Chemical Ionization Mass Spectrometry. X. Temperature Studies with Substituted Benzyl Acetates

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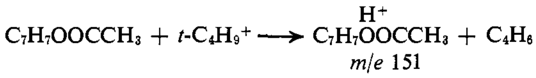
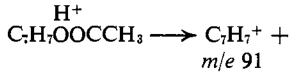
Abstract: Isobutane chemical ionization mass spectra have been determined for five *para*-substituted benzyl acetates as a function of the temperature of the mass spectrometer ionization chamber: *p*-methoxy, fluoro, methyl, chloro, and nitrobenzyl acetates. The spectra are strongly temperature dependent. For all compounds except *p*-nitrobenzyl acetate the dominant ions at low temperature are $(M + 1)^+$, but at high temperatures the dominant ions are fragment ions formed by decomposition of $(M + 1)^+$. Temperature-dependent equilibrium reactions are also observed. Rate constants for the decomposition of $(M + 1)^+$ are deduced from the observed ion intensities, and the rate constants at different temperatures follow the Arrhenius relationship. Activation energies and frequency factors are given. The activation energies depend on the nature of the *para* substituent, decreasing as the electron-releasing propensities of the substituents increase. Hammett plots of the rate constants against σ^+ show a satisfactory correlation except for *p*-nitrobenzyl acetate, for which the rate constant is much too slow. It is concluded that the activation energies obtained from chemical ionization rate determinations are meaningfully related to the relative energies of the ions produced, although there is reason to think that the differences in activation energy are not exactly equal to the differences in the ion energies. Ions with general formula $(2M + 1)^+$ and $(M + 39)^+$ are formed by reactions which appear to be equilibrium reactions. Equilibrium constants are calculated, and from the temperature variation of the equilibrium constants enthalpies and entropies for the reactions are obtained. As was found in a previous study the surprising result was obtained that the entropy changes for these reactions are positive.

In a recent paper[1] we reported that with i-C_4H_{10} as reactant the chemical ionization mass spectra of benzyl acetate and *t*-amyl acetate show a marked temperature dependence, and from this temperature dependence one can deduce kinetic parameters for reactions involved in the formation of the mass spectra. Furthermore, we tentatively postulated that the activation energies obtained are related to the relative energies of certain ionic species which are formed, but we emphasized that more experimental evidence was needed in order to determine the validity of the postulate. The purpose of the present paper is to provide some of this evidence, and we present the results of studies of five *para*-substituted benzyl acetates, namely, *p*-methoxy, fluoro, methyl, chloro, and nitrobenzyl acetate.

To illustrate using benzyl acetate as a specific example, we reported that this compound is initially protonated by *t*-butyl ion, and the protonated benzyl acetate thus formed can undergo a decomposition to benzyl ion and acetic acid, that is



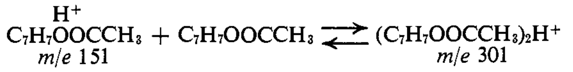
$$C_7H_7OOCCH_3 + t\text{-}C_4H_9^+ \longrightarrow \underset{m/e\ 151}{\overset{H^+}{C_7H_7OOCCH_3}} + C_4H_8 \qquad (1)$$



$$\overset{H^+}{C_7H_7OOCCH_3} \longrightarrow \underset{m/e\ 91}{C_7H_7^+} + CH_3COOH \qquad (2)$$

The amount of $C_7H_7^+$ ion formed by (2) depends upon the temperature of the ionization chamber of the mass spectrometer, and it varies between only a few per cent of the total benzyl acetate ionization at 40° and about 80% of the total ionization at 200°. The t-$C_4H_9^+$ ion appearing in (1) is the major ion formed from the i-C_4H_{10}, which in these experiments is used as the chemical ionization reactant material. From the relative intensities of the benzyl ion (*m/e* 91) and the protonated benzyl acetate ion (*m/e* 151) one can deduce the rate constants for (2), and from an Arrhenius plot of the rate constants obtained at several temperatures one obtains the activation energy and preexponential factor for the reaction. We postulate that the activation energy is related to the energy of the ion formed, and thus the activation energies obtained for reactions analogous to (2) for different acetate esters may be measures of the relative energies of the several ions produced.

We have also reported[1] that several of the ions found in the chemical ionization mass spectra of benzyl acetate and *t*-amyl acetate enter into equilibrium reactions under the chemical ionization conditions. For example, an equilibrium exists between protonated benzyl acetate and protonated benzyl acetate dimer, that is



$$\underset{m/e\ 151}{\overset{H^+}{C_7H_7OOCCH_3}} + C_7H_7OOCCH_3 \rightleftharpoons \underset{m/e\ 301}{(C_7H_7OOCCH_3)_2H^+} \qquad (3)$$

The equilibrium constants for these reactions vary with temperature, and from this one obtains in the usual way the enthalpy and entropy changes for the reactions. Similar equilibria are observed with the substituted benzyl acetates and are reported here.

Chemical ionization mass spectrometry is a form of mass spectrometry wherein the ionization of the substance under investigation is effected by reactions between the molecules of the substance and a set of ions which serve as ionizing reactants. Review papers describing the techniques and containing references to previous work have recently been published.[2,3]

Experimental Section

The apparatus used for these studies was the Esso chemical physics mass spectrometer described previously,[4,5] and the pro-

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[1] F. H. Field, *J. Am. Chem. Soc.*, **91**, 2827 (1969).

(2) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(3) F. H. Field in "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., Institute of Petroleum, London, 1968.

