g (0.040 mole) of sodium hydroxide in another run. The product was exclusively 3-homoadamantanol (**25**) in each case.

Preparative Solvolysis of 3-Homoadamantyl Bromide (23) in Aqueous Ethanol in the Presence of Sodium Carbonate. A mixture of 65 ml of 20% water–80% ethanol (v/v), 0.57 g (0.0025 mole, molarity = 0.04) of 3-homoadamantyl bromide (**23**), and 0.53 g (0.0050 mole) of anhydrous sodium carbonate was heated under reflux for 10 hr, and was then worked up as described for the similar solvolysis of 3-adamantylcarbinyl tosylate (**15**, X = OTs). The crude semisolid product, 0.49 g, was subjected to vpc on the silicone oil column and showed two peaks, of relative areas 37.5 and 62.5%, with the major component eluted first. The major product was identified as 3-homoadamantanol (**25**) and the minor product as 3-homoadamantyl ethyl ether (**18**, X = OEt) by their vpc retention times. Control vpc experiments were run which showed that 1% of primary alcohol **15** (X = OH) or primary ether **15** (X = OEt) could have been detected if present.

Neopentyl *p*-Nitrobenzenesulfonate. Commercially available neopentyl alcohol was converted to its nosylate by the standard procedure, mp 111.8–112.0°. *Anal.* Calcd: C, 48.35; H, 5.23. Found: C, 48.53; H, 5.55.

Kinetic Procedures. Standard titrimetric ampoule procedures were employed.[4,5,11,13,15,16,19,21,22,35,51,55] The solvents were carefully dried and fractionally distilled. Two separate runs to about three half-lives were made by each investigator at each temperature; agreement between runs was generally good. Table IV provides examples of the kind of agreement found between different investigators. Three separate studies, years apart, of the acetolysis of 1-adamantylcarbinyl tosylate (**15**, X = OTs) gave excellent agreement of the rate constants at a common temperature, 100°, and of the activation parameters. On the other hand, two studies on the corresponding nosylate, while giving moderately good agreement at 100° (11%), gave widely different activation parameters. This illustrates just one of the possible pitfalls of overenthusiastic interpretation of small differences in enthalpies and entropies of activation.[56]

Acknowledgments. We wish to thank the National Science Foundation for support of this research at Western Reserve University, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research at Princeton University.

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(55) See footnote *g*, Chart I.

(56) See also H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956).

Substituent Effects in Unimolecular Ion Decompositions. III. Elucidation of Competing Alternative Pathways for the Formation of a Particular Ion[1]

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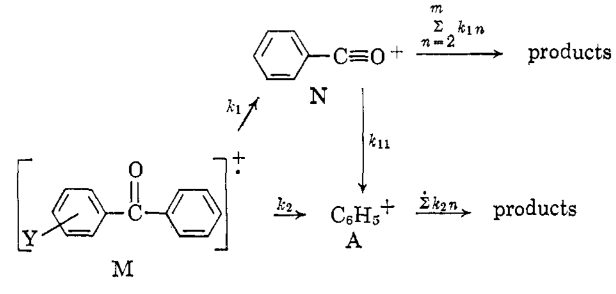
Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. *Received April 29, 1966*

Abstract: Substituent effects may be used to indicate the existence of two pathways for the formation of an ion in mass spectra. For example, the $C_6H_5^+$ ion in the mass spectra of substituted benzophenones is indicated to be formed by two pathways: directly from the molecular ion, and also through the intermediacy of the benzoyl ion. This mechanism is confirmed by elimination of the first process at low voltages. Similar data are found for the $C_3H_7^+$ ion in the spectra of substituted butyrophenones. Further use of the low-voltage technique is demonstrated in the determination of the origin of the $C_2H_3O^+$ ion in *m*- and *p*-*t*-butylacetophenone.

Substituent effects offer promise in the unraveling of structural detail of ions formed in the mass spectrometer and of the kinetic processes relating them. A significant correlation with Hammett σ constants[2] obtained in solution indicates similarity in the structure and behavior of the gas phase ion to that of species found in solution chemistry, both for ion abundance data[3] and for appearance potentials.[4–7]

In the previous paper of this series,[3] ion-abundance data were demonstrated to yield useful information about the structures of ions and transition states in the formation of acyl ions (N) from substituted acylbenzenes (M), M → N in Scheme I. This simple case was ideal for study, since there are no alternative pathways for the formation of the acyl ion, nor is there a substituent effect on further decomposition of this ion. The present paper extends this technique to the more complex system in which a particular product ion can be formed from a particular precursor ion by competing reaction paths. To our knowledge no techniques for the study of such a situation have been discussed previously; isotopic labeling will not distinguish these

Scheme I



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

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[3] M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

[4] A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, 1, 1 (1963).

