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(13) Anisotropy in the absence of extra mobility could in principle account for the C-9 result, if the required number of linearly independent C-H vectors to detect anisotropic motion were not present at C-3 to C-8, but the requirement was met by the C-9 protons. However, it appears that in all reasonable conformations the requirement will be satisfied by C-7 or C-8 protons, so that very probably there is rotational mobility around the C-8–C-9 bond.

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Stability of Some C_7 Tertiary Alkyl Carbonium Ions

Sir:

The stabilities of gaseous carbonium ions have been investigated in this laboratory by pulsed, high-pressure mass spectrometric equilibrium measurements.[1,2] The temperature variation of the equilibria

$$t\text{-}C_4H_9{}^+ + RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + i\text{-}C_4H_{10}\ (RH = \text{tertiary } C_4\text{-}C_7 \text{ alkanes}) \quad (1)$$

were used to obtain the enthalpies of formation of C_4-C_7 carbonium ions. The values obtained for the C_7 ion derived from 2,4-dimethylpentane showed unexpected stability and an unexpectedly large negative entropy of formation. Similar results for C_7 alkyl ions have been obtained by Goren and Munson[3] using a continuous ionization mass spectrometric method.

We report here that C_7 alkyl carbonium ions undergo thermal decomposition at temperatures >480 K, and this decomposition caused the previously reported enthalpy and relative entropy for the carbonium ion derived from 2,4-dimethylpentane to be seriously in error. New and more accurate values for C_7 ions have been obtained and are given in this communication.

The decomposition reaction is

$$t\text{-}C_7H_{15}{}^+ \xrightarrow{k_2} t\text{-}C_4H_9{}^+ + C_3H_6 \quad (2)$$

The occurrence of this reaction is masked by reaction (−1) when the t-C_7H_{15} ion is produced from t-$C_4H_9{}^+$, but it is readily apparent when $C_3H_7{}^+$ from propane serves as the reactant ion. However, we confirm that eq 2 also occurs with isobutane as reactant gas, for when deuterated 2-methylhexane was used as the C_7 hydrocarbon, deuterated butyl ions were observed.

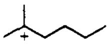
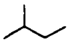
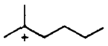
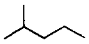
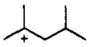
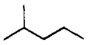
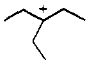
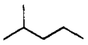
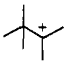
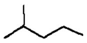
Both (2) and (−1) lead from the $C_7H_{15}{}^+$ to the $C_4H_9{}^+$ ion. The rates r_2 (= k_2) for eq 2 have been investigated in a study which will be reported separately, and the values of k_2 generally fall in the range $(1\text{-}20) \times 10^3$ s^{-1}. The rate for (−1) is usually much smaller than 10^3 s^{-1} under our conditions. For example, for RH = 2,4-dimethylpentane we find k_{-1} at 500 K from the values of k_1[4] and the value of the equilibrium constant for eq 1 to be 3.0×10^{-15} cm^3/(mol s). With a typical values of (i-C_4H_{10}) = 2×10^{16} mol/cm^3 this gives for the rate $r_{-1} = 0.6$ s^{-1}, which is $\ll (1\text{-}20) \times 10^3$ s^{-1}. Consequently, in the system of reactions 1 and 2, a constant ion ratio is established by the steady-state situation $r_1 = r_{-1} + r_2$ and

$$1 \equiv \left(\frac{r_{-1} + r_2}{r_1}\right)_{ss} = \frac{k_{-1}[t\text{-}C_7H_{15}{}^+][i\text{-}C_4H_{10}] + k_2[t\text{-}C_7H_{15}{}^+]}{k_1[t\text{-}C_4H_9{}^+][C_7H_{16}]} \cong \frac{k_2}{k_1}\frac{[t\text{-}C_7H_{15}{}^+]}{[t\text{-}C_4H_9{}^+][C_7H_{16}]};\ K_a = \frac{[t\text{-}C_7H_{15}{}^+]}{[t\text{-}C_4H_9{}^+][C_7H_{16}]} \quad (3)$$

where the apparent equilibrium constant K_a is defined as $K_a = k_2/k_1$ and is the quantity experimentally determined when $r_2 \gg r_{-1}$. In our previous work[2] $K_a[i\text{-}C_4H_{10}]$ was taken as the true equilibrium constant for eq 1. The temperature dependence of K_a is determined mainly by the activation energy of k_2 and is not related to the enthalpy change of eq 1. The unexpected thermochemical behavior of the 2,4-dimethylpentyl ion found previously appears to be an artifact caused by the unexpected and previously unknown thermal pyrolysis reaction (2).

