Chemical Ionization Mass Spectrometry. XVI. Temperature Effects in Tertiary Alkyl Acetates

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Abstract: The chemical ionization mass spectra of seven tertiary alkyl acetates have been determined at several temperatures using isobutane or isopentane as reactant gas. The major ions observed are the protonated molecular ions and the tertiary alkyl ions formed from them. Rate constants, activation energies, and frequency factors are given for the reactions forming the tertiary alkyl ions. The rate constants show an increase from *tert*-butyl acetate ($k_{350} = 4.5 \times 10^4$ sec^{-1}) to 2,3-dimethyl-2-pentyl acetate ($k_{350} = 5.9 \times 10^6$ sec^{-1}). The activation energies for these reactions are essentially constant (about 9 kcal/mol) and the changes in rates result from changes in the frequency factors and, hence, the entropies of activation of the reactions. These results have been rationalized on the basis of steric interactions in the protonated ester ions.

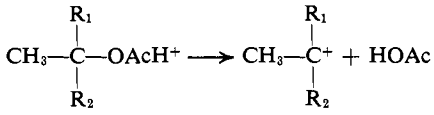
Temperature has been shown markedly to affect under certain conditions the chemical ionization mass spectra of organic esters, and from measurements of the temperature coefficients of the spectra information about the kinetics of the gaseous ionic reactions involved can be deduced.[1-4] This technique has a large potential usefulness for obtaining information about the reactions and properties of ions uncomplicated by the presence of solvent molecules. The technique is a new one, and much of the information obtained (rate constants, activation energies, and frequency factors for the reactions of gaseous ions) is without precedent. Certain assumptions are made in utilizing the technique, and prudence requires the exercise of caution in the immediate acceptance of the technique and the exercise of diligence in the accumulation of information to serve as a basis for its ultimate evaluation. This paper is directed to the latter requirement, but at the same time the information obtained is of much intrinsic value.

The important assumptions made are: (1) Sufficient collisions occur between ions, molecules, and surfaces in the ionization chamber of the mass spectrometer to establish thermal equilibrium in general and to maintain a Boltzmann distribution in the reacting ions. (2) The decomposition of $(M + 1)^+$ ions illustrated by

$$\mathrm{ROOCCH_3H^+} \longrightarrow \mathrm{R^+} + \mathrm{CH_3COOH} \qquad (1)$$

for protonated acetates is sufficiently independent of the $(M + 1)^+$ formation that the decompositions such as (1) can be treated as first-order reactions. (3) The presence of small electrical fields in the ionization chamber does not seriously distort the kinetics. (4) The reacting ion residence time can be calculated from ion mobilities obtained from the Langevin equation.[1,5] (5) The ion intensities observed are proportional to the ion concentrations within the ion chamber, and negligible ion decompositions take place outside the ionization chamber.

The results obtained to date[1-4] have yielded satisfactory correlations between structure and reactivity, and reasonably linear Arrhenius plots have been obtained by ion source temperature variations. In order further to test the validity of these postulates, and thus this approach to a study of gaseous ionic chemistry, we decided to examine a series of closely related tertiary alkyl acetates which differ only in the length and/or the degree of branching of the alkyl group. As a kind of zero-order approximation one expects the energy of the charged group in a tertiary carbonium ion (the tertiary ion group equivalent as defined by Franklin[6]) to be unaffected by substitution on the alkyl group at some distance from the charge center. Consequently, we expect also as a zero-order approximation that the kinetics of the reaction



$$\mathrm{CH_3}\!-\!\underset{\mathrm{R_2}}{\overset{\mathrm{R_1}}{\mathrm{C}}}\!-\!\mathrm{OAcH^+} \longrightarrow \mathrm{CH_3}\!-\!\underset{\mathrm{R_2}}{\overset{\mathrm{R_1}}{\mathrm{C}^+}} + \mathrm{HOAc} \qquad (2)$$

will be independent of the size of the alkyl groups R_1 and R_2, but perhaps with some dependence on the degree of branching. We would expect the chemical ionization kinetics obtained for (2) to exhibit little or no dependence on R_1 and R_2 if the temperature coefficient technique is free of artifacts and sources of systematic error. In short we make minimal variations in the structures of the acetates, and we expect to see minimal effects on the chemical ionization kinetics. However, in varying the size of the alkyl groups, the mass, the number of internal degrees of freedom, and possibly the amount of steric interaction of the protonated acetates are varied, and we thus have the opportunity of observing the effect of these factors on the chemical ionization kinetics. The acetate esters studied are those where $R_1 = CH_3$ and $R_2 = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, and s-C_4H_9; $R_1 = C_2H_5$ and $R_2 = n$-C_3H_7, a total of seven compounds.

Experimental Section

The experiments were carried out in the Esso chemical physics mass spectrometer which has been described elsewhere.[7] The ion source used was that designated in previous work[8] as source III,

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(1) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).
(2) F. H. Field, *ibid.*, **91**, 6334 (1969).
(3) D. P. Weeks and F. H. Field, *ibid.*, **92**, 1600 (1970).
(4) F. H. Field and D. P. Weeks, *ibid.*, **92**, 6521 (1970).
(5) E. W. McDaniel, "Collision Phenomena in Ionized Gases," Wiley, New York, N. Y., 1964.
(6) J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953).
(7) (a) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966); (b) F. H. Field, *ibid.*, **83**, 1523 (1961).
(8) D. P. Beggs and F. H. Field, *ibid.*, **93**, 1567 (1971).

