

tained spectra. Small rate constants and relatively large activation energies were found. This suggests ion-pairing effects are important in the benzene, toluene, and *p*-xylene systems investigated.

At present large experimental errors involved in experiments of this type do not allow one to assess very accurately the effects of changes in system parameters upon rate constants. More sophisticated observation techniques involving spectrum averaging devices and accurate frequency and field measuring equipment, all coupled with computer simulation, should soon allow one to investigate the more subtle aspects of such electron-transfer reactions. The experimental difficulties are probably at a maximum for the systems we have studied, although the time involved in computer simulation is a minimum because of the relatively small number of hyperfine energy levels to deal with for these

molecules. More ambitious studies with larger, more easily prepared and more stable anions should lead to important chemical information and are in progress.

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Chemical Ionization Mass Spectrometry. XII. Alcohols

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Abstract: The isobutane chemical ionization mass spectra of 23 saturated, monohydroxylic alcohols have been determined. The ionization chamber temperature was 180°. The main ions produced are $(M - 17)^+ = R^+$ of ROH, $(M - 1)^+$, $(M + 1)^+$, $(M + 39)^+$, $(M + 57)^+$, and $(2M + 1)^+$. The relative intensities of the several ions depend upon the structure of the alcohol. For alcohols with three or fewer carbon atoms the $(M + 1)^+$ ion dominates the spectrum, but for alcohols with five or more carbon atoms the R^+ ion dominates. Thus for the larger alcohols the chemical ionization technique emphasizes the hydrocarbon portion of the molecule. The $(M + 39)^+$ intensity is significantly larger in the secondary alkanols with five or more carbon atoms than in the corresponding primary alkanols. By contrast the $(M + 57)^+$ ion is larger in the primary alkanols. The magnitude of the total ionization of the alcohols depends on the structure and is significantly smaller for the primary alcohols. Speculations on the origin of the observed relations between structure and spectra are given.

As part of a program in these laboratories to determine the chemical ionization mass spectra of different types of compounds, we have measured the isobutane chemical ionization spectra of a number of alcohols, and we here report the results of the investigation. The study is of the nature of a survey in that the spectra of a relatively large number of alcohols have been determined to establish general behavior patterns in a qualitative or semiquantitative manner.

In some preliminary investigations which have been partially reported,¹ it was found that when methane is used as the reactant in the chemical ionization technique extensive decomposition of the alcohols occurs, and in particular the intensity of ions in the molecular weight region (the quasi-molecular ions) tends to be rather small. To diminish the amount of fragmentation occurring, the present investigation was made using isobutane as reactant. As we have pointed out previously,² the main ion in the isobutane plasma is

t-C₄H₉⁺. In our experience so far this ion often acts as a Brønsted acid, and it is a much milder protonating agent than the CH₅⁺ and C₂H₅⁺ ions found in methane plasma.

More details about the chemical ionization technique may be found in recent articles.^{3,4}

Experimental Section

The spectra were obtained with the Esso chemical physics mass spectrometer.^{1,5} All measurements were made at a single ionization chamber temperature, namely, 180°. The isobutane was research grade material obtained from Lif-O-Gen Co. of Lumberton, N. J. Its pressure in the ionization chamber of the mass spectrometer was maintained at 0.50 ± 0.01 Torr, and it was demonstrated that the spectra of the alcohols did not change significantly over the pressure range 0.5–0.7 Torr.

The alcohols used were obtained from the laboratory library of pure compounds, and the samples used were for the most part API standard samples or were samples from the Standards Project on Oxygenated Compounds of the Pennsylvania State University. Smaller alcohols such as methanol, ethanol, etc., were obtained from conventional commercial sources. For all of the compounds

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

(2) F. H. Field, *ibid.*, **91**, 2827 (1969).

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

(4) F. H. Field, *Advan. Mass Spectrom.*, **4**, 645 (1968).

(5) F. H. Field, *J. Amer. Chem. Soc.*, **83**, 1523 (1961).