Table I. Chemical Ionization Mass Spectra of *p*-Fluorobenzyl Acetate at Three Temperatures[a]

m/e	Ion formula	Ion type	Relative intensity[b] at temp = 38°	108°	152°
109	$p\text{-FC}_6\text{H}_4\text{CH}_2^+$	R^+	0.215	0.488	0.772
110	^{13}C isotope		0.016	0.043	0.062
165	$\text{C}_{11}\text{H}_{14}\text{F}^+$	$(M - 3)^+$	0.023	0.071	0.054
168	$p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAc}^+$	M^+	0.043	0.032	0.019
169	$p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAcH}^+$	$(M + 1)^+$	0.494	0.293	0.075
170	^{13}C isotope		0.054	0.031	0.006
187	$p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAcH}\cdot\text{H}_2\text{O}^+$	$(M + 1 + 18)^+$	0.012		
207	$p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAcH}\cdot\text{C}_3\text{H}_3^+$	$(M + 39)^+$	0.019	0.004	
225	$p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAcH}\cdot\text{C}_4\text{H}_9^+$	$(M + 57)^+$	0.008		
337	$(p\text{-FC}_6\text{H}_4\text{CH}_2\text{OAc})_2\text{H}^+$	$(2M + 1)^+$	0.081	0.022	
338	^{13}C isotope	0.019	0.004		

[a] Reactant = $i\text{-C}_4\text{H}_{10}$; $P_{i\text{-C}_4\text{H}_{10}} = 0.70$ Torr; $P_{\text{FBzOAc}} = 4.6 \times 10^{-5}$ Torr; mol wt$_{\text{FBzOAc}}$ = 168. [b] In this and subsequent tables the relative intensity is the fraction of the total ionization attributed to the additive compounds (substituted benzyl acetates in this work).

cedures used for making the temperature effects studies are identical with those used for the previously reported work on benzyl acetate and *t*-amyl acetate.[1] One minor difference in procedure is that in the present work measurements were made using ion repeller voltages of both 5.0 and 10.0 V. In the previous work all measurements were made at 5.0 V. We find that the ions are extracted from the ionization chamber more effectively by the use of the higher repeller voltage, and this improvement is particularly marked at lower ionization chamber temperatures. The pressure of the $i\text{-C}_4\text{H}_{10}$ used as reactant was 0.70 Torr.

The calculation of the rate constants for the decompositions of the substituted benzyl acetates analogous to (2) requires a knowledge of the residence times of the protonated benzyl acetates in the ionization chamber of the mass spectrometer. These values are calculated from drift velocity considerations identical with those described in ref 1. As a matter of practical necessity it is assumed that the collision diameters for all the substituted benzyl acetates are the same, and thus the Hassé *A* factors are the same for these compounds. Consequently, the residence time will depend only upon the *m/e* value for the protonated ester. A value of 0.32 was taken for the Hassé *A* factor. It is deemed that no significant error in the kinetic results is introduced by the utilization of the constant Hasse *A* factor.

The pressures of the several substituted benzyl acetates in the ionization chamber of the mass spectrometer were obtained using the same considerations as those applied previously.[1] It was assumed that the flows of the several acetates were identical, and thus the pressures were calculated relative to the pressure of benzyl acetate simply from the ratios of densities.

To make a temperature run on a compound the spectra were determined at approximately 10° intervals over the range of temperatures of interest. For all the compounds except *p*-nitrobenzyl acetate three replicate runs were made with repeller voltage of 5.0 V and three runs with a repeller voltage of 10.0 V for a total of six replicate runs. For the *p*-nitrobenzyl acetate only three replicate runs with repeller voltage of 5.0 V were made.

The *p*-methylbenzyl acetate was purchased from a commercial source, but the other esters were prepared from the corresponding alcohols by acetylation with acetic anhydride using sodium acetate as an accelerating agent. The *p*-chloro-, nitro-, and methoxybenzyl alcohols were obtained commercially, but the *p*-chloro alcohol had to be prepared by LiAlH_4 reduction of *p*-chlorobenzaldehyde. The physical constants on the several products agreed satisfactorily with accepted values. In addition to this, except for *p*-nitrobenzyl acetate, the materials used in the mass spectrometric measurements were purified by preparative scale gas chromatography. The *p*-nitrobenzyl acetate was too involatile to make this procedure feasible, and it was purified by triple recrystallization. For all compounds the final purity was checked by analytical gas chromatography, and no extraneous peaks were found. It is estimated that the impurity levels of the compounds measured were significantly below 0.1%.

Results

Mass Spectra. The spectra of the substituted benzyl acetates other than *p*-nitrobenzyl acetate are very similar and can be represented by the spectra of *p*-fluorobenzyl acetate given in Table I. The *p*-nitrobenzyl acetate spectra will be discussed separately. The spectra given in Table I are completely analogous to those discussed previously.[1] At the low temperature the most abundant ion is the $(M + 1)^+$ ion formed by a reaction analogous to (1). The ions with *m/e* values larger than that of $(M + 1)^+$ are formed by various equilibrium reactions involving entities in the ionization chamber of the mass spectrometer. Thus the *m/e* 187 ion is formed from the reaction of protonated acetate with water impurity in the mass spectrometer. The ions with *m/e* 207 and 225 are formed by reaction of the acetate with the C_3H_3^+ and C_4H_9^+ components of the isobutane plasma. The *m/e* 337 ion is produced by a dimerization reaction analogous to (3). The most important ion with *m/e* smaller than that of $(M + 1)^+$ is that with *m/e* 109, which is the *p*-fluorobenzyl ion produced by a reaction analogous to (2). The M^+ ion at *m/e* 168 is formed by electron transfer with an unknown component of the isobutane plasma, and the $(M - 3)^+$ ion with *m/e* 165 will be discussed below. From Table I it may be seen that as the source temperature is increased the intensities of the ions formed by the various equilibrium processes, *i.e.*, those with *m/e* greater than that of $(M + 1)^+$ decrease, and the intensity of R^+ increases. This behavior has been observed and discussed previously,[1] and it results from the fact that the equilibria such as (3) are exothermic for the reaction proceeding to the right, and the reactions analogous to (2) involve an activation energy.