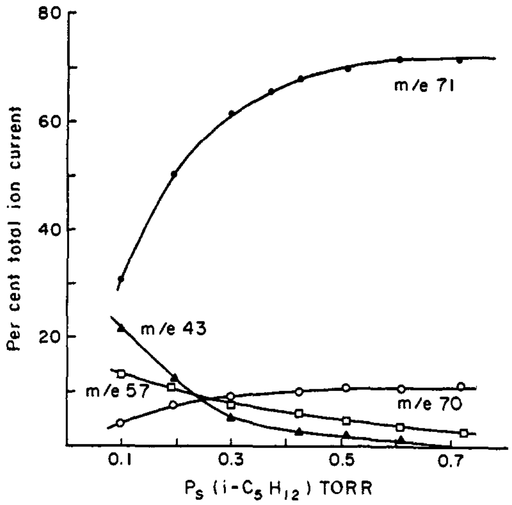

Figure 1. Variation of major ion intensities of isopentane with source pressure (source temperature 86°).

and it is constructed to allow cooling by blowing air or liquid nitrogen through a channel in the source. Thus by a combination of heating and cooling, wide-source temperature ranges can be covered. Isobutane was used as reactant for all the experiments save two, for which isopentane was used. The experimental and computational techniques were described previously[1] except for the following modifications. (1) The insertion of a fine mesh gauze between the focus electrode and the ground electrode[8] prevents ion accelerating voltage penetration into the ion chamber. The ion focus electrodes and repeller voltages were kept at the minimum values compatible with reasonable ion beam intensity and stability. Typically these were −5 V for the focus electrodes and +8 V for the repeller, both measured with respect to the ionization chamber. When operating under these conditions, the satellite peaks discussed previously[1] were not observed. (2) The partial pressures of the acetates in the ionization chamber were maintained at somewhat lower values than previously in order to reduce ion association reactions at low temperatures. This lessens the problem of how to treat these equilibria in the kinetic equations. Association ions formed in spite of this precaution are treated in the calculations as part of the initial concentration of the protonated ester ions. (3) In previous experiments ions were observed at *m/e* 113–116 at low temperatures. We know now that these ions result from association reactions occurring in the isobutane plasma alone, and hence in the calculations the intensities of these ions are excluded from the summation used to obtain the initial concentration of $(M + 1)^+$ ions. Ions with *m/e* 117 and 121 are also excluded from the $(M + 1)^+$ initial concentration summation for reasons given in the Discussion of this paper. (4) In the calculation of ion source residence times[1,5] the calculation of the Hassé *A* factor involved in the term D_{12} was wrongly taken previously to involve the sum of diameters of the ion and gas molecule. This should be the sum of the radii. Using the correct procedure, the Hassé *A* factor was estimated at one temperature for each of the esters studied. The temperatures used were in the middle of the temperature ranges involved for the several compounds, and this procedure is acceptable because the Hassé *A* factors are not very temperature dependent. The faulty calculation causes previously obtained[1-4] rate constants and frequency factors to be in error by somewhat less than a factor of 2.

Spectra at all temperatures were obtained in the present work at a reactant gas pressure of 0.70 Torr. Duplicate temperature coefficient runs were made for all the compounds. The reactant gases were passed through a bath of solid CO_2 and isopropyl alcohol to to remove water. Water, when present, forms association ions with the protonated acetates and complicates the calculations. The isobutane was Matheson instrument grade (99.5%) and the isopentane was Matheson Coleman and Bell spectroquality grade. The *tert*-butyl acetate was a commercial sample which contained no impurities detectable by glc. The other acetates were prepared by a standard procedure[9] from the commercially available alcohols. They were purified by glc, and no impurities were observed in the glc or mass spectra.

Results and Discussion

A. Reactant Gases. Difficulties are encountered in chemical ionization mass spectrometry when the compounds under study are closely related to the reactant ions and, in particular, when interesting ions from the additive occur at the same *m/e* values as reactant ions. When isobutane is used as reactant, substances producing important ions at *m/e* 57 cannot be studied. Also, at low source temperatures association reactions occur giving ions in the *m/e* 113–116 mass region, which may produce interferences. Therefore, to extend the range of this study, we investigated the use of isopentane as a reactant gas.

The major reactant ion in the high pressure spectrum of isopentane is *m/e* 71, presumably the *tert*-pentyl ion. The variation of the major ion intensities with pressure (Figure 1) is very similar to that of isobutane. The spectrum varies somewhat with temperature, and this temperature variation was measured over an appropriate temperature range. The isopentane spectrum contains ions of small intensity at *m/e* 56 and 57, and the intensities of ions at these *m/e* values produced from additive substances were corrected for the intensities from the isopentane. In making these corrections temperature variations were taken into account. Using this technique we were able, for example, to study the formation of *tert*-butyl ion from *tert*-butyl acetate.