Table I. Chemical Ionization Spectra of Alcohols^a

| Ion | <i>m/e</i> | RI | <i>m/e</i> | RI | <i>m/e</i> | RI | <i>m/e</i> | RI | <i>m/e</i> | RI | <i>m/e</i> | RI | <i>m/e</i> | RI |
|-----------------------|---|-------|---|-------|--|-------|---|-------|--------------------------------------|-------|-------------------------------------|-------|-------------------------------------|-------|
| | CH ₃ OH | | C ₂ H ₅ OH | | <i>n</i> -C ₃ H ₇ OH | | <i>i</i> -C ₃ H ₇ OH | | 1-C ₆ H ₁₁ OH | | 2-C ₆ H ₁₁ OH | | 3-C ₆ H ₁₁ OH | |
| R ⁺ | | | | | | | | | 71 | 0.716 | 71 | 0.803 | 71 | 0.810 |
| (M - 1) ⁺ | | | 45 | 0.038 | 59 | 0.162 | 59 | 0.159 | 87 | 0.086 | 87 | 0.028 | 87 | 0.017 |
| (M + 1) ⁺ | 33 | 0.958 | 47 | 0.841 | 61 | 0.599 | 61 | 0.716 | 89 | 0.006 | 89 | 0.053 | 89 | 0.058 |
| (M + 39) ⁺ | | | | | | | | | | | 127 | 0.010 | 127 | 0.012 |
| (M + 57) ⁺ | | | | | 117 | 0.084 | 117 | 0.027 | 145 | 0.071 | 145 | 0.010 | 145 | 0.004 |
| (2M + 1) ⁺ | 65 | 0.031 | 93 | 0.076 | 121 | 0.078 | 121 | 0.046 | | | | | | |
| Others | | | | | 119 | 0.020 | | | 86 | 0.024 | | | | |
| ΣI ^b | | 570 | | 620 | | 300 | | 800 | | 660 | | 2790 | | 1210 |
| | 1-C ₆ H ₁₃ OH | | 2-C ₆ H ₁₃ OH | | 3-C ₆ H ₁₃ OH | | <i>c</i> -C ₆ H ₁₁ OH | | 1-C ₇ H ₁₅ OH | | 2-C ₇ H ₁₅ OH | | 3-C ₇ H ₁₅ OH | |
| R ⁺ | 85 | 0.655 | 85 | 0.794 | 85 | 0.826 | 83 | 0.658 | 99 | 0.549 | 99 | 0.802 | 99 | 0.829 |
| (M - 1) ⁺ | 101 | 0.079 | 101 | 0.051 | 101 | 0.012 | 99 | 0.101 | 115 | 0.096 | 115 | 0.043 | | |
| (M + 1) ⁺ | | | 103 | 0.021 | 103 | 0.028 | 101 | 0.072 | | | | | | |
| (M + 39) ⁺ | | | 141 | 0.016 | 141 | 0.015 | 139 | 0.031 | | | 155 | 0.019 | 155 | 0.012 |
| (M + 57) ⁺ | 159 | 0.124 | 159 | 0.011 | 159 | 0.003 | 157 | 0.023 | 173 | 0.132 | 173 | 0.007 | | |