[5] A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), 42, 221 (1964).

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

[7] F. Meyer and A. G. Harrison, *Can. J. Chem.*, 42, 1762 (1964).

pathways, because both produce ions of identical formulas.

For the formation of the $C_6H_5^+$ ion from substituted benzophenone ions the pathways depicted in Scheme I are probable.[8] Absence of other pathways involving the substituent in the formation of the benzoyl ion (N) has been demonstrated, as has the substituent dependence of the rate k_1.[3] One way to simplify the study of the formation of A from M is to eliminate one of the two pathways. If one has a sufficiently higher energy requirement, it may be possible to remove this path by lowering the ionizing voltage.

Low-Voltage Studies. It is a fairly common analytical practice to simplify complex spectra by recording them at low voltage, and thus remove ion products of high-energy reactions. Such techniques may be made quantitative, so that ionization potentials and appearance potentials may be determined for electron-impact processes.[10,11] The distinction in the present case is that the interfering fragment ion is identical with (or at least has the same elemental composition as) the fragment ion of lower energy.

On application of the steady-state approximation to the consecutive two-step pathway M → N → A of Scheme I, the rato of [A] to [M] is given by eq 1. We have shown[3] that the substituent effect for the processes

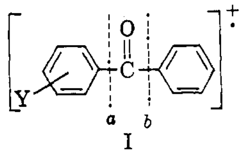
$$Z = \frac{[A]}{[M]} = \frac{k_{11}k_1}{(\Sigma k_{1n} + \Sigma k'_{\text{inst}})(\Sigma k_{2n} + \Sigma k'_{\text{inst}})} \qquad (1)$$

M → N is determined by the Hammett equation (ρ = 1.01), but the reaction N → A is independent of substituent. Inspection of eq 1 indicates that for the two-step process M → N → A substituent effects will be governed by the same Hammett equation, namely, eq 2.

$$\frac{Z}{Z_0} = \frac{k_1}{k_1^0} = \exp(1.01\sigma/2.3) \qquad (2)$$

On the other hand, the prediction of the substituent effect on the assumption of only the one-step process requires some argument. In the molecular ion I, an electron-withdrawing substituent should weaken bond b and produce more $C_6H_5^+$ ions than in the parent compound (as it does for bond a).[5] However, because of the additional bond and cross-conjugation of the carbonyl group between the substituent and the reaction site, the magnitude of the substituent effect would be quite small in comparison with the effect on the cleavage of bond a. If the Hammett equation holds, as it does for the cleavage of bond a, the reaction constant ρ for the direct formation M → A will be small and positive, and eq 3 will be followed (where $0 < \rho \ll 1.01$).

$$\frac{Z}{Z_0} = \frac{k_2}{k_2^0} = \exp(\rho\sigma/2.3) \qquad (3)$$



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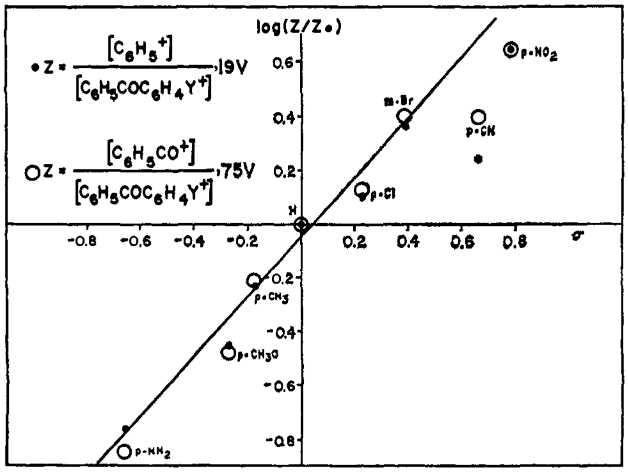

Figure 1. Correlation of substituent effects on the formation of $C_6H_5^+$ ions from substituted benzophenones at 19 v with Hammett σ constants.[12] The line is the correlation line determined previously for benzophenones,[3] with ρ_1 = 1.01.