An approximate calculation,[1] assuming the proton affinity of esters to be 195–200 kcal/mol, shows that the enthalpy change involved in the formation of $(M + 1)^+$ by protonation of the esters is exothermic, *i.e.*

$$CH_3COOR + t\text{-}C_4H_9^+ \longrightarrow CH_3COORH^+ + i\text{-}C_4H_8 \quad (3)$$

$$\Delta H = -(9\text{–}14)\ \text{kcal/mol}$$

This calculation used 176 kcal/mol as the best available[10] heat of formation of *tert*-butyl ion. It has recently been shown[11] that this value is too high. Using the new value of 167 kcal/mol for ΔH_f (t-$C_4H_9^+$) we get ΔH for reaction 3 to be 0-5 kcal/mol. Hence the formation of the $(M + 1)^+$ ion is even less exothermic than originally believed,[1] and it is thus even more probable than originally thought that the $(M + 1)^+$ ions can achieve a Boltzmann distribution of energies. A similar calculation for reaction 4 indicates $\Delta H =$

$$CH_3COOR + t\text{-}C_5H_{11}^+ \longrightarrow CH_3COORH^+ + i\text{-}C_5H_{10} \quad (4)$$

−(4-9) kcal/mol. Thus the tertiary pentyl ion should protonate the esters as does the *tert*-butyl ion. To the extent that reactions 3 and 4 have different exothermicities, comparison of results obtained with isopentane and isobutane as reactant gases conceivably may show the effects of different initial distributions of energy in the $(M + 1)^+$ ion.

B. Mass Spectra. The chemical ionization mass spectra of the tertiary esters used in this study were very similar to the *tert*-amyl acetate spectrum.[1] In all cases, initial protonation of the ester was followed by alkyl oxygen cleavage to form the tertiary alkyl ion.

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(9) E. C. Horning, Ed., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 142.

(10) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NBS-NSRD 26, U. S. Government Printing Office, Washington, D. C., 1969.

(11) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

This latter process is strongly temperature dependent, and, in some instances, in order to observe $(M + 1)^+$ ions, the ion source had to be cooled as described in the Experimental Section. This process gave rise to experimental difficulties below about 0°. Pressure surges were observed with both isopentane and isobutane at those temperatures, and this was accompanied by the occurrence of ion accelerating voltage breakdown. The results given in this paper were all obtained at temperatures somewhat higher than the onset temperatures for these difficulties. The strong temperature dependence of the spectra is illustrated for 2-methyl-2-hexyl acetate (Table I).

Table I. Chemical Ionization Mass Spectra of 2-Methyl-2-hexyl Acetate at Three Temperatures[a]

		% total ion current at T		
m/e	Ion	17°	49°	89°
95	$C_7H_{11}^+$ (?)			1.6
97	$C_7H_{13}^+$		2.4	1.9
98	$C_7H_{14}^+$	1.7	3.4	3.7
99	$t\text{-}C_7H_{15}^+$	25.2	59.9	72.9
100	^{13}C isotope	2.7	5.8	7.7
117	$C_4H_9OAcH^+$	10.6	10.0	7.2
121	$(CH_3COOH)_2H^+$			4.3
137	?	1.9		
155	?	1.8		
156	?	1.5		
157	$C_7H_{14}OAc^+$	1.5		
158	$C_7H_{15}OAc^+$	3.0		
159	$t\text{-}C_7H_{15}OAcH^+$	34.0	15.4	2.4
160	^{13}C isotope	4.9	3.5	
177	$t\text{-}C_7H_{15}OAcH \cdot H_2O^+$	6.0		
219	$t\text{-}C_7H_{15}OAcH \cdot HOAc^+$ (?)	1.7		
275	?	1.6		
317	$(t\text{-}C_7H_{15}OAc)_2H^+$	5.4		

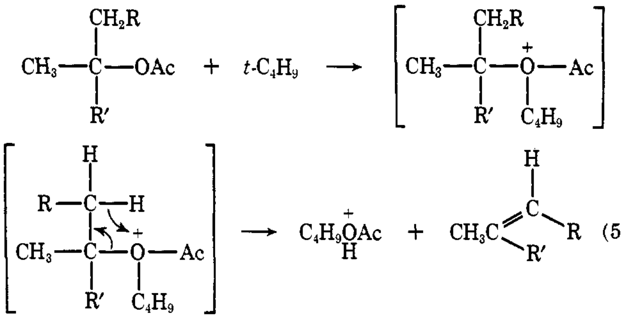
[a] Reactant = $i\text{-}C_4H_{10}$, $P_{i\text{-}C_4H_{10}}$ = 0.70 Torr, mol wt$_{t\text{-}C_7H_{15}OAC}$ = 158.