| (2M + 1) ⁺ | | | | | | | | | | | | | | |
| Others | 83 | 0.023 | | | | | 81 | 0.010 | 97 | 0.026 | | | 71 | 0.008 |
| | 84 | 0.016 | | | | | | | 98 | 0.013 | | | 85 | 0.012 |
| | 100 | 0.020 | | | | | | | | | | | 97 | 0.010 |
| ΣI ^b | | 723 | | 3270 | | 3255 | | 3700 | | 670 | | 2600 | | 1645 |
| | 2,4-Me ₂ C ₅ OH-3 | | 4,4-Me ₂ C ₅ OH-2 | | 2,3-Me ₂ C ₅ OH-3 | | 1-C ₈ H ₁₇ OH | | 2-C ₈ H ₁₇ OH | | 2-MeC ₇ OH-2 | | 3-MeC ₈ OH-3 | |
| R ⁺ | 99 | 0.886 | 99 | 0.903 | 99 | 0.853 | 113 | 0.488 | 113 | 0.733 | 113 | 0.829 | 127 | 0.872 |
| (M - 1) ⁺ | 115 | 0.012 | 115 | 0.006 | | | 129 | 0.115 | 129 | 0.079 | | | | |
| (M + 1) ⁺ | | | | | | | | | | | 169 | 0.021 | | |
| (M + 39) ⁺ | | | | | | | | | | | 187 | 0.011 | | |
| (M + 57) ⁺ | | | | | | | 187 | 0.153 | 187 | 0.011 | | | | |
| (2M + 1) ⁺ | | | | | | | | | | | | | | |
| Others | | | | | 85 | 0.010 | 71 | 0.045 | 71 | 0.019 | 71 | 0.025 | 113 | 0.015 |
| | | | | | 97 | 0.010 | 111 | 0.024 | 111 | 0.012 | 99 | 0.018 | 125 | 0.013 |
| | | | | | 98 | 0.027 | 112 | 0.012 | | | 111 | 0.027 | | |
| ΣI ^b | | 4630 | | 3910 | | 3870 | | 509 | | 2010 | | 2255 | | 1645 |
| | 1-C ₁₀ H ₂₁ OH | | 1-C ₁₁ H ₂₃ OH | | Others | | 1-C ₁₀ H ₂₁ OH | | 1-C ₁₁ H ₂₃ OH | | | | | |
| R ⁺ | 141 | 0.434 | 155 | 0.454 | | | 71 | 0.071 | 71 | 0.029 | | | | |
| (M - 1) ⁺ | 157 | 0.091 | 171 | 0.087 | | | 85 | 0.058 | 83 | 0.018 | | | | |
| (M + 1) ⁺ | | | | | | | 99 | 0.029 | 85 | 0.037 | | | | |
| (M + 39) ⁺ | | | | | | | 113 | 0.025 | 96 | 0.014 | | | | |
| (M + 57) ⁺ | 215 | 0.086 | 229 | 0.214 | | | | | 98 | 0.022 | | | | |
| (2M + 1) ⁺ | | | | | | | | | 112 | 0.013 | | | | |
| | | | | | | | | | 152 | 0.013 | | | | |
| | | | | | | | | | 154 | 0.014 | | | | |
| | | | | | | | | | 156 | 0.047 | | | | |
| ΣI ^b | | 400 | | | | | | | | | | | | |