The correlation of substituent effect data recorded at an ionizing energy of 19 v with Hammett σ values is shown in Figure 1. It is apparent from the slope of the line that the two-step process applies, for the substituent effects are within experimental error to those found for the production of benzoyl ion.[3] Further, the two-step process is supported by metastable ion formation. The "metastable" ion for the loss of CO from benzoyl ion (calcd m/e 56.5, obsd 56.5) in the spectra of the compounds studied is still present at 19 v and indicates that the process N → A is still important. No "metastable" ion corresponding to other paths of formation of $C_6H_5^+$ from the molecular ion is found even at normal ionizing voltages; only the substituent effect data indicate the singularity of the mode of $C_6H_5^+$ formation.

Data at Normal Ionizing Voltages. If the kinetic scheme for substituent effects at normal ionizing voltages is complicated by the existence of an additional process for formation of the $C_6H_5^+$ ion, the rate of its appearance is given by eq 4. Combining this with the

$$0 = \frac{d[A]}{dt} = k_2[M] + k_{11}[N] - (\Sigma k_{2n} + \Sigma k'_{\text{inst}})[A] \qquad (4)$$

formation of N from M, as in Scheme I, gives the rate dependence of the ion intensity ratios. For a series of ratios, eq 5 holds, since the denominator is constant

$$\frac{[A]/[M]}{[A_0]/[M_0]} = \frac{Z}{Z_0} = \frac{k_{11}k_1 + (\Sigma k_{1n} + \Sigma k'_{\text{inst}})k_2}{k_{11}k_1^0 + (\Sigma k_{1n} + \Sigma k'_{\text{inst}})k_2^0} \qquad (5)$$

for all substituents. Incorporation of the substituent dependences ρ_1 and ρ_2 of k_1 and k_2, respectively, permits writing of an equation relating substituent constants to the expected abundance behavior of product ion A

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[8] Natalis and Franklin[9] report the decomposition of benzophenone by loss of CO to $C_{12}H_{10}\cdot^+$, an ion of considerable excitation energy and rearranged structure. Thus $C_6H_5^+$ could also be formed by Y–C_6H_4-$COC_6H_5\cdot^+$ → Y–$C_{12}H_9\cdot^+$ → $C_6H_5^+$; this possibility is discussed later.

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

[10] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 26.

[11] R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 162.

[12] Values tabulated by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964), were used.

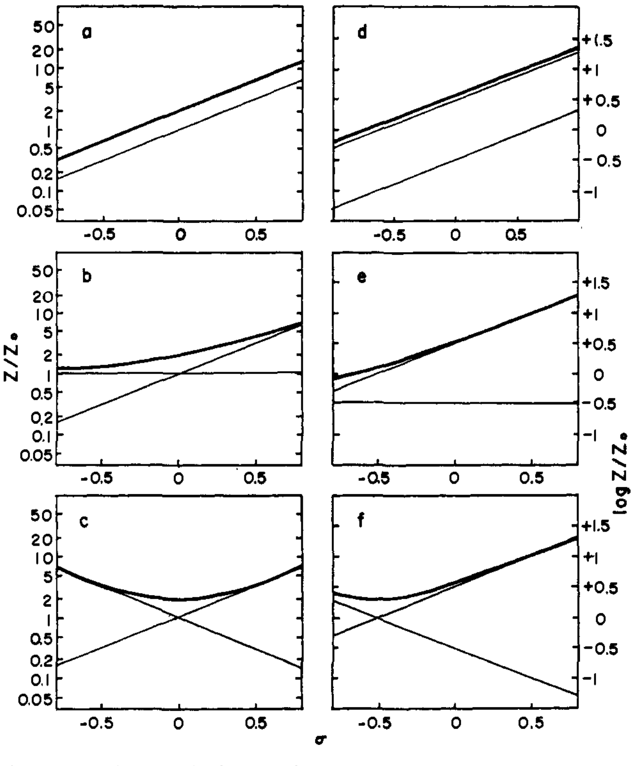


Figure 2. Hypothetical examples of eq 9: (a) $A = B, \rho_2 = 1$; (b) $A = B, \rho_2 = 0$; (c) $A = B, \rho_2 = -1$; (d) $A = 10B, \rho_2 = 1$; (e) $A = 10B, \rho_2 = 0$; (f) $A = 10B, \rho_2 = -1$. The heavy lines are the sum of the contributions from the two lighter lines.