Table II. Mass Spectra of 2-Methyl-2-hexyl Acetate Using Different Reactant Gases[a]

		Rel intensities for reactant	
m/e	Ion	Isobutane	Isopentane
95	?		2.8
97	$C_7H_{13}^+$		3.0
98	$C_7H_{14}^+$		6.3
99	$C_7H_{15}^+$	40.7	37.4
100	^{13}C isotope	4.8	5.8
117	$C_4H_9OAcH^+$	12.1	
121	$(AcOH)_2H^+$ (?)		3.0
131	$C_5H_{11}OAcH^+$		3.3
158	$C_7H_{15}OAc^+$	3.4	2.8
159	$C_7H_{15}OAcH^+$	29.4	27.1
160	^{13}C isotope	5.1	5.5
177	$C_7H_{14}OAcH \cdot H_2O^+$	4.9	2.9

[a] P_{reactant} = 0.70 Torr, mol wt$_{t\text{-}C_7H_{15}OAc}$ = 158, T = 30°.

Table II compares the spectra obtained for 2-methyl-2-hexyl acetate using isobutane and isopentane as reactant gas. The spectra are very similar, and, most important from the point of view of this study, the intensities of the $(M + 1)^+$ and R^+ ions are similar using the two reactants. The change of reactant gas gives a clue to the identity of m/e 117 from *tert*-amyl acetate, which was previously not understood.[1] This ion is present in the spectra of all the acetates using isobutane as the reactant gas suggesting the acetate portion of the molecule is involved in its formation. However, when using *tert*-pentyl ion as the reactant ion, no m/e 117 is observed, but an ion is seen at m/e 131, suggesting the *tert*-pentyl group is involved in its formation. These observations are consistent with the following mechanism for formation of these ions (illustrated with *tert*-butyl ion).


(5)

Reaction 5 is a hitherto unreported analog of the transesterification reaction previously observed in methane chemical ionization spectra of esters,[12] *e.g.*

$$C_2H_5COOR + C_2H_5^+ \longrightarrow C_2H_5COOC_2H_5 \cdot H^+ + R'CH{=}CH_2 \quad (6)$$

No evidence was advanced previously[1] as to the mode of formation of m/e 121 in the *tert*-amyl acetate spectrum. This ion was observed in the spectra of all the acetates and it was relatively more intense when the ester pressure in the source was higher. The only possible ion of the mass is $(CH_3COOH)_2H^+$ formed by the protonation and subsequent association of acetic acid. This probably arises by slight thermal decomposition in the inlet system, but it is conceivable that the formation of the ion involves not understood complex ion molecule reactions. It also may result from a trace of acetic acid as impurity in the esters.

In accord with the findings, m/e 117 (or m/e 131) and 121 were not included in the initial $(M + 1)^+$ ion concentrations.

C. Kinetic Parameters for Tertiary Alkyl Ion Formation. The modified experimental approach described above was used to obtain rate constants for the decompositions of the protonated ester ions. The variation of the rate constants with temperature gives Arrhenius plots and hence the activation energies and frequency factors for the reactions.

A typical Arrhenius plot is illustrated in Figure 2, the compound being 2-methyl-2-hexyl acetate. It is of particular relevance to note that one point (at $1/T$ = 0.00360) is somewhat removed from the least-squares line, and as a matter of interest, the least-squares line was calculated first with this point included and then with it excluded. The effect of omitting this point from the calculations is shown in Table III, from which one sees that this one point affects E_a to the extent of 0.6 kcal/mol and A to the extent of a factor of about 3. The value of k_{350} is unchanged. This calculation illustrates the behavior we have usually encountered; namely, the activation energies and A values are sensitive functions of the experimental scatter, but the k_{350} values are less so and are thus more reliable. Obviously, our experience with kinetic studies of gaseous

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(12) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 4337 (1966).

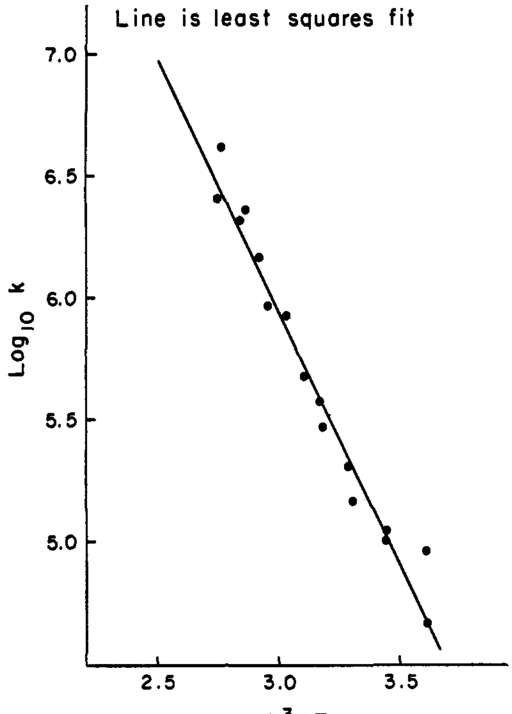

Figure 2. Log k *vs.* $1/T$ for $t\text{-}C_7H_{15}OAcH^+ \rightarrow t\text{-}C_7H_{15}^+ + HOAc$.

ions is no different from that encountered in other types of kinetic studies. It should be noted that in general the Arrhenius plots give rise to results in which more reliance should be placed on relative rather than absolute values.[13]

Table III. Kinetic Data for $t\text{-}C_7H_{15}^+$ Formation from $t\text{-}C_7H_{15}OAcH^+$

Calcn	E_a, kcal/mol	A, sec^{-1}	k_{350}, sec^{-1}
1[a]	9.4	1.3×10^{12}	1.7×10^6
2[b]	10.0	3.2×10^{12}	1.7×10^6

[a] Point at $1/T = 0.00360$ included. [b] Point at $1/T = 0.00360$ omitted.