Table I. Thermodynamic Values[a] from

$$R' + RH \rightleftharpoons R^+ + R'H$$

R^+	R'H	ΔH_f (R^+), kcal/mol	$\Delta\Delta S_f$ (R^+)[b] eu	D(R^+–H^-), kcal/mol
		150.5	32.7	231.8
		151.5	37.1	232.7
		148.4	29.3	231.2
		150.6	33.8	230.5
		144.5	15.8	228.1

[a] ΔH_f and ΔS_f values for neutral reactants from D. W. Scott, *J. Chem. Phys.*, **60**, 3144 (1974). $\Delta H_f(H^-)$ = 34.7 kcal/mol calculated from R. S. Berry, *Chem. Rev.*, **60**, 533 (1969). [b] $\Delta\Delta S_f(R^+) = \Delta S_f(R^+) - \Delta S_f(t\text{-}C_4H_9{}^+)$.

In our kinetic studies we observed that eq 2 does not proceed at observable rates below 450 K. We therefore measured thermodynamic values for several tertiary carbonium ions by the equilibrium method between 300 and 450 K. In these measurements mixtures of ~15% of the appropriate heptane in 2-methylpentane (2-MP) were used, at a total particle density of ≈1.5×10^6 mol/cm^3. These conditions assured that the reactant to product ion ratios in the equilibrium constant

$$K = \frac{I_{C_7H_{15}{}^+}}{I_{C_6H_{13}{}^+}}\frac{P_{2\text{-MP}}}{P_{(C_7H_{16})}} \quad (4)$$

remained within the dynamic range of the mass spectrometer throughout our experiments.

At least duplicate sets of equilibrium measurements at several temperatures were made for each system. The van't Hoff plots from each set of data exhibited an acceptably small amount of scatter. The reproducibility of the thermodynamic values was found to be within ±0.3 kcal/mol and ±3 eu except for the values for 2,4-dimethylpentyl ion, where differences of ±0.6 kcal/mol and 6 eu between four repetitive runs occurred for unknown reasons. The stability of the 2-methylhexyl ion was measured in the reaction system consisting of 2-methylpentane and 2-methylhexane and also in a three-component equilibrium system where, in addition, 2-methylbutane was also present. The results obtained in the two-component system were in satisfactory agreement with those obtained in the three-component system.

Values (averages of replicate measurements) of heats of formation, relative entropies, and hydride ion affinities for four tertiary C_7^+ alkyl carbonium ions are given in Table I. Two sets of values are given for 2-methylhexyl ion, where each set is obtained using a different reactant ion. The heats of formation of the reactant ions, i.e., 2-methylbutane and 2-methylpentane, had in turn previously been measured[2] in their reaction with isobutane. The agreement of the values for the 2-methylhexyl ions thus provides a measure of the internal consistency in a cycle involving four different equilibrium studies. The average of the two values of hydride affinity for this ion is virtually identical with the value obtained previously[2] for 2-methylpentyl ion (232.1 kcal/mol). Thus the additional methylene group does not affect the intrinsic stability of the ion. The hydride affinity of 2,4-dimethylpentyl ion is lower than that of 2-methylhexyl ion by an amount which is only marginally significant. The values for 3-ethylpentyl ion and 2,2,3-trimethylbutyl ion are somewhat lower. The results can be rationalized by the idea that the intrinsic ion energy is affected by the number of alkyl groups attached to carbon atoms α to the nominal charge center.

In evaluating the results as presented in Table I it must be remembered that the structures of ions in our reaction systems cannot be demonstrated. If rearrangements occur, our observed equilibrium constants are actually steady-state constants for reactions involving different isomers, and the thermodynamic values are incorrect to an unknown extent. This question requires further studies of ion structures by independent techniques.