The $(M - 3)^+$ ion appearing in Table I at *m/e* 165 is observed in the *p*-chloro- and *p*-methylbenzyl acetates as well as in *p*-fluorobenzyl acetate. It was also observed previously[1] in benzyl acetate, but the reaction producing it was not understood. *p*-Methoxy- and *p*-nitrobenzyl acetates do not produce measurable amounts

Table II. Tabulation of $(M - 3)^+$ Relative Intensities (temp = 100–110°)

Substituent	$I_{(M - 3)^+}$
CH_3O	0
NO_2	0
F	0.068
Cl	0.095[a]
CH_3	0.079
H	0.016[b]

[a] Sum of intensities corresponding to ions containing ^{35}Cl and ^{37}Cl. [b] From ref 1, t = 126°.

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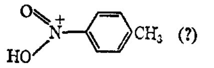
(4) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

(5) F. H. Field, *ibid.*, **83**, 1523 (1961).

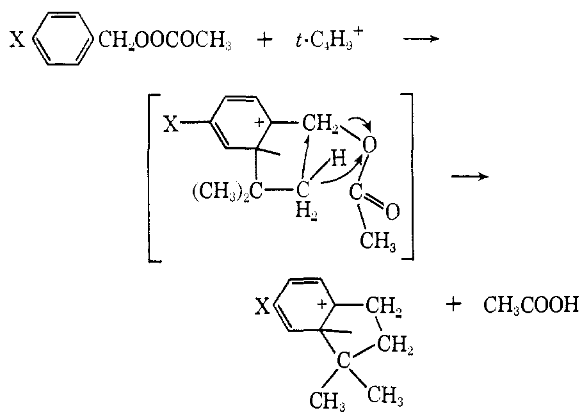
Table III. Chemical Ionization Mass Spectra of *p*-Nitrobenzyl Acetate at Three Temperatures[a]

m/e	Ion formula	Ion type	Relative intensity at temp = 51°	143°	254°
138	 (?)				0.107
196	$O_2NC_6H_4CH_2OAcH^+$	$(M + 1)^+$	0.138	0.744	0.794
197	^{13}C isotope		0.017	0.079	0.080
198	^{13}C isotope		0.001	0.008	0.017
214	$O_2NC_6H_4CH_2OAcH \cdot H_2O^+$	$(M + 1 + 18)^+$	0.029		
234	$O_2NC_6H_4CH_2OAc \cdot C_3H_3^+$	$(M + 39)^+$	0.018		
251	?		0.023		
252	$O_2NC_6H_4CH_2OAc \cdot C_4H_9^+$	$(M + 57)^+$	0.611	0.069	
253	^{13}C isotope		0.092	0.009	
391	$(O_2NC_6H_4CH_2OAc)_2H^+$	$(2M + 1)^+$	0.044	0.077	
392	^{13}C isotope		0.006	0.013	

[a] Reactant = $i\text{-}C_4H_{10}$; $P_{i\text{-}C_4H_{10}} = 0.70$ Torr, $P_{NO_2BzOAc} \cong 4.6 \times 10^{-5}$ Torr; mol $wt_{NO_2BzOAc} = 195$.

of this ion. The relative intensities observed in the several compounds are given in Table II. The intensities show a weak dependence on temperature, and it is sufficient for present purposes to give the intensities at only a single temperature.

Investigations in progress in this laboratory[6] on the isobutane chemical ionization behavior or methoxymethyl acetate and methoxymethyl formate show that in the former compound the $(M - 3)^+$ ion is the most intense in the spectrum, but in the latter compound the most intense ion is the $(M + 11)^+$ ion. The molecular weights of acetic acid, formic acid, and $t\text{-}C_4H_9^+$ are 60, 46, and 57, respectively, and the observed *m/e* values suggest that the $(M - 3)^+$ and $(M + 11)^+$ ions produced involve displacement of acetic acid and formic acid, respectively, by *t*-butyl ion. We suggest that $(M - 3)^+$ ions observed in the several benzyl acetates result from the acetic acid displacement reaction, *i.e.*,



(4)

$m/e = (M - 3)^+$

The failure to observe $(M - 3)^+$ ions in *p*-methoxybenzyl acetate may be ascribed to the fact that, as will be shown later, protonated *p*-methoxybenzyl acetate decomposes very rapidly to *p*-methoxybenzyl ion and acetic acid; that is, the rate for the analog of (2) is very high. The sum of analog (1) and (2) on the one hand and analog (4) on the other are in competition, and we conclude that for the methoxy-substituted ester the path *via* analog (1) and (2) dominates. By contrast, the opposite explanation is to be invoked for the lack of formation of $(M - 3)^+$ ions in *p*-nitrobenzyl acetate; namely, essentially no decomposition at all occurs with this compound, presumably because of the destabilizing influence of the nitro group.

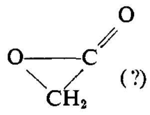
The spectra of *p*-nitrobenzyl acetate are sufficiently different from the spectra of the other compounds that a separate discussion is warranted. Spectra at three temperatures are given in Table III. Two striking differences are: (1) at the lowest temperatures the $(M + 57)^+$ ion dominates the spectrum, and (2) even at the highest temperature obtained no observable amount of *p*-nitrobenzyl ion is formed. At intermediate and high temperatures the $(M + 57)^+$ ion diminishes in intensity, and in its place the $(M + 1)^+$ ion grows to dominate the spectrum. The ions formed by the various equilibrium processes ($(M + 19)^+$, $(M + 39)^+$, and $(2M + 1)^+$) are to be observed in the spectra, and in addition one observes at the highest temperature the formation of the ion with *m/e* 138, which is assumed to be protonated *p*-nitrotoluene. As much care as possible was taken in making this *m/e* assignment in view of the possibility of formation of *p*-nitrobenzyl ion with *m/e* 136. So far as we can tell, no ion with *m/e* 136 is formed.