We found that the rate constants obtained at temperatures below the lowest represented in Figure 2 (about 0°) did not form linear Arrhenius plots but rather exhibited positive deviations from linearity. At the lowest temperatures investigated (−20 to −30°) the rate constants changed but little with temperature. We speculate that this indicates the presence of nonthermal (nonequilibrium) factors in the $(M + 1)^+$ decomposition reactions. Possible examples of such factors are (1) collision-induced dissociations involving the irreducible electric fields associated with the ionization chamber and (2) dissociations of $(M + 1)^+$ ions occurring immediately following proton transfer from the reactant ion and before sufficient collisions occur to produce an equilibrium distribution.

Obviously, we must be quite concerned with the question of the extent to which such factors are operating at temperatures where the Arrhenius plots are linear and to what extent the results in the linear range are distorted by these factors. We have no unequivocal answer, but we point out that the protonated tertiary acetates decompose very easily, and the magnitudes of the thermal energies involved in the reactions at low temperatures are relatively small. Thus the magnitude of nonthermal factors which distort results at low temperatures will also be relatively small. At higher temperatures where the thermal energies are larger, the nonthermal factors will be of less importance and possibly negligible. The good linearity of the Arrhenius plots at higher temperatures over relatively large ranges of k values is an indication, although not a proof, that at these temperatures the distorting effects are negligible and the results obtained are trustworthy.

The kinetics of the decomposition of protonated *tert*-amyl acetate were investigated in the first chemical ionization temperature coefficient study from this laboratory,[1] and a comparison of the previous results with those obtained in the present investigation is given in Table IV. Two sets of values resulting from the present study are included, namely, set 1 obtained using calculational techniques identical with those used in the early work and set 2 obtained using improved calculational techniques as described in the Experimental Section of this paper. The k_{373} value included in set 1 is within a factor of 3 of the early value, which we deem to be acceptable agreement, especially in view of the fact that the apparatus used in the two studies differ somewhat as described in the Experimental Section. The agreement between the E_a values in set 1 and the early work is much poorer, as is the agreement of the A values. This is doubtless a manifestation of the greater difficulties encountered in obtaining accurate E_a and A values as described above, and except to reiterate the fact that somewhat different apparatus was used in the two studies, we have no explanation for the discrepancies. Better agreement can be obtained between results obtained with the same apparatus and in the same series of experiments, as is illustrated by the agreement between replicate runs made in the present work. For example, replicate runs done on different days with *tert*-butyl acetate both gave E_a values of 9.4 kcal/mol and A values of 2.9×10^{10} and 4.4×10^{10} sec^{-1}, and the corresponding log k_{350} values were 3.65 and 3.78.

Table IV. Kinetic Data for Formation of *tert*-$C_5H_{11}^+$ from $t\text{-}C_5H_{11}OAcH^+$

	E_a, kcal/mol	A, sec^{-1}	k_{373}, sec^{-1}
Set 1	9.5	1.1×10^{11}	2.5×10^5
Set 2	9.3	2.0×10^{11}	6.9×10^5
Previous work[a]	12.4	2.5×10^{12}	1.1×10^5

[a] Reference 1.

A comparison of the rate constants, activation energies, and frequency factors calculated for five tertiary acetates is given in Table V. These compounds have identical structures except for the length of one alkyl group. The rate constants (k_{350}) increase by a factor of nearly 40 between *tert*-butyl acetate and 2-methyl-2-hexyl acetate, but it remains essentially unchanged in proceeding to 2-methyl-2-heptyl acetate. The increase observed in k_{350} seems to result primarily from changes in the values of the A factors, since the E_a values found

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(13) G. R. Hulett, *Quart. Rev., Chem. Soc.*, **18**, 227 (1964).

Table V. Kinetic Data for *tert*-Alkyl Ion Formation from Protonated Acetates

Ion	E_a, kcal/mol	A, sec^{-1}	k_{350}, sec^{-1}
$(CH_3)_3C^+$	9.4	3.6×10^{10}	4.5×10^4
$(CH_3)_2C^+C_2H_5$	9.3	2.0×10^{11}	3.0×10^5
$(CH_3)_2C^+C_3H_7$	8.2	8.0×10^{10}	4.7×10^5
$(CH_3)_2C^+C_4H_9$	9.4	1.3×10^{12}	1.7×10^6
$(CH_3)_2C^+C_5H_{11}$	9.8	1.9×10^{12}	1.4×10^6

for the five compounds probably must be considered to be essentially the same within experimental error. The E_a value for 2-methyl-2-pentyl acetate is somewhat lower than the others, but we feel that this reflects the larger experimental scatter we observed with different runs of this compound rather than real difference in activation energies. The magnitude of the difference in the decomposition rates is depicted graphically in Figure 3 for *tert*-butyl acetate and 2-methyl-2-heptyl acetate, and one sees clearly the equality of the slopes and the difference in the A factors.