(eq 6), assuming no substituent effect on k_{11}. This is simplified to eq 7 for further discussion. The shape of

$$\frac{Z}{Z_0} = \frac{k_{11}k_1{}^0 \exp(\rho_1\sigma/2.3) + (\Sigma k_{1n} + \Sigma k'_{\text{inst}})k_2{}^0 \exp(\rho_2\sigma/2.3)}{k_{11}k_1{}^0 + (\Sigma k_{1n} + \Sigma k'_{\text{inst}})k_2{}^0} \qquad (6)$$

$$\frac{Z}{Z_0} = A \exp(\rho_1\sigma/2.3) + B \exp(\rho_2\, \sigma/2.3) \qquad (7)$$

the correlation line is therefore a function of $k_1{}^0$, $k_2{}^0$, k_{11}, Σk_{1n}, and both ρ values. In Figure 2, several cases are illustrated in which ρ_1 is maintained equal to 1. For a sufficiently different ρ_2 value and sufficiently similar A and B, the observed ratio (which is the sum of the two contributions represented by the two lines below it) does not correlate linearly with Hammett substituent constants, but curves instead.

The relative intensities of the $C_6H_5{}^+$ ion in the mass spectra of substituted benzophenones at 75 ev are plotted *vs.* Hammett σ constants[2,12] in Figure 3. An approximate fit to the data may be obtained with the curved line, which is the logarithm of the sum of the Z/Z_0 values of the two straight lines below it, and which resembles the curve of Figure 2b. The slope of one line corresponds to $\rho_1 = 1.0$, the value found for the formation of $C_6H_5{}^+$ ion at 19 v; the other has a slope of approximately zero. The latter (ρ_2) corresponds to the low ρ value predicted previously for the direct formation of the $C_6H_5{}^+$ from the molecular ion, reflecting the very slight influence of substituents on the strength of the bond being broken in the direct process. Although the possible third path for formation of $C_6H_5{}^+$ through $Y{-}C_{12}H_9\cdot{}^+$ cannot be ruled out on this basis, the data found would demand a surprising combination of kinetic terms. By comparison to Figure 2b again, the coefficients A and B are nearly the same; a graphical solution yields the relation $A = 1.2B$. The chief product of decomposition of $C_6H_5CO^+$ is logically $C_6H_5{}^+$, so that k_{11} accounts for most of Σk_{1n}; a conservative lower limit is 50%. If $\Sigma k_{\text{inst}}'$ is small compared to Σk_{1n}, it follows that $1.2 < k_1{}^0/k_2{}^0 < 2.4$ at 75 v. In benzophenones substituted by electron-donating groups, the preponderance of the $C_6H_5{}^+$ product is formed by the one-step process. On the other hand, for compounds with electron-withdrawing substituents, formation of benzoyl ion from the molecular ion is so greatly accelerated that the two-step process overwhelms the one-step process.

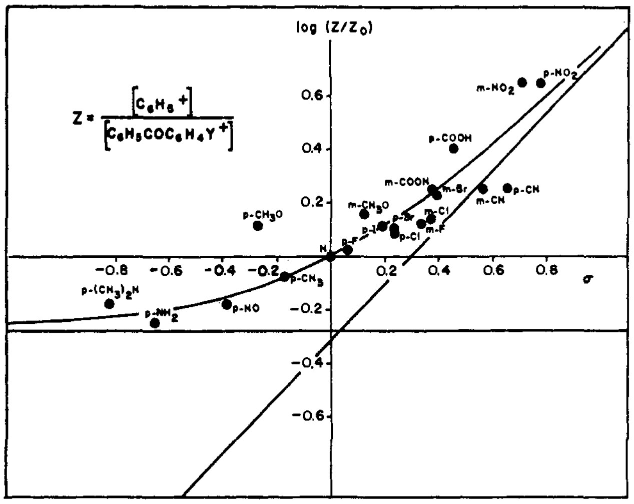


Figure 3. Correlation of substituted effects on the formation of $C_6H_5{}^+$ ions from substituted benzophenones at 75 v with the sum of predicted contributions from two reaction pathways.