The new reactions occurring in *p*-nitrobenzyl acetate are postulated to be

$$O_2NC_6H_4CH_2OAc + t\text{-}C_4H_9^+ \longrightarrow \underset{m/e\ 252}{O_2NC_6H_4CH_2OAc \cdot C_4H_9^+} \quad (5)$$

$$O_2NC_6H_4CH_2OAc \cdot C_4H_9^+ \longrightarrow \underset{m/e\ 196}{O_2NC_6H_4CH_2OAcH^+} + C_4H_8 \quad (6)$$

$$O_2NC_6H_4CH_2OAcH^+ \longrightarrow \underset{m/e\ 138}{O_2NC_6H_4CH_3H^+} +$$



(7)

Since the ions with *m/e* 196 and *m/e* 138 increase in intensity with increasing temperature, we conclude that (6) and (7) involve activation energies. The question of the structures of the *m/e* 252, 196, and 138 ions, and particularly the point of attachment of the $t\text{-}C_4H_9^+$ ion or proton, remains very much open. The occurrence of (7) can be rationalized most easily if the proton is considered to be attached to one of the oxygens in the nitro group, and the ion formula given in Table III is written as if this were the case. However, this is not meant to imply that attachment of the proton to the acetoxy group of *p*-nitrobenzyl acetate does not occur. In any event, it is obvious from the large intensity observed at low temperatures for the *p*-nitrobenzyl acetate–butyl complex ion that the presence of the nitro group very

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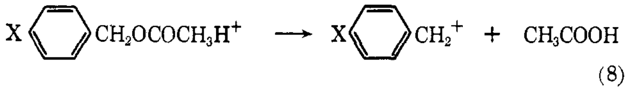
(6) D. Weeks and F. H. Field, unpublished results.

profoundly affects the nature of the electrophilic attack of the *t*-butyl ion. The different behavior observed may be the result of attack of the *t*-butyl ion on the nitro group, or it may decrease the proton affinity of the carboxyl group sufficiently to affect the nature of the reaction.

Kinetic Considerations. We showed in the previous work[1] that rate constants for reactions analogous to (2) can be obtained from appropriate intensities in the spectra of a compound. From measurements at different temperatures, activation energies and preexponential factors can be evaluated.

We are concerned with the rate constants for the reaction



(8)

where X is methoxy, methyl, fluoro, chloro, and nitro. We give in Figure 1 as illustration the Arrhenius plot applicable to (8) when X is F. As was mentioned earlier, replicate measurements have been made using repeller voltages of 5.0 and 10.0 V, and the data points corresponding to the two different conditions are represented in Figure 1 by different symbols. To take into account the possibility that the kinetics are affected by the repeller voltage, the data were fitted by a multiple regression analysis to a line, the equation of which is

$$\log k = A + \frac{B}{T} + CV \qquad (9)$$

where V = repeller volts. The values of the constant C for the different compounds obtained from the analyses varied from 0.03 to 0.11. Thus a small dependence of the rate constant upon the repeller voltage does in fact exist, and the two lines drawn through the points in Figure 1 correspond to (9) evaluated for repeller voltages of 5.0 and 10.0 V.

The preexponential factors, A, are obtained directly from the intercepts of (9), and the activation energies are obtained from the regression coefficients B. The kinetic quantities thus obtained are free from the influence of the repeller voltage V. The values of the kinetic quantities obtained for the several compounds are given in Table IV. The uncertainties associated with the activation energies are calculated from twice the standard error in the regression coefficients B, and thus they correspond to 95% confidence limits. The uncertainties associated with the log k quantities are calculated from the uncertainties given for the activation energies by assuming that all of the uncertainties should be associated with log k. The activation energies and log k values are used to calculate values of log k_{300} where k_{300} is the rate constant at 300°K. These values are also given in Table IV. The kinetic quantities for unsubstituted benzyl acetate are taken from ref 1. As was mentioned earlier, even at the highest temperature attainable in the mass spectrometer (254°) no decomposition of protonated *p*-nitrobenzyl acetate to nitrobenzyl ion was observed, and we assume for the sake of discussion that this is the consequence of a very high activation energy for the process. Our experiments are such that we could easily detect a relative intensity of nitrobenzyl ion of 1%, and assuming a log A value of 13, the failure to observe the nitrobenzyl ion corresponds to a minimum value for the activation energy of 24 kcal/mole, and this figure is included in Table IV.

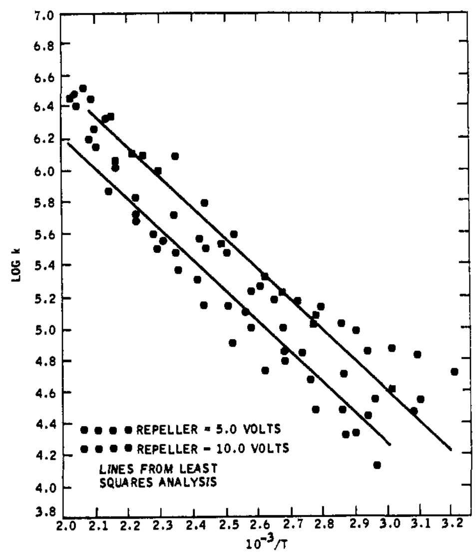


Figure 1. Log k *vs.* $1/T$ for *p*-$FC_6H_4CH_2OCOCH_3H^+ \rightarrow$ *p*-$FC_6H_4CH_2^+ + CH_3COOH$.

Table IV. Kinetic Quantities for *para*-Substituted Benzyl Acetates

Substituent	E_a, kcal/mole	Log A	Log k_{300}
CH_3O	4.3 ± 0.7	9.0 ± 0.5	5.9
F	9.0 ± 0.7	9.8 ± 0.5	3.3
CH_3	10.3 ± 1.0	12 1.± 0.7	4.6
H[a]	12.3 ± 0.9	11.2 ± 0.7	2.3
Cl	12.5 ± 0.9	11.8 ± 0.6	2.7
NO_2	>24[b]	13[c]	<−4.5

[a] Taken from ref 1. [b] Calculated from failure to observe formation of $NO_2C_6H_4CH_2^+$ at 254°. [c] Assumed.