Thus, the increase in rate appears to be the result of some kind of entropy effect which is operating in the decompositions of these gas-phase ions. Indeed, it would seem unlikely that there would be much increase in inductive stabilization of the carbonium ion formed by simply lengthening one alkyl group, and any increase in stabilization resulting from inductive effects may be opposed by some loss of hyperconjugative stabilization energy (Baker–Nathan effect) by loss of the hydrogen atoms of the α-methyl groups. The expectation of a small energy effect is in accord with the essential constancy of the E_a values observed experimentally. On the other hand, examination of Dreiding models shows that replacement of one of the methyl groups of *tert*-butyl acetate by alkyl chains of increasing length leads to the possibility of larger steric interactions between the various groups. The formation of the planar tertiary carbonium ion eliminates the interactions with the acetate group and decreases the alkyl–alkyl interactions. More freedom of internal motion results, which would manifest itself in the entropies of activation (A factors) as is experimentally observed. However, it should be noted that steric interactions are fundamentally energetic interactions. For example, Benson[14] points out that the two gauche conformations of n-butane are 0.8 kcal/mol less stable than the trans conformation. Our experimental method should be sensitive to energies of this magnitude, but our results indicate that energy effects are not occurring.

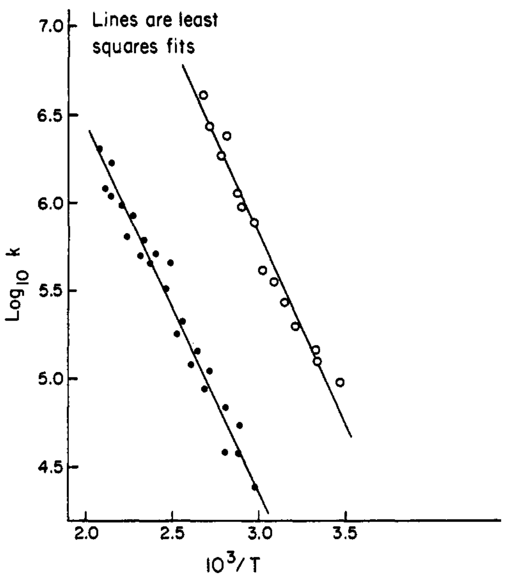
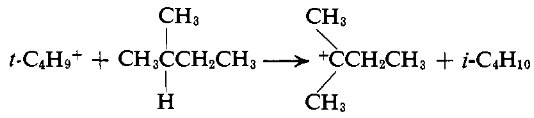


Figure 3. Log k *vs.* $1/T$ for $t\text{-}C_4H_9OAcH^+ \rightarrow t\text{-}C_4H_9^+ + HOAc$ (●) and $t\text{-}C_8H_{17}OAcH^+ \rightarrow t\text{-}C_8H_{17}^+ + HOAc$ (○).

A few comparisons of our results with those of previous investigations can be made. The most direct comparison is with a study of the kinetics of gas-phase ionic reactions made by Ausloos and Lias.[15] Using their radiation chemistry–deuterium tracer technique they have determined the relative rates of hydride ion transfer from 22 C_5–C_8 alkanes (predominantly tertiary) to *tert*-butyl ion. Variations of the rates with structure are observed, and of particular interest to us are their results in the series of compounds from 2-methylbutane to 2-methylheptane. An example of the reactions they observe is



$$t\text{-}C_4H_9^+ + CH_3\overset{CH_3}{\underset{H}{C}}CH_2CH_3 \longrightarrow {}^{+}\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3 + i\text{-}C_4H_{10} \qquad (7)$$

The relative rates they obtain in the above pentane–octane series are given in Table VI, and we also include our relative rates for the production of the corresponding ions produced from the protonated acetates by reaction 2.

Table VI. Relative Rates of Formation of *tert*-Alkyl Ions

Ion	Relative rates	
	Ausloos and Lias[a]	This work[b]
$(CH_3)_3C^+$		0.15
$(CH_3)_2C^+C_2H_5$	1	1
$(CH_3)_2C^+C_3H_7$	1.54	2.9
$(CH_3)_2C^+C_4H_9$	2.59	5.7
$(CH_3)_2C^+C_5H_{11}$	4.89	4.7

[a] Reference 15 using reaction 7. [b] Using reaction 2.

The agreement between the relative rates obtained in the two studies is remarkably good, but one must be very cautious with regard to the significance of the agreement. In particular, the carbonium ions are formed by a bimolecular reaction in the Ausloos–Lias work (reaction 7), but by a unimolecular reaction (2) in our work, and clearly the rates of the two kinds of reactions can be influenced by different factors. However, we think that one is justified in drawing the conclusion that the rates of gas-phase ionic reactions can be influenced by rather small changes in molecular structure. We point out as a matter of interest that Ausloos and Lias imply that the changes in rates that they observe in the series of compounds given in Table VI are to be ascribed to energy effects but, as discussed above, our rates seem to depend upon entropy effects. Further comment on this difference in origins of effects does not seem to be warranted at this time.