^a Reactant = *i*-C₄H₁₀, temperature = 180°, and pressure of *i*-C₄H₁₀ = 0.50 Torr; RI = relative intensity. ^b Summation of ions attributed to alcohol additive.

investigated purity was checked by glpc analysis, and when impurities were found the samples were purified by preparative scale gas chromatography. The volume of sample charged to the mass spectrometer was 2 μl, which produced a partial pressure of alcohol in the ionization chamber of ~2 × 10⁻⁴ Torr.

The gas handling system of the mass spectrometer contains two metal valves with which the alcohol vapors can come in contact, and to eliminate dehydrogenation of the alcohols the temperature of the gas handling system was reduced to 130°. Comparison of the spectra of a given alcohol introduced through the gas handling system and by the use of the solids introduction probe (with which the vapors do not come in contact with metal surfaces) did not reveal any meaningful differences.

For all of the compounds except for four branched alcohols (3-methyl-3-octanol, 2,4-dimethyl-3-pentanol, 2,3-dimethyl-3-pentanol, and 4,4-dimethyl-2-pentanol) several replicate determinations of the spectra were made over a period of time of several months. The agreement of the replicate spectra was invariably satisfactory, and consequently it is believed that the spectra of the four compounds for which only single measurements were made are reliable.

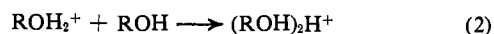
Results

The spectra of the 23 saturated monohydroxylic alcohols investigated in this work are given in Table I. Intensities due predominantly to ¹³C isotope ions are omitted for simplicity. The spectra are quite

simple, and the following ion types comprise a large fraction of the spectra: the alkyl ion formed from the hydrocarbon portion of the molecule (R⁺), the ion formed by abstracting a hydride from the molecule ((M - 1)⁺), the protonated molecule ((M + 1)⁺), the association complex of the molecule with the *m/e* 39 ion of the isobutane plasma ((M + 39)⁺), the association complex of the molecule with the *m/e* 57 ion of the isobutane plasma ((M + 57)⁺), and the protonated dimer of the molecule ((2M + 1)⁺). Other ions are found in certain compounds, but the intensities of these are invariably small. The intensities of these different ions are given in Table I, and in addition we give the values for ΣI, which is the sum of the intensities of all of the ions to be attributed to the alcohol, and as such is a measure of the extent of ionization of the alcohol in the chemical ionization process. The accuracies of these total ionizations are not high, but they are sufficient to show semiquantitatively trends in the probabilities of ionization of the different compounds.

The variations in the mass spectra with the structures of the alcohols is interesting both from the

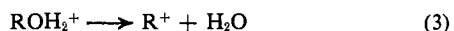
point of view of the utility of the spectra for analytical purposes and from that of the gaseous ionic chemistry operating. For the smallest alcohols, methanol through the propanols, the protonated molecules ($(M + 1)^+$) dominate the spectra, and these protonated molecules react with another molecule of alcohol even at the low alcohol pressures which obtain to produce protonated dimers. The reactions occurring are



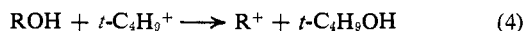
In a recent isobutane chemical ionization study of acetate esters² it was found that the $(2M + 1)^+$ ions are formed by a temperature-sensitive equilibrium reaction, and by analogy we suspect that reaction 2 also will be strongly temperature dependent and probably is an equilibrium reaction.

A very sharp drop in the $(M + 1)^+$ intensity occurs between the propanols and the pentanols, and the ion is no longer detectable in the heptanols and higher alcohols. Unfortunately, butanol could not be studied because of interference with the mass spectra by the $t\text{-C}_4\text{H}_9^+$ ion used as reactant. Alcohols with the same carbon number but different structures exhibit a significant variation in the intensity of $(M + 1)^+$, the 1-alkanols having a lower intensity than the 2- and 3-alkanols. For example, $(M + 1)^+$ in 2-pentanol is more intense than in 1-pentanol by a factor of approximately 10. Particularly noteworthy is the fact that the $(M + 1)^+$ intensity in cyclohexanol is larger than the intensities of this ion in 2- and 3-hexanol by factors of 2-3.

The decrease in the $(M + 1)^+$ intensity which occurs between the propanols and the pentanols is accompanied by a corresponding increase in the intensity of R^+ , and this ion dominates the spectra for all of the alcohols with five or more carbon atoms. Here also a dependency on structure exists, for, comparing alcohols with equal numbers of carbon atoms, the R^+ intensities for the 1-alkanols are smaller than the intensities of the other isomers. The R^+ intensities for the branched alkanols are greatest. Obviously the R^+ ions are formed by removal of the hydroxyl group, but we have no way of distinguishing between the two possible reactions

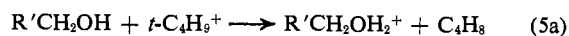


or



$(M - 1)^+$ ions are found for all the alcohols except methanol, 3-heptanol, and the three tertiary alcohols (2,3-dimethyl-3-heptanol, 2-methyl-2-heptanol, and 3-methyl-3-octanol). The intensities are greatest for the 1-alkanols, less for the 2-alkanols, and still less for the 3-alkanols. The value in cyclohexanol is higher than in any other secondary alcohol. Because of the polar nature of the alcohol molecule, one expects that the attack of the reactant ion will occur predominantly at the hydroxyl group or at adjacent parts of the molecule. When this is coupled with the fact that no $(M - 1)^+$ ions are formed from the tertiary alcohols, one is led to suspect that $(M - 1)^+$ ions are formed predominantly by hydride ion abstraction from the α carbon. Deuterium labeling studies obviously will

be very useful, but these have not been undertaken as part of the investigation reported here. Furthermore, in the $\text{C}_5\text{-C}_8$ alcohols the $(M - 1)^+$ intensities are, on the average, 2.1 times greater in the 1-alkanols than in the 2-alkanols, and this behavior is compatible with the formation of $(M - 1)^+$ ions by hydride ion abstraction from the α carbon. However, other explanations for this behavior may be operating in view of the fact that a fourfold difference in intensity exists between the 2- and 3-alkanols. We tentatively postulate that the $(M - 1)^+$ ions are formed either by



or by



or by both. Analogous reactions can be written for secondary alcohols.