One may observe from Table IV that significant trends with the nature of substituent occur for all the quantities tabulated. As is well known, a useful way of correlating substituent effects in condensed phase chemistry is to apply the Hammett equation.[7] The application of this concept to reactions induced by electron impact in the mass spectrometer has been made in recent years, and a useful review of this work has been given by Bursey.[8] We give in Figure 2 a conventional Hammett plot for the substituted benzyl acetates; that is, we plot log k_X/k_H against the quantity σ^+ devised by Brown and Okamoto.[9] The rate constants used are the 300°K values given in Table IV. The line drawn through the points was fitted by eye, and because of the approximate nature of the point for the nitro substituent, no weight was given to it in drawing the line.

It is clear that except for the nitro compound a correlation exists between log k_X/k_H and σ^+, and the magnitude of the scatter of the points is within acceptable limits. The point for the nitro substituent deviates from the line significantly, but even so it may be seen that the effect of the nitro substituent is qualitatively in the direc-

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(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184 ff.

(8) M. M. Bursey, *Org. Mass Spectrom.*, 1, 31 (1968).

(9) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958).

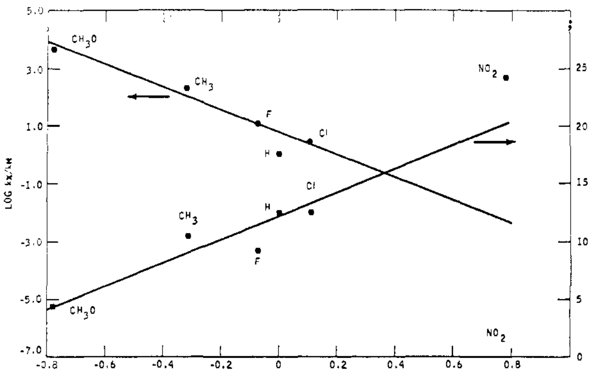

Figure 2. Correlation of log k_x/k_H and E_a with σ^+.

tion one would expect. The slope of the line, which is the term ρ in the Hammett equation, is $\rho = -3.9$. Values of ρ in the range -3 to -5 are observed[10] in condensed phase reactions in which the formation of carbonium ions may plausibly be considered to be the rate-determining process. The fact that our value of ρ for a gas phase reaction falls within this range is perhaps significant.

As a matter of interest we also include in Figure 2 a plot of the several activation energies, E_a, against σ^+. A correlation exists, although with more scatter than is found in the log k_X/k_H plot. One also finds in this plot a large deviation from the line of the point for the nitro substituent. The slope of the line is $\Delta E_a/\Delta\sigma^+ = 10.1$ kcal/mole/σ^+, and for purposes of comparison we have converted this value into the ρ value of the conventional Hammett relation. The temperature chosen for the conversion is 300°K, and the assumption is made that the preexponential factors for the various reactions are identical. The value thus obtained is $\rho = -7.4$, which is to be compared with $\rho = -3.9$ from log k_X/k_H *vs.* σ^+.

The difference between the two values of ρ may formally be ascribed to the fact that the Hammett relationship is a linear free energy relationship, but the plot of E_a *vs.* σ^+ is a linear enthalpy relationship. The difference between the two is the preexponential factor A, and it may be seen from Table IV that the preexponential factors tend to decrease as the activation energy decreases. The one exception to the trend is methylbenzyl acetate. The change in A is included in the log k_X/k_H *vs.* σ^+ relationship and accounts for the smaller value of ρ. Interrelationships between activation energies and preexponential factors are oftentimes encountered in kinetic considerations, and Ritchie and Sager[11] give an extended discussion of the question of interrelationship between enthalpies and entropies in the context of Hammett equation considerations. No very clear-cut conclusion about the matter can be drawn.

We can offer no very meaningful explanation for the observed variation in the preexponential factors. It is, however, necessary to discuss one possible explanation for the low frequency factors observed in the fluoro- and methoxybenzyl acetates; namely, that because of the relatively low pressure and limited number of collisions occurring in the ionization chamber of the mass spectrometer, reactions such as (2) follow second-order kinetics. That is, the rate of reaction depends upon the rate of collisional activation. This effect is of importance here because, as Benson[12] points out, the activation energy of a unimolecular reaction depends somewhat upon whether it is in the pressure region in which first- or second-order kinetics are followed.

To investigate this point we have in this work studied the effect of varying the i-C_4H_{10} pressure on the decomposition of protonated p-fluorobenzyl acetate, and previously we reported[1] a similar experiment with unsubstituted benzyl acetate. The pressure range used was 0.5–1.3 Torr with p-fluoro compound and 0.5–1.0 Torr with the unsubstituted compound. While these ranges are limited by experimental factors, we still think it significant that no increase in the amounts of decomposition of the protonated molecule ions resulted from the increase in i-C_4H_{10} pressure.

Further to treat the matter, we have calculated the magnitude of the preexponential factor for the decompositions of the $(M + 1)^+$ ions assuming the reaction to be following pure second-order kinetics. The calculations were made taking $P_{i\text{-}C_4H_{10}} = 0.70$ Torr, collision cross section for the ions with i-$C_4H_{10} = 50 \times 10^{-16}$ cm^2, and ion velocity $= 3 \times 10^5$ cm/sec. One obtains a value of the preexponential factor $A = 3 \times 10^7$, which is appreciably smaller than the smallest value of A given in Table IV, log $A_{CH_3O-} = 9.0$, $A_{CH_3O-} = 1 \times 10^9$.

Thus the evidence available leads one to believe that the decomposition rates of the protonated benzyl acetates are not determined to any significant extent by the rate of collisional activation; that is, second-order falloff phenomena do not seem to be occurring to a significant extent. If this be the case, the variation in the preexponential factors given in Table IV must be accepted (at least tentatively) as real, even though its significance with respect to the relationship between molecular structure and reactivity is presently not known. Moreover, it may be concluded with greater certainty that the activation energies given in Table IV are not significantly subject to errors resulting from the occurrence of second-order falloff.