Natalis and Franklin[9] find that both $C_6H_5CO^+$ and $C_6H_5{}^+$ are formed from benzophenone with excess energy. This should not necessarily affect the applicability of the Hammett equation to the abundance of $C_6H_5{}^+$ from $YC_6H_4COC_6H_5\cdot{}^+$, since a good correlation was found for the abundance of $C_6H_5CO^+$.[3] Energetics would predict that the direct formation of $C_6H_5{}^+$ would be the lower energy process, if cleavage of the $YC_6H_4{-}CO$ bond is not required. The fact that the opposite is the case shows that the $C_6H_5{}^+$ ion product from one-step reaction has even greater excess energy than the two-step process product, which has been postulated to be an open-chain structure.[9]

Deviations of Substituents from Solution Behavior. We discussed deviations from the correlation line for formation of the benzoyl ion with respect to σ constants in terms of alteration of the structure of substituents which show large deviations.[3] Figure 4 shows that deviations of $C_6H_5{}^+$ data appear to follow qualitatively the deviations found earlier for the benzoyl ion data; there is an improvement in correlation over that in Figure 3. The data for the cyano and nitro substituents in particular show much greater accord with mass spectral data (Figure 4) than solution data (Figure 3). The rearranged structures suggested to explain these deviations of these substituents from solution behavior

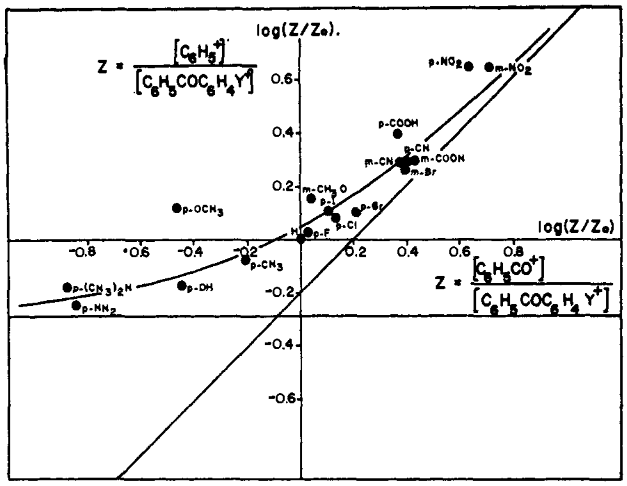


Figure 4. Correlation of the formation of $C_6H_5^+$ and $C_6H_5CO^+$ ions from substituted benzophenones.

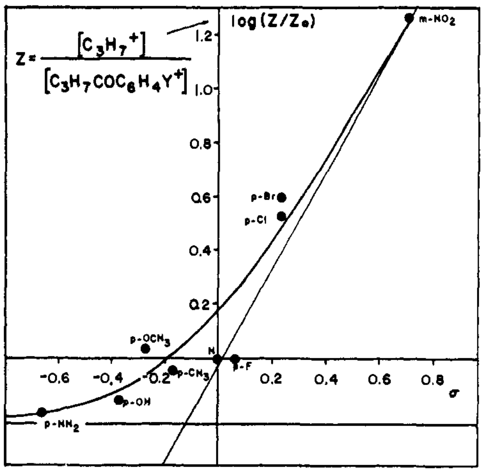


Figure 5. Correlation of the relative intensities of $C_3H_7^+$ ions in the mass spectra of substituted *n*-butyrophenones with Hammett σ constants.[12]

in the benzoyl ion data may also be operative in the formation of $C_6H_5^+$.

Just as no other contributions to the formation of benzoyl ion from other pathways were detected by substituent effects,[3] so also it may be deduced that the contributions of other pathways for individual substituents to the formation of $C_6H_5^+$ are not large, for they are significant only to the extent of deviation of individual points from the correlation line of Figure 4. Only the *p*-methoxy substituent gives much more $C_6H_5^+$ than is predicted. This substituent has been noted to yield anomalous substituent effects: in the formation of substituted C_7 ions from substituted toluenes, the *p*-methoxy substituent appears to prevent skeletal rearrangement, in contrast to the other substituents examined.[6] The cause of this behavior has been suggested as localization of charge on the oxygen; establishment of an alternate reaction site would therefore provide an additional source of $C_6H_5^+$ ion. The process involving the intermediacy of $CH_3OC_6H_4^+$ (Scheme II) is

Scheme II

$$CH_3OC_6H_4COC_6H_5\cdot^+ \longrightarrow \underset{107}{CH_3OC_6H_4^+} \longrightarrow \underset{77}{C_6H_5^+}$$

supported by a "metastable" ion (calculated *m/e* 55.4, found 55.5). The evidence does not rule out other pathways, nor indicate the importance of this route relative to other possibilities. The substituent effect can do these, however. Other routes (*e.g.*, Schemes III and IV) are also analogous to the expulsion of the elements of formaldehyde from anisole,[13] but these should have given rise to abnormal amounts of $C_6H_5CO^+$ as well.