Acknowledgment. This study was supported by a grant from the National Science Foundation. We thank Mr. R. Ciccarone for carrying out the measurements reported here.

References and Notes

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Catalyzed Oxidation Reactions. I. Picolinic Acid Catalysis of the Chromic Acid Oxidation of Isopropyl Alcohol[1]

Sir:

We have reported earlier that the oxidation of alcohols by chromic acid is accelerated by several orders of magnitude if it is carried out in the presence of oxalic acid[2] or α-hydroxy acids.[3,4] In these cases the fast reaction resulted not only in the oxidation of the alcohol but also of the added acid; these reactions thus represented examples of cooxidations.

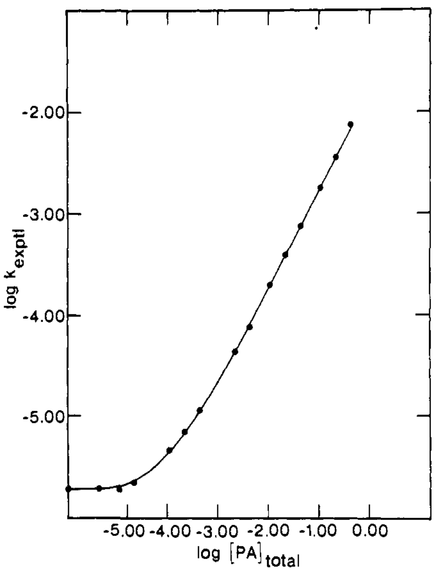

Figure 1. Picolinic acid catalysis: initial chromium(VI) = 4.50×10^{-4} M; isopropyl alcohol = 0.0186 M; H^+ = 0.1 M; ionic strength = 0.596 M; 25°.

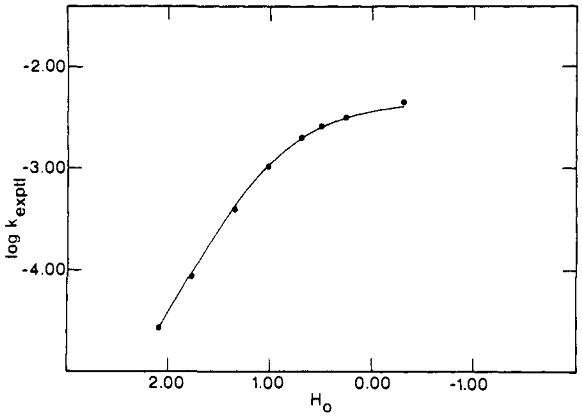

Figure 2. Acidity Dependence: initial chromium(VI) = 4.50×10^{-4} M; isopropyl alcohol = 0.0261 M; picolinic acid = 0.0472 M; ionic strength = 1.18 M; 25°. (Curve calculated from eq 1.)

Table I. Chromic Acid Oxidation Rates[a] with Pyridine Carboxylic Acids in 0.185 M Perchloric Acid at 25° [b]

Pyridinecarboxylic acid (concn, M)	$10^4 k_{exptl}$, s^{-1}
None	4.25
Picolinic acid (1.54×10^{-2})	306
2,4-Pyridinedicarboxylic acid (1.54×10^{-2})	1210
2,6-Pyridinedicarboxylic acid (1.32×10^{-2})	24.2
Nicotinic acid (1.47×10^{-2})	3.06
Isonicotinic acid (1.46×10^{-2})	3.43
2-Pyridylacetic acid (1.54×10^{-2})	3.79

[a] Rates were determined spectrophotometrically at the absorption maximum for chromium acid (350 nm) under pseudo-first-order conditioning. [b] Isopropyl alcohol = 0.928 M.

We now wish to report the first example of a specifically catalyzed oxidation of an organic substrate by chromic acid. While picolinic acid alone reacts with chromic acid only very slowly, it exhibits a very strong rate accelerating effect on the reaction between chromic acid and isopropyl alcohol (Figure 1). Nevertheless, practically quantitative yields of acetone are obtained.

The picolinic acid catalysis is highly specific and is related to the proximity of the nitrogen atom and the carboxylic group: 2,6- and 2,4-pyridinedicarboxylic acids also catalyze