It is evident from Figure 2 that neither the rate nor the activation energy for protonated p-nitrobenzyl acetate decomposition correlates well with the corresponding quantities for the other substituted benzyl acetates. We can offer no definitive explanation for the behavior of this compound, but we pointed out earlier that its behavior is anomalous in that it protonates with much more difficulty than do the other compounds investigated, and at the highest temperatures the protonated p-nitrobenzyl acetate ion decomposes to produce an ion with m/e 138, which we interpret as being the protonated nitrotoluene ion. No p-nitrobenzyl ion seems to be formed. The kinetic quantities plotted in Figure 2 are minimum and maximum values (rates and activation energies) based on this lack of formation of the p-nitrobenzyl ion. However, we cannot exclude the possibility that in this compound the protonation occurs on the nitro group rather than the acetoxy group, in which case

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(10) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 97.

(11) C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitweiser, Jr., and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1964, p 352 ff.

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 230–239.

no correlation with the other benzyl acetates should be expected. The formation of the *m/e* 138 ion is compatible with the occurrence of protonation on the nitro group. The nmr spectrum of *p*-nitrobenzyl acetate dissolved in HSO_3F-SbF_5 indicates that some protonation occurs on the nitro group.[13] On the other hand, we have obtained the chemical ionization mass spectrum of *p*-nitrobenzyl acetate using methane as reactant, and we observe that *p*-nitrobenzyl ion is formed with this strongly acidic reagent. This suggests that protonation can occur on the acetoxy group under certain conditions. The evidence does not permit a clear understanding of the behavior of this compound, but obviously a number of possible reasons exists for the lack of correlation by the Hammett relationship.

It is of interest to compare our results with a Hammett correlation of the ionization potentials of substituted benzyl radicals made by Lossing and coworkers.[14] The slope of the plot of ionization potentials against the Brown σ^+ values is $\Delta E/\Delta\sigma^+ = 27$ kcal/mole/σ^+, and if this is converted to the conventional Hammett relationship involving the ratio of rate constants (calculated assuming a constant preexponential factor) one obtains the value $\rho = -19.6$. These values should be compared with the value $\Delta E_a/\Delta\sigma^+ = 10.1$ kcal/mole/σ^+, which corresponds to the value $\rho = -7.4$. We are unable to reconcile these differences in the ρ values obtained by the two different experiments. In both cases free, gaseous carbonium ions are produced, and we can think of no reason why the effect of substituents on the energies of the ions would be different in the two experiments. Conceivably the difference in behavior might be due to a different substituent effect in the reactant species involved in the two experiments. Lossing and coworkers point out that the substituent effect on benzyl free radicals is negligibly small, and consequently the observed substituent effect must result completely from effects in the benzyl ion. Unfortunately, we have no information concerning the magnitude of substituent effects on the energies of the protonated molecule ions involved in the chemical ionization reactions, and thus we have no evidence to exclude the possibility that the small observed substituent effect results from compensatory effects in protonated benzyl acetate ion and in the product benzyl ion. However, if the protonation occurs on the acetoxy group as we postulate, there is no obvious mechanism by which a resonance effect can be transmitted from a *para* substituent on the benzene, and the distances are such that a significant inductive interaction does not seem very probable.

Because of this disagreement between the chemical ionization and the ionization potential experiments, the present results cannot be interpreted as support for the hope[1] that the activation energies for the decompositions of protonated acetates would be exact, quantitative measures of the differences in energies of the ions produced in the decompositions. However, it is clear that the qualitative trend in the activation energies (even including *p*-nitrobenzyl acetate) is in accordance with the known energies of the ions, and the Hammett correlation which is found for all of the compounds other than the nitro-substituted compound indicates that the activation energies obtained from these measurements are meaningfully related to the relative energies of the different ions. The rather surprising similarity of the ρ values obtained in the chemical ionization experiments and in condensed phase ionic processes leads one to think that the chemical ionization results will be quite applicable to condensed phase phenomena. One can hope that further work will yield a better understanding of the discrepancy between the gas phase results found using chemical ionization and ionization potential techniques.

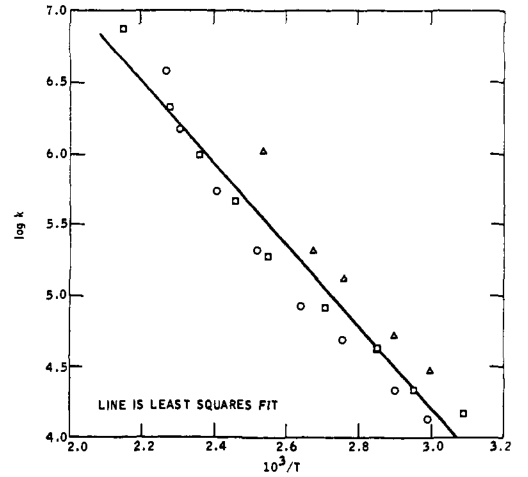
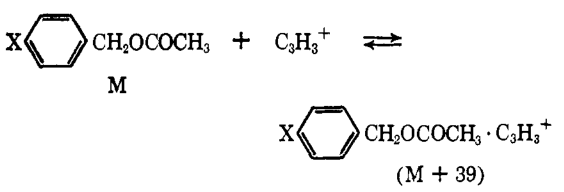


Figure 3. Log *k vs.* 1/*T* for $p\text{-}NO_2C_6H_4CH_2OCOCH_3 \cdot C_4H_9^+ \rightarrow p\text{-}NO_2C_6H_4CH_2OCOCH_3 \cdot H^+ + C_4H_8$.