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(14) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 25–26.

(15) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, 92, 5037 (1970).

Table VII. Rates of (1) Acid Hydrolysis, (2) Alkaline Hydrolysis, and (3) Gaseous Ionic Decompositions of Tertiary Alkyl Compounds

Compound	Relative rates Acid hydrol[a]	 Alk hydrol[b]	 This work[c]
$(CH_3)_3CX$	1.0	1.0	1
$(CH_3)_2C(X)CH_2CH_3$	1.7	0.45	6
$(CH_3)_2C(X)CH_2CH_2CH_3$	1.6	0.42	15
$(C_2H_5)_2C(X)CH_3$	2.6	0.21	
$(C_2H_5)(C_3H_7)C(X)CH_3$			91

[a] Reference 16, X = Cl, solvolysis in 80% ethanol at 25°. [b] Reference 17, X = CH_3COO, solvolysis in H_2O at 20°. [c] X = CH_3COOH^+, source temperature at 25°.

Turning now to a comparison of our results with condensed phase results, we list in Table VII some pertinent values for acid hydrolysis (first-order reactions),[16] alkaline hydrolysis (second-order reactions),[17] and our gas-phase results. The acid hydrolyses exhibit small increases in rates analogous to those observed in the gas phase, but the magnitude of the differences is much less. An obvious possible cause for this difference in behavior is the presence of ion solvation in solution as contrasted with its absence in the gas phase, but much more gas-phase data will have to be accumulated before a detailed understanding of these behavioral differences is achieved.

Similar but reversed effects of structure are observed in the alkaline hydrolysis experiments, that is, the increasing length of the alkyl groups produces a decrease in rate. Presumably this results from a hindrance of the attack of the base by the longer alkyl chains and constitutes another piece of evidence that small structural changes can effect rates of ionic reactions. The magnitude of the effect in the alkaline hydrolysis case is also significantly less than that observed in the gas phase.

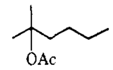
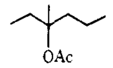
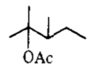
Table VIII. Kinetic Data for Formation of $C_7H_{15}^+$ from 2-Methyl-2-hexyl Acetate

Reactant gas	E_a, kcal/mol	A, sec^{-1}	k_{350}, sec^{-1}
Isobutane	9.4	1.3×10^{12}	1.7×10^6
Isopentane	9.0	5.3×10^{12}	1.3×10^6

Table VIII gives a comparison of results obtained for 2-methyl-2-hexyl acetate using isobutane and isopentane as reactant gases. The agreement between k_{350} values is good, and that between the E_a and A values is of the order usually observed in replicate determinations, and we deem it to be acceptable. These results indicate that the kinetic values obtained from our temperature studies of tertiary acetates are not highly sensitive to the identity of the reactant gas. Isobutane and isopentane are obviously similar compounds, but they differ in mass and number of internal degrees of freedom, and the acidities of the reactant ions formed from them (t-$C_4H_9^+$ and t-$C_5H_{11}^+$) may be slightly different. Furthermore, the calculational details used with the two reactants are slightly different. We think that the agreement obtained with the two reactants is evidence that the kinetic values obtained with the temperature coefficient chemical ionization technique are at least to a considerable extent intrinsic properties of the ions being studied (protonated tertiary acetates in this case), which is, of course, the situation one desires.

We give in Table IX kinetic results for three isomeric heptyl acetates, which differ in the amount of substitution or branching adjacent to the charge site. One sees that the most highly branched compound (2,3-dimethyl-2-pentyl acetate) exhibits the fastest decomposition reaction of all the compounds studied, and the next fastest is the 3-methyl-3-hexyl acetate. In solution it has been shown[16,18] that successive substitution of methyl groups for the β hydrogens of *tert*-butyl chloride increases the acid-catalyzed solvolysis rates of the compounds. For example, 3-methyl-3-pentyl chloride solvolyzes faster than 2-methyl-2-pentyl chloride (Table VII). Very extensive substitution for the β hydrogens produces marked acceleration of solvolysis rates. Thus, the solvolysis of $[(CH_3)_3C]_3COOCC_6H_4$-p-NO_2 occurs 13,500 times faster than the solvolysis of t-C_4H_9Cl.[18] Our gas-phase results are in keeping with one's expectations based on these solution results.

Table IX. Kinetic Data for *tert*-Heptyl Ion Formation from Isomeric Heptyl Acetates

Compound	E_a, kcal/mol	A, sec^{-1}	k_{350}, sec^{-1}
	9.4	1.3×10^{12}	1.7×10^6
	9.9	7.4×10^{12}	4.7×10^6
	9.0	2.4×10^{12}	5.9×10^6

Ausloos and Lias[15] have determined the effect of β substitution on the rates of gas-phase hydride abstraction reactions, and they find that the rates *decrease* as the degree of substitution increases. The hydride abstraction reaction 7 is bimolecular, and Ausloos and Lias attribute the rate changes to steric hindrance in the approach of the *tert*-butyl ion to the tertiary hydrogen to be abstracted. This factor is not operative in our unimolecular decomposition experiments, and thus the difference in behavior is not worrisome. However, perhaps it is fair again to draw the conclusion that both studies are in agreement in demonstrating that the rates of reaction of gaseous ions considered in these studies are dependent upon small structural variations.