Scheme III

$$CH_3OC_6H_4COC_6H_5\cdot^+ \longrightarrow CH_3OC_6H_4CO^+ \longrightarrow C_6H_5CO^+ \longrightarrow C_6H_5^+$$

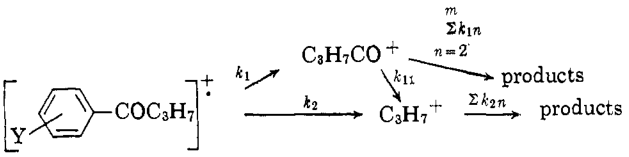
Scheme IV

$$\begin{tikzcd}
 & & C_6H_5CO^+ \\
CH_3OC_6H_4COC_6H_5\cdot^+ \arrow[r] & C_6H_5COC_6H_5\cdot^+ \arrow[ur] \arrow[dr] & \\
 & & C_6H_5^+
\end{tikzcd}$$

Since there is no abnormal amount of benzoyl ion detected in *p*-methoxybenzophenone,[3] these alternate pathways are not important. The excess $C_6H_5^+$ from Scheme III amounts to 1.1 times that from the direct process, according to this reasoning.

Other Systems. The applicability of this approach to study ions arising from several sources in other sets of compounds is illustrated by the analysis of the intensity of the $C_3H_7^+$ ion in the mass spectra of substituted *n*-butyrophenones (Figure 5). Although the data points are somewhat scattered, the same characteristics are observed: the apparent decrease in the effect of electron-donating substituents on the intensity of the product produces a curve indicating a similar mechanism of formation to that for the $C_6H_5^+$ ion in the benzophenones. The correlation of $C_3H_7^+$ to $C_3H_7CO^+$ is not indicated; there is significant scatter in it, probably related to the surprisingly low intensity of the $C_3H_7CO^+$ ion in these spectra, and to possible contributions from alternate structures connected with rearrangements.[14] The pertinent reactions are given in Scheme V. Since the butyryl ion is so weak (2% of molecular ion intensity in *n*-butyrophenone), k_{11} is apparently large; the product possesses especial stability and may be cationated cyclopropane.[15] Because both processes are important in determining the intensity of $C_3H_7^+$ in *n*-butyrophenone, we may use these data from the more intense $C_3H_7^+$ to comment on the substituent dependence of the formation of the much weaker *n*-butyryl ion exclusive of rearrangement products which may obscure its true substituent dependence; and by analysis of the relative contributions of the two pathways, the relative importance of k_1 and k_2 may be assessed. Thus, for direct formation of $C_3H_7^+$ from

Scheme V



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(13) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, 16, 219 (1963).

(14) F. W. McLafferty, *Anal. Chem.*, 31, 82 (1959).

(15) P. N. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, 78, 5799 (1956).

substituted butyrophenones, ρ is approximately 0.0; and for the formation of butyryl ion, ρ equals 1.8, and $k_1{}^0 = 3.2\,k_2{}^0$ if $k_{11} - 0.50\Sigma k_{1n}$ and $\Sigma k'_{\text{inst}} \ll \Sigma k_{1n}$.

As a further application of this technique, consider the effect of lowering the ionizing electron energy on the competition of the two pathways for the formation of acetyl ion from *t*-butylacetophenones. To explain the abnormal amount of acetyl ion produced from these compounds,[3] we suggested earlier that part of this ion is produced from the intermediate from which a methyl radical has been lost, as in Scheme VI. If the contribution of the one-step path is increased, log Z/Z_0 should decrease, approaching the values predicted by solution σ constants.[16,17] If the two-step path becomes more important, log Z/Z_0 should increase; Table I indicates that the latter occurs.

