

for both molecules, electrostatic forces must play an important role in the bonding.

The molecular structure can also be understood in terms of molecular orbitals. By a straightforward application of group theory, it is easy to construct 20 symmetrized molecular orbitals using as a basis set the 8 hydrogen 1s orbitals and the 12 beryllium and boron 2s and 2p orbitals. From an examination of the nodal planes of the orbitals of a D_{3d} model, one would expect six bonding orbitals ($2A_{1g} + 2A_{2u} + E_g + E_u$), three nonbonding orbitals ($A_{1g} + A_{2u} + E_u$), and six antibonding orbitals ($2A_{1g} + 2A_{2u} + E_g + E_u$). Distortion to a C_{3v} structure will only result in a slight mixing of the A_{1g} and A_{2u} functions and of the E_g and E_u functions. The six bonding orbitals can just accommodate the 16 available electrons and the electronic configuration for the ${}^1A_{1g}$ ground state can be written $(1A_{1g})^2(1A_{2u})^2(2A_{1g})^2(2A_{2u})^2(1E_u)^4(1E_g)^4$. The first two orbitals essentially localize four electrons in the terminal BH bonds and the remaining 12 electrons are distributed in the bridging regions. In the absence of the bridging protons, the electron density distribution would be cylindrically symmetric but addition of the protons so as to minimize electrostatic repulsions would give a D_{3d} configuration. It seems likely that the resistance to torsion would be small and thus the inac-

tive torsional frequency, ν_9 , is apt to be quite low. It is noteworthy that the electronic configuration is quite analogous to that of the isoelectronic molecule CO_2 [${}^1\Sigma_g^+ = (3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$] and thus the comparable coupling of the symmetric and asymmetric stretches noted earlier for the two molecules is understandable. Similarly, no electronic transitions would be expected in the visible region for BeB_2H_8 , a prediction supported by the transparency of the vapor down to 1900 Å.

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Chemical Ionization Mass Spectrometry. XVIII. Effect of Acid Identity on Decomposition Rates of Protonated Tertiary Alkyl Esters

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Abstract: Kinetic studies were made using the chemical ionization technique of the decompositions of four esters: *tert*-amyl *n*-propionate and *tert*-amyl *n*-butyrate using isobutane as reactant gas and *tert*-butyl *n*-propionate and *tert*-butyl *n*-butyrate using isopentane as reactant gas. It is found that the rates of decomposition are independent of the chain length of the acid portion of the ester. This is in contrast to the effect found previously of the length of complexity of the chain in the alcohol portion of the ester. As a further illustration of this effect, the rate of decomposition of gaseous protonated 3-ethyl-3-pentyl acetate was found to be faster than any acetate investigated so far.

We have recently reported¹ the results of a study of the decomposition kinetics of seven gaseous protonated tertiary alkyl acetates. The rates of decomposition of the protonated molecule ions to the tertiary alkyl ions and acetic acid were measured, and a good correlation with structure was obtained. In brief, as the size and complexity of the alkyl groups increased the rates of decomposition increased. In this study we have investigated the importance of the identity of the acidic function in the reaction. The compounds studied were *tert*-amyl *n*-propionate and *n*-butyrate using isobutane as reactant gas, and *tert*-butyl *n*-pro-

pionate and *n*-butyrate using isopentane as the reactant gas. Synthetic difficulties limited the extension of the study to acids with longer chains. 3-Ethyl-3-pentyl acetate was also measured, which provides a further link with the previous work.

Experimental Section

The experiments were carried out on the Esso Chemical Physics mass spectrometer which has been described elsewhere.¹⁻⁶ The

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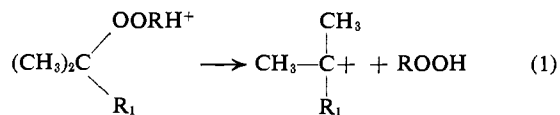
(6) (a) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 2621 (1966); (b) F. H. Field, *ibid.*, **83**, 1523 (1961).

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experimental and computational techniques were as described previously.¹ Duplicate temperature coefficient runs were made for all compounds. The compounds were prepared by a standard procedure⁷ from the commercially available alcohols and the acyl halide. They were purified by preparative glc, and their purity was checked by glc and mass spectrometry.

