of its precursor ion (P), *i.e.*, $[A^+]/[P^+]$. The usual custom of comparing $[A^+]$ to the abundance of the base peak or of the total ions in the spectrum indicates the importance of A^+ *relative* to the rest of the molecule. Consider an example in which the addition

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[27] F. L. Mohler, V. M. Dibeler, and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).

[28] (a) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965); (b) E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.*, **87**, 4234 (1965).

[29] H. E. Zimmerman, *Tetrahedron Suppl.*, **2**, 393 (1963).

[30] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2935, 2943 (1965).

[31] Appearance potential data for YC_6H_4O from $YC_6H_4OCH_3$ have a large negative ρ value.[15]

[32] R. W. Taft, I. R. Fox, and I. C. Lewis, *J. Am. Chem. Soc.*, **83**, 3349 (1961).

of a functional group to a molecule halves the relative abundances of both the molecular ion M^+ and a particular primary decomposition product A^+. Although the decompositions produced by the new substituent are of major importance compared to the reaction $M^+ \rightarrow A^+$, the unchanged *absolute* rate of the latter (as shown by $[A^+]/[M^+]$) indicates that the new substituent does *not* influence the molecular environment for $M^+ \rightarrow A^+$.

Substituent Effects as an Additional Method for the Study of Gaseous Ions. Techniques employing spectral correlations, high resolution, appearance potentials, metastable ions, and isotopic labeling have produced a surprisingly consistent picture of the structures and unimolecular reactions of gaseous ions in mass spectra, although rigorous proof has often been unobtainable. However, these tools are limited in their extent and ease of application, and for further progress in the field there appear to be a number of important areas in which substituent effects can provide definitive answers or corroborative evidence. Such areas include particular ion structures, the electron distribution in the transition state, and identification and estimation of the contributions of different kinetic pathways for formation of an ion.

For example, poor general correlation of data of *meta* substituents for a particular system would indicate that at least part of the molecular ions decompose from an electronically excited state. If a good correlation exists, the sign of the ρ value provides information about the electron distribution in the transition state in the usual manner. As data accumulate, more precise interpretations of the relative magnitude of the ρ value should provide better information about the ability of certain molecular components to stabilize and to transmit charge in the transition states for fragmentation of unsolvated ions.

Deviations of individual points in a generally good correlation, on the other hand, indicate rate phenomena singular to the substituents. Consider the general situation for the decomposition

$$\begin{tikzcd}
 & & N^+ \arrow[dr] & & \\
 & M^+ \arrow[ur] \arrow[rr] \arrow[dd, shift left] \arrow[ddrr] & & A^+ \arrow[r] \arrow[dd, shift left] & \text{product} \\
M \arrow[ur] \arrow[dr] & & & & \\
 & M'^+ \arrow[uu, shift left] \arrow[uurr] \arrow[rr] & & A'^+ \arrow[r] \arrow[uu, shift left] & \text{product}
\end{tikzcd} \tag{9}$$

Greater abundance than the value predicted from the correlation line may be explained by the presence of the following pathways.

the intermediacy of another ion between reactant and product

$$\begin{tikzcd}
 & N^+ \arrow[dr] & & \\
M^+ \arrow[ur] \arrow[rr] & & A^+ \arrow[r] & \text{product}
\end{tikzcd} \tag{10}$$

This explanation would be supported in general by metastables for the sequential steps.

The following pathways can give either greater or lower values, depending on the relative rate constants involved.

rearrangement in the molecular ion

$$\begin{tikzcd}
 & M^+ \arrow[r] \arrow[dd, shift left] & A^+ \arrow[r] & \text{product} \\
M \arrow[ur] \arrow[dr] & & & \\
 & M'^+ \arrow[uu, shift left] \arrow[uur] & &
\end{tikzcd} \tag{11}$$

This may affect the structure of the substituent alone so that a new σ constant may be used or be so deep seated that the new reaction must be regarded as an entirely different process, requiring a new ρ value.[33]

formation of a rearranged product ion

$$\begin{tikzcd}
M^+ \arrow[r] \arrow[dr] & A^+ \arrow[r] \arrow[d, shift left] & \text{product} \\
 & A^+ \arrow[r] \arrow[u, shift left] & \text{product}
\end{tikzcd} \tag{12}$$

No evidence was seen in this study for such a situation; it is possible that certain substituents may be found which have this general behavior. The term "rearrangement" in eq. 11 and 12 includes even electronic rearrangements, or excited states, to include such possibilities as the case mentioned in the discussion of kinetics where the energy distribution is dependent on the mode of formation.

Extension of the Present Results. There are a number of ways in which it appears possible to extend the applicability of substituent effects to the study of structures and mechanisms of gas phase ions. Work is currently in progress on the correlation of substituent effects with ion intensities resulting from combinations of formation and/or decomposition routes, on the use of substituent effects to investigate mechanisms in mass spectral rearrangements, and on the further evaluation of molecular environment at reaction centers by absolute ion intensities. These topics will form the basis for forthcoming papers.