Conclusion

We here have examined a series of compounds in which the structural variation is minimal with the expectation that the experimental method, if valid, should give kinetic results which exhibit a corresponding

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[16] A. G. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 92–94.

[17] M. S. Newman in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 222.

[18] P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, 90, 4421 (1968).

minimal amount of variation. The rate constants obtained vary somewhat, and the question arises whether the amount of variation should be interpreted as indicating flaws in the method. We can only state an opinion at this time because too many unknowns still exist for us to advance a definitive proof. However, we have shown that the kinetic variations we observed are not unreasonable by comparison with such other gas-phase and condensed-phase data which exists, and thus we are of the opinion that the experimental method is valid and thus that the observed variations are real properties. If this really be the case (as only more extensive work can show), it is clear that the chemical ionization method is a sensitive one which will reflect and be useful for the determination of small variations in molecular properties.

Acknowledgment. We wish to acknowledge with thanks the gift by Esso Research and Engineering Co., Linden, N. J., of the Esso chemical physics mass spectrometer.

An Electron Spin Resonance Study of a Spirotetraene and a Spirodienone Radical Anion

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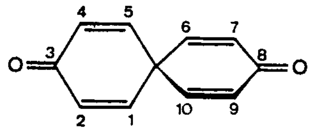
Abstract: Esr spectra of the radical anions obtained by electrolytic reduction of spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione (**1**) and spiro[5.5]undeca-1,4-dien-3-one (**2**) have been recorded and analyzed. The similarity in the hyperfine structures of two radical anions (large splittings by two protons only) points to an essential localization of the spin population on one dienone moiety in $\mathbf{1}^-$. This statement is substantiated by a simple HMO model. All-valence-electrons calculations account satisfactorily for the spin distribution in both $\mathbf{1}^-$ and $\mathbf{2}^-$, if a minute perturbation is applied to one of the oxygen atoms in $\mathbf{1}^-$. A reasonable assignment of the coupling constants to sets of equivalent protons could be based on the results of INDO calculations. This procedure also allows conclusions to be drawn about the mechanisms of spin transfer to hydrogen 1s orbitals. Although the singly occupied orbitals of $\mathbf{1}^-$ and $\mathbf{2}^-$ are essentially localized on one dienone moiety, the extent of delocalization over the spiro-carbon atom is considerable.

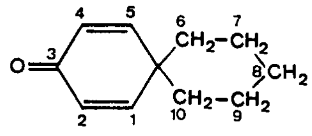
A theoretical treatment of spiroconjugation[2] has stimulated research in this field.[3-6] Although esr spectroscopy is a tool well suited to the study of π-electron delocalization in the radical ions of spiroconjugated compounds, to our knowledge, only one such study has been reported.[7] The observed spectrum of the radical anion of bis(2,2′-biphenylene)methane suggested that spin delocalization occurs over the two mutually perpendicular π systems; however, neither an analysis of the esr hyperfine structure nor a detailed discussion of the results was presented. It is noteworthy that spin delocalization over two formally orthogonal but not spiroconjugated π systems has been recently observed in the radical anion of 2,4,6,2′,4′,6′-hexa-*tert*-butylacetylene.[8]

A few years ago, spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione (**1**), a member of the class of compounds named "spirotetrenes," was synthesized.[3] Subsequently, a MO model of **1** was put forward, which is consistent with its electronic spectrum.[4]

In the present paper we wish to report an esr study of the radical anions of spirotetraene **1** and spiro[5.5]undeca-1,4-dien-3-one (**2**).[3]



1



2

Preparations of the Radical Anions and Analysis of Their Esr Spectra

The radical anions, $\mathbf{1}^-$ and $\mathbf{2}^-$, were obtained upon electrolytic reduction of the parent compounds in a 1 : 1 mixture of *N*,*N*-dimethylformamide (DMF) and acetonitrile (ACN), with tetraethylammonium perchlorate as supporting salt. The use of this mixture instead of pure solvent (DMF or ACN) provided an extension of the temperature range (down to −90°) for the generation of the radical anions and the observation of their

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(1) (a) Universität Basel; (b) deceased January 1972; (c) Universität Zürich.

(2) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. Zeiss, *ibid.*, **89**, 5215 (1967).

(3) G. Farges and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966).

(4) R. Boschi, A. S. Dreiding, and E. Heilbronner, *J. Amer. Chem. Soc.*, **92**, 123 (1970).

(5) G. Haas, P. B. Hubert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, **54**, 491 (1971).

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(7) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

(8) H. E. Zimmerman and J. R. Dodd, *J. Amer. Chem. Soc.*, 92, 6507 (1970).