Results and Discussion

The chemical ionization mass spectra of the *tert*-alkyl esters corresponded well with those observed before.¹ The most important ions were the $(M + 1)^+$ ion and the ion formed by alkyl-oxygen cleavage (reaction 1). As described previously,¹ there appeared



to be some thermal decomposition of the esters in the heated inlet system. Thus the spectrum of *tert*-amyl butyrate, for example, showed an ion at m/e 89 corresponding to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}_2^+$. The protonated acid dimer was observed as was an ion at m/e 107, which would be $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}_2 \cdot \text{H}_2\text{O}^+$. The latter two ions were eliminated and m/e 89 was minimized by running the heated inlet at 100–115°.

When studying *tert*-butyl esters it is obviously necessary to avoid isobutane as the reactant gas, and we have used isopentane.¹ However, this does give rise to some *tert*-butyl ions, which have to be subtracted from the spectrum of the additive. Because of this correction to the *tert*-butyl ion intensity, the measurements with isopentane are intrinsically less accurate than the measurements with isobutane, and more emphasis is to be placed on the latter experiments.

The results obtained for the *tert*-amyl and *tert*-butyl *n*-propionate and *n*-butyrate are shown in Table I.

Table I. Effect of Lengthening Acid Chain on Decomposition Kinetics^a

Compound	k_{350} , sec ⁻¹	E_a , kcal/mol	A , sec ⁻¹
<i>t</i> -BuOOCCH ₃ ^b	4.4×10^4	9.4	3.4×10^{10}
<i>t</i> -BuOOCCH ₂ CH ₃	1.9×10^5	5.5	5.2×10^9
<i>t</i> -BuOOCCH ₂ CH ₂ CH ₃	2.9×10^4	9.4	2.1×10^{10}
<i>t</i> -AmOOCCH ₃ ^b	2.8×10^5	9.4	2.1×10^{11}
<i>t</i> -AmOOCCH ₂ CH ₃	4.2×10^5	8.4	7.6×10^{10}
<i>t</i> -AmOOCCH ₂ CH ₂ CH ₃	3.0×10^5	8.3	5.4×10^{10}

^a $P_{i-C_4H_{10}}$ or $P_{i-C_5H_{12}} = 0.8$ Torr. Repeller = 8 V. ^b From ref 1.

They are compared with the results for the acetates obtained previously under the same conditions.¹ Lengthening of the acid chain has little effect on the rate of reaction 1. The activation energies and frequency factors are in agreement within the range of experimental error usually observed. The activation energy for the *tert*-butyl *n*-propionate reaction is much lower than those observed in the other *tert*-butyl compounds, and the rate constant is somewhat higher. This result is an average of three separate determinations,





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

and in spite of our best efforts a rather large scatter in the data was encountered. It is quite possible as a consequence that the error in this result is relatively high. We have pointed out above¹ that measurements of *tert*-butyl esters are subject to difficulties, and we tend to discount the significance of the low activation energy found for *tert*-butyl *n*-propionate.

In contrast to the lack of dependence shown in Table I of the decomposition rates upon the length of the acid chain, we found previously¹ that the addition of one methylene group to the alcohol portion of the ester causes a substantial rate increase in all cases. We suggest that the rate increases observed with longer alcohol chains resulted from the higher entropies associated with the longer chains in the planar carbonium ion center of the products than in the nonplanar protonated ester reactants. No such change in configuration would be expected to occur in the acid portion of the protonated ester as a result of reaction, and thus the lack of dependence actually observed constitutes confirmatory evidence for our explanation of the phenomenon.

We wish to report here one further example of the effect on decomposition rates of the structure of the alcohol portion of protonated esters. We give in Table II the kinetic data for reaction 1 when the re-

Table II. Comparison of Kinetics of Decomposition of Tertiary Heptyl Acetates^a

Compound	k_{350} , sec ⁻¹	E_a , kcal/mol	A , sec ⁻¹
	1.7×10^6	9.4	1.3×10^{12}
	5.9×10^6	9.0	2.4×10^{12}
	4.7×10^6	9.9	7.4×10^{12}
	1.2×10^7	9.2	6.7×10^{12}

^a $P_{i-C_4H_{10}} = 0.8$ Torr. Repeller = 8 V. ^b From ref 1.

actant is protonated 3-ethyl-3-pentyl acetate. The results are compared with those of three other isomeric heptyl acetates determined previously.¹ The trend of faster reaction rates with more crowding around the reactive center is continued with this compound. We have noted before¹ that the relative reaction rates for these reactions are more significant in the sense of being less subject to error than the activation energies or frequency factors. Consequently, the values shown in Table II for E_a and A are too close for us to observe trends or to determine the roles played in establishing the observed rates.

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