Experimental Section

Spectra were recorded on a Hitachi RMU-6A single-focusing instrument using 75-ev electrons at an emission current of 100 μa. The sample inlet system was maintained at 185 ± 5° and the source at 170 ± 5°; at 200° slight increases in the product ion intensity ratios for several substituted compounds relative to the parent compound ratio were observed, indicating partial decomposition by some thermal route. At temperatures lower than those used, no decrease in ratios was observed, and it was thus concluded that no thermal decomposition could be detected at 185°. The standard deviation for eight replicate recordings of the same sample in the benzophenone series was, on the average, 1%; ratios of fragment ion intensities to molecular ion intensities were constant to within 1% from day to day for standard compounds. The acetophenone data were recorded in duplicate and showed the same reproducibility as that of the benzophenones. No multiplier effect on relative collection efficiencies was observed. Several compounds in which interference from isobaric ions might plausibly occur were examined on a CEC 21-110B high-resolution instrument; data for *p*-dimethylaminobenzophenone, *p*-dimethylaminoacetophenone, and the *t*-butylacetophenones reflect such corrections, which were not warranted for any of the other compounds examined.[34]

Chemical samples were either donated or were commercial samples of high purity. No indication of impurities was detected in the mass spectrum of any compound.

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(33) For an elegant series of related studies on appearance potentials, see ref 12; F. Meyer and A. G. Harrison, *Can. J. Chem.* **42**, 1762, 2008 (1965); and also F. Meyer, Thesis, University of Amsterdam, 1965.

(34) Edward Chait and Laurence Dusold assisted with several spectra.

Acknowledgments. We appreciate stimulating discussions with Dr. Louis P. Hammett, Dr. Herbert C. Brown, and Dr. Robert W. Taft. Samples of several of the compounds used in the study were donated by Dr. Herbert C. Brown, Dr. Saul G. Cohen, Dr. Thomas DeVries, Dr. George C. Fraenkel, Dr. J. J. Norman, and Dr. Paul J. Ricca. We are grateful for their generosity. We are indebted to the National Science Foundation and the National Aeronautics and Space Administration for generous support of this work.

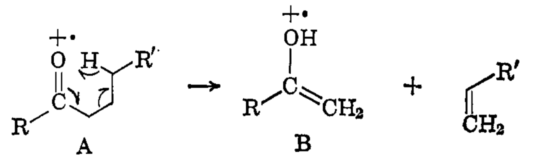
Mass Spectrometry in Structural and Stereochemical Problems. XCIII.[1] Further Observations on the Importance of Interatomic Distance in the McLafferty Rearrangement. Synthesis and Fragmentation Behavior of Deuterium-Labeled 12-Keto Steroids[2,3]

Carl Djerassi and Laszlo Tökés

Contribution from the Department of Chemistry, Stanford University, Stanford, California. Received September 13, 1965

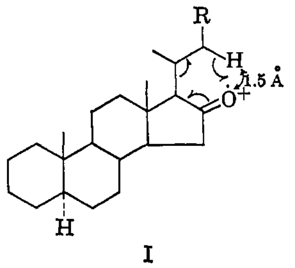
Abstract: Earlier work with deuterium-labeled 11-, 15-, and 16-keto steroids had indicated that the McLafferty rearrangement of ketones (β-cleavage with concomitant transfer of a γ-hydrogen atom) proceeds only if the interatomic distance between the itinerant hydrogen and the receptor oxygen is less than 1.8 Å. 12-Ketopregnanes, therefore, should not undergo a McLafferty rearrangement with transfer of a C-20 hydrogen atom, because the interatomic distance in the *intact* steroid is approximately 3.0 Å. Deuterium labeling has shown that the C-20 hydrogen atom is, in fact, transferred and this apparent discrepancy is rationalized by the assumption that the 13–17 bond is broken *prior* to hydrogen transfer, thus permitting close approach of the C-12 oxygen and the C-20 hydrogen atoms. The nature of all of the significant peaks in the high mass range of the mass spectrum of 5α-pregnan-12-one could be explained through the concept of charge localization by means of appropriate deuterium labeling, which also uncovered a reciprocal double hydrogen transfer involved in the genesis of the m/e 246 peak.

The electron impact induced fission of a β bond with simultaneous transfer of a γ-hydrogen atom (A → B) in carbonyl compounds appears to be of wide generality. Its recognition is due to McLafferty[4] and the experimental evidence, principally based on deuterium labeling, has already been summarized in various forms.[5–8]

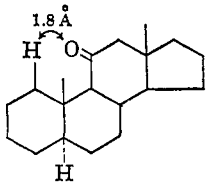


A B

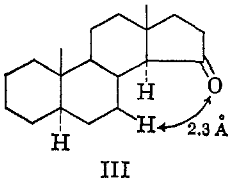
Recent studies in our laboratory with isotopically labeled ketones have shed considerable light on some of the more subtle factors affecting the McLafferty rearrangement such as the preference for abstraction of a secondary over a primary hydrogen atom,[1,9] the operation of restricted rotation,[10] and the existence of an appreciable deuterium isotope effect.[11] Through the use of suitably labeled steroids, it could be shown that the specific transfer of a γ-hydrogen did occur (see arrows in I) in 16-keto steroids (I),[9] where the γ-



I



II



III

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[2] Financial assistance by the National Institutes of Health (Grant No. CA-07195) of the U. S. Public Health Service is gratefully acknowledged.

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