We mentioned earlier and showed in Table III that *p*-nitrobenzyl acetate exhibits a $(M + 57)^+$ ion at *m/e* 252 which is temperature dependent, and we postulate that (5) and (6) are involved in its formation and disappearance. We can calculate rate constants for (6), and Figure 3 is an Arrhenius plot of these rate constants. The kinetic quantities obtained from the plot are $E_a = 13.1$ kcal/mole and $\log A = 12.8$. We do not know the significance of this activation energy, but the overall behavior suggests the possibility that the protonation of *p*-nitrobenzyl acetate by $t\text{-}C_4H_9^+$ is an endothermic process, and the activation energy may then be a measure of the endothermicity. None of the other benzyl acetates studied has a significant amount of $(M + 57)^+$ ion in its spectrum, and the conclusion to be drawn is that the presence of the *p*-nitro group decreases the proton affinity of the molecule. We discussed above the possibility that the low value of ρ applying to Figure 2 results from changes in proton affinity with substituent, and these considerations are based to a considerable extent on the behavior of *p*-nitrobenzyl acetate.

Equilibrium Considerations. Equilibrium reactions analogous to (3), which involves the formation of the protonated dimer ions, have been observed for all the substituted benzyl acetates studied except *p*-methoxybenzyl acetate, and the reaction



(10)

producing $(M + 39)^+$ ions has been observed for all the

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[13] Communication from G. M. Kramer of this laboratory.

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

Table V. Thermodynamic Quantities for *para*-Substituted Benzyl Acetates

Substituent	$(M + 1)^+ + M \rightleftarrows (2M + 1)^+$			$M + 39^+ \rightleftarrows (M + 39)^+$		
	ΔH^a	ΔS^b	$K_{P300}{}^c$	ΔH	ΔS	K_{P300}
CH_3–	−4.5 ± 1.9	16.8 ± 6.2	9.1×10^6	−7.8 ± 1.1	8.0 ± 3.8	2.6×10^7
Cl–	−2.9 ± 1.8	21.4 ± 5.9	6.8×10^6	−7.3 ± 3.6	8.5 ± 11.9	1.6×10^7
F–	−4.3 ± 1.1	17.3 ± 1.2	7.8×10^6	−7.8 ± 1.8	7.8 ± 6.0	2.3×10^7
NO_2–	−7.7 ± 1.5	9.2 ± 4.8	4.1×10^7			

[a] ΔH in kcal/mole. [b] ΔS in cal/deg mole. [c] Standard state for K_P is 1 atm.

substituted benzyl acetates except *p*-methoxybenzyl acetate.

The failure of *p*-methoxybenzyl acetate to form a protonated dimer is understandable in view of the very large rate constant for the decomposition of the protonated monomer: the protonated monomer decomposes so rapidly that it has little opportunity to collide with a *p*-methoxybenzyl acetate molecule. We can offer no explanation for the failure of this compound to form a $(M + 39)^+$ ion.

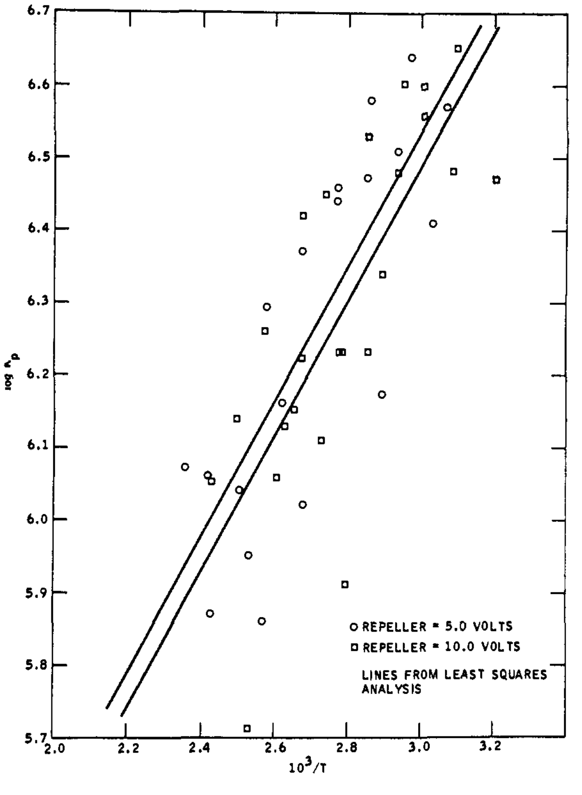

Figure 4. Log K_p *vs.* $1/T$ for $p\text{-}FC_6H_4CH_2OCOCH_3H^+ + p\text{-}FC_6H_4CH_2OCOCH_3 \rightleftarrows (p\text{-}FC_6H_4CH_2OCOCH_3)_2H^+$.

Since the purpose of this work is primarily to study the kinetics of the decompositions of protonated molecule ions of the various substituted benzyl acetates, experiments designed specifically for the elucidation of equilibrium phenomena have not been undertaken. In particular, no studies have been made of the effect of varying the pressures of the several substituted benzyl acetates to determine whether equilibria had been established completely. However, we showed[1] that the protonated monomer–dimer equilibrium was indeed established in unsubstituted benzyl acetate, and the conditions and behavior involved in the present measurements do not differ from those involved in the benzyl acetate measurements. Consequently we have used the observed ion intensities to calculate a quantity which we shall refer to as an equilibrium constant. For the $(M + 1)^+$–$(2M + 1)^+$ equilibrium we write

$$K_P = \frac{I_{(2M+1)^+}}{(I_{(M+1)^+})(P_{XBzAc})} \tag{11}$$

where P_{XBzAc} is the pressure of the substituted benzyl acetate in atmospheres. An analogous expression may be written for the formation of the $(M + 39)^+$ ions.