Scheme VI

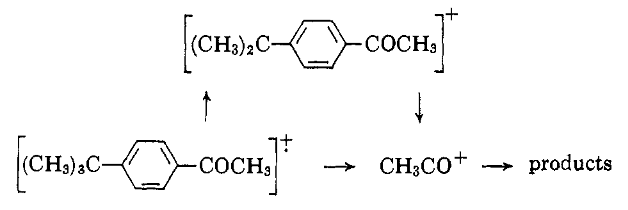

Table I

Y	Log Z/Z_0 at 75 v	Log Z/Z_0 at 16.3 v	Log Z/Z_0 predicted for one-step process
m-$(CH_3)_3C$	0.72	1.02	−0.07
p-$(CH_3)_3C$	0.69	0.97	−0.14

Application of Substituent Effects to Appearance Potential Studies. Knowledge of the mode of formation of an ion is necessary in appearance potential studies for calculation of the energy involved. If two paths of formation are operative, this fact must be recognized for the accurate determination of appearance potentials.[18] Some methods of calculation[19,20] utilize fractional intensities, *i.e.*, intensities relative to the intensity at some higher voltage. Differing relative contributions from the competing paths could be estimated by a study with substituents, so that the intensity due to the low-voltage process alone may be used for further calculation. For example, the intensity of $C_6H_5^+$ in *p*-aminobenzophenone at 19 v is about 1.5% of its value at 75 v, but only about 10% of the intensity at normal ionizing voltage arises from a process kinetically significant near the appearance potential, according to our interpretation. Thus the value at 19 v is more properly 15% of its relevant intensity at 75 v.

Conclusions

Substituent effects may be used to detect and evaluate two routes of formation for a particular ion, if the effects are sufficiently different; and their processes may be detected for a particular derivative by the deviation from the expected substituent behavior. Analysis of complex curves leads to evaluation of relative magnitudes of competing rates of decomposition for the molecular ion. Substituent dependences of these rates seem to be predicted by the usual arguments relative to interposition of resonating groups to determine ρ values, and Hammett substituent constants appear to be generally useful in such analyses. Even for such complex competing reactions ρ values and relative base rate constants may be collected for analysis of unresolved systems. Such studies on more complex systems will be continued in this series.

Experimental Section

Samples were either commercial samples or gifts, and did not contain any impurities detectable by mass spectrometry.

Spectra were recorded at least in duplicate on a Hitachi RMU-6A single-focusing instrument with inlet at 185 ± 5° and source at 160 ± 10°. Ionizing current for high-voltage spectra was 80 μa; electron energy was 75 v.

The low-voltage spectra of the benzophenones were recorded under similar temperature conditions, with repellers tied at 1.5 v and trap current at 2 μa. The voltage was standardized against an Ar sample; it was adjusted until the intensity of the Ar^+ ion was 10% of its value at 48 v (maximum voltage on low-voltage scale) and the entire spectrum was recorded. Although it is subjective to choose a point of departure for voltages based on peak intensities of a standard, the 10% value for Ar^+ occurs 3.2 v higher than its 1% value, which was arbitrarily taken as 15.8 v, the reported appearance potential.[21,22]

Data for the acetophenones were recorded at a voltage at which the intensity of the *m/e* 43 ion of acetophenone was equal to 4% of its value at 75 v; this value was 2.6 above the energy at which the *m/e* 43 ion is 1% of its high-voltage value. The voltage for the 1% value again was arbitrarily taken to equal the reported appearance potential, 13.7 v.[23] Data for various compounds were compared after standardization against the relative intensity of the $C_2Cl_3^+$ ion of tetrachloroethylene, which attains 20% of its intensity at 75 v, at this voltage.

Acknowledgments. The donation of samples by Dr. Herbert C. Brown, Dr. Saul G. Cohen, Dr. Thomas DeVries, and Dr. Paul G. Ricca is noted with thanks. This work was supported by grants from the National Science Foundation (GP 4335) and the National Aeronautics and Space Administration (NGR 15-005-021).

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(16) Log $Z/Z_0 = \rho\sigma$, where $Z = [CH_3CO^+]/[C_4H_9C_6H_4COCH_3\cdot^+]$, $\rho = 0.7$,[3] and $\sigma = -0.10$ and -0.20 for *m*- and *p*-$(CH_3)_3C$.[17]

(17) Values tabulated by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(18) For an alternate source of difficulty, a high-voltage decomposition leading to depletion of the molecular ion; see C. Lifschitz and F. A. Long, *J. Chem. Phys.*, 41, 2468 (1964).

(19) F. P. Lossing, A. W. Tickner, and W. A. Brice, *ibid.*, **19**, 1254 (1951).

(20) R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).

(21) W. Bleakney, *Phys. Rev.*, **35**, 1303 (1930).

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(23) J. R. Majer, C. R. Patrick, and J. C. Robb, *Trans. Faraday Soc.*, **57**, 14 (1961).