Values of K_P have been calculated for the various equilibria at different temperatures, and van't Hoff plots have been constructed. From these various thermodynamic quantities may be calculated. A typical plot (for the $(M + 1)^+$–$(2M + 1)^+$ equilibrium for *p*-fluorobenzyl acetate) is given in Figure 4, and the various thermodynamic quantities obtained are given in Table V. The lines through the experimental points were obtained by a multiple regression analysis involving the reciprocal temperature and the repeller voltage (analogous to (9)). The two lines drawn in Figure 4 are the regression lines for the two repeller voltages, and it may be seen that the dependence of log K_P on this quantity is not very strong. The enthalpies obtained from the slopes of the lines are independent of repeller voltage. The uncertainties in the enthalpies given in Table V are obtained from twice the standard error in the regression coefficient, and thus they correspond to 95% confidence limits. The uncertainties associated with the entropies are calculated from the uncertainties given for the enthalpies by assuming that all of the uncertainties in the equilibrium constants should be associated with entropies. Also given in Table V are values of K_{P300}, the value of the equilibrium constant at 300°K. The behavior of the $(M + 39)^+$ ion for *p*-nitrobenzyl acetate was rather erratic, and while we are of the opinion that this ion is indeed formed, it did not seem wise to calculate thermodynamic quantities for it.

The quantities of greatest interest in Table V are the positive values of ΔS found for both equilibria with all of the compounds. Positive values of ΔS have been found previously[1] for equilibria in unsubstituted benzyl acetate and *t*-amyl acetate, and the present results are in keeping with these findings. The reactions forming the $(2M + 1)^+$ and the $(M + 39)^+$ ions both involve the association of two molecular entities, and because of the loss of three translational degrees of freedom one would *a priori* expect values of ΔS for reactions on the order of −30 cal/deg mole. Thus the observed ΔS values are anomalously high in the amount of 30–50 cal/deg mole. These results are very difficult to accept, but if they result from some kind of experiment error or artifact, it is indeed a well-hidden one. The results in Table V are also of interest in that except for the *p*-nitrobenzyl acetate (which seems uniformly to behave anomalously) no significant effect of substituent on the thermodynamic quantities exists for either reaction, but a difference does seem to exist between the values for each reaction. Further comment on this observation is not warranted at present.

Acknowledgment. The author wishes to thank Mr. W. A. Petersen, Mr. W. C. Ehrhardt, and Mr. F. C. Petronis for making the measurements reported here. He also wishes to acknowledge with thanks valuable consultations with Professor H. C. Brown of Purdue University.

The Cyclopropylmethyl Cation Series Subjected to the Complete Neglect of Differential Overlap Approximation (CNDO)

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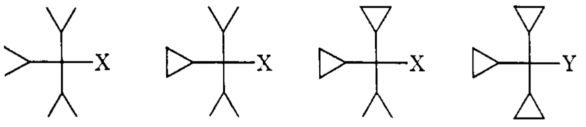
Abstract: The calculations show that the introduction of one cyclopropyl group on methyl cation does not appreciably diminish the charge density on the central carbon atom, but the charge densities on the ring carbons are changed dramatically. The variation of the charge on the ring carbon atoms with successive replacement of hydrogen atoms of methyl cation by cyclopropyl groups suggests a homoallylic type structure. This effect is most pronounced for tricyclopropylmethyl cation.

It is well known that a cyclopropyl group is unusually effective in stabilizing a positive charge on an adjacent carbon. Although the nonclassical explanation for this unusual stabilizing ability is attractive, it has not received unquestioned acceptance.[2] Hart has shown that the replacement of an isopropyl group by a cyclopropyl group in triisopropylmethyl esters increases the solvolysis rate in a regular fashion.[3] The magnitude of the effect produced by successively substituting a cyclopropyl for an isopropyl group becomes more dramatic when one considers that (a) cyclopropyl groups are inductively electron withdrawing relative to an isopropyl group,[4] (b) the steric requirements of the cyclopropyl group are less than of an isopropyl group. Thus, one would expect a slower rate of solvolysis for the cyclopropyl analogs because of less nonbonded repulsions in the ground state relative to the planar transition state for a first-order reaction. A qualitative explanation proposed by Hart to explain the unusual solvolysis rates was set forth in terms of electron delocalization into the cyclopropyl rings.[3b]

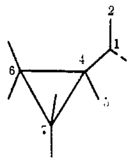


K_{rel} 1 246 2.4×10^4 $\sim 2.0 \times 10^7$

80% aqueous dioxane at 60°

X = *p*-nitrobenzoate; Y = benzoate

In order to ascertain whether this qualitative explanation is consistent with molecular orbital calculation using a fairly sophisticated method, an electron density study was undertaken on the cyclopropyl methyl cation system using the CNDO/2 approximation (complete neglect of differential overlap).[5] Wiberg has applied this approximation to the unsubstituted cyclopropylmethyl cation in both the "bisected" and "in-plane" conformations.[6a] It was concluded from these calculations that the "bisected" conformation (one in which the plane of atoms 1, 2, 3, 4, and 5 bisects the C_6–C_7 bond) was preferred by 8 kcal/mol and that 51.3% of the charge remained outside of the ring. Similar results were obtained by the extended Hückel method.[7]



In view of these findings, our CNDO/2 calculations were carried out on the methyl cation, the cyclopropylmethyl cation with C_s symmetry, the dicyclopropylmethyl cation with both C_s and C_{2v} symmetry, and the tricyclopropylmethyl cation with C_{3h} symmetry. The results of this study are shown in Figures 1–5.

Experimental Section

The computations were carried out on a Burroughs B5500 computer using a Burroughs-ALGOL translation of the CNDO/2 program No. 91, obtained from the Quantum Chemistry Program Exchange (University of Indiana).[8] Although the program was

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(1) (a) Phillip F. du Pont Predoctoral Fellow, 1968–1969; (b) National Institutes of Health Predoctoral Fellow, 1968–1969.

(2) Review article: M. Hannack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(3) (a) H. A. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959); (b) H. A. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962); **86**, 2957 (1964).

(4) T. L. Brown, J. M. Sandri, and H. A. Hart, *J. Phys. Chem.*, **61**, 698 (1957).

(5) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

(6) (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (b) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).

(7) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

(8) (a) The description of the method is given in an article by J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); (b) O. Bastiansen, F. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964); (c) "Tables of Interatomic Distances and Configuration in Molecules