An interesting and curious dependence upon structure is to be observed for the formation of the $(M + 39)^+$ and the $(M + 57)^+$ ions. We had previously found² that with acetates the $(M + 39)^+$ association complex is formed by an equilibrium reaction between the m/e 39 ion of the isobutane plasma and the acetate compound under investigation, and we suspect that a similar phenomenon may be occurring with the alcohols. Similarly, we have recently found⁶ that the $(M + 57)^+$ association complex is formed with acetates by an equilibrium reaction at higher pressures of acetate; and again, we suspect that an equilibrium is involved in the formation of this ion with alcohols. Regardless of whether or not the reactions are equilibrium reactions, one observes that a $(M + 39)^+$ ion appears in $2\text{-C}_5\text{H}_{11}\text{OH}$ and is found consistently in all the higher secondary alkanols investigated. The intensities of the ions are small, but the distinction between the formation of the ions in the secondary alkanols and their absence in primary and tertiary alkanols is clear cut. One exception of unknown origin and significance is that no $(M + 39)^+$ is observed with $i\text{-C}_3\text{H}_7\text{OH}$.

By contrast, one finds the opposite behavior in the formation of $(M + 57)^+$ ions. The ratios of the intensities of $(M + 57)^+$ ions in 1-alkanols to those in 2-alkanols are tabulated for different alcohols in Table II. Clearly the tendency to form $(M + 57)^+$

Table II. Intensity Ratios of $(M + 57)^+$ Ions

| Carbon number of alcohol | $I_{(M+57)^+}$ in 1-alkanol/ $I_{(M+57)^+}$ in 2-alkanol | $I_{(M+57)^+}$ in 2-alkanol/ $I_{(M+57)^+}$ in 3-alkanol |
|--------------------------|---|---|
| 3 | 3.1 | |
| 5 | 7.1 | 2.5 |
| 6 | 11.3 | 3.7 |
| 7 | 18.9 | Large |
| 8 | 13.9 | |

ions is greatest in the 1-alkanols, and the tendency is larger in the larger alcohols. Somewhat similarly, the tendency for the formation of this ion is larger in the 2-alkanols than in the 3-alkanols, although the number of cases which are observed is relatively small. It is worthy of notice that in the 1-alkanols the $(M + 57)^+$ ions are formed with moderate intensities, and, indeed,

(6) Unpublished results.

often constitute the second most intense ions in the spectra.

Finally, an interesting variation in the magnitude of the additive total ionization (designated in Table I by ΣI) with structures of the alcohols is to be observed. For equal pressures of the alcohols in the ionization chamber of the mass spectrometer the total ionization is a measure of the average reaction cross-section (or, alternatively, the average reaction rate constant) for the reaction between the reactant ions from the isobutane plasma and the alcohol molecules. In these experiments the numerical values of the alcohol pressures are not known, but equal volumes of liquid alcohols are charged to the mass spectrometer. Thus, as a good approximation the pressures of isomeric alcohols will be equal, and the total ionizations will be measures of the relative reaction cross-sections.

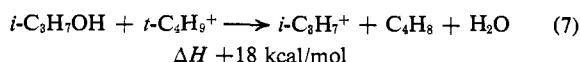
One observes from Table I that the total ionization values for 1-alkanols are consistently significantly lower than those for the 2-alkanols. This is represented more quantitatively in Table III, from which one sees

Table III. Ratio of Total Ionizations of 1- and 2-Alkanols

| Carbon number of alcohol | ΣI for 2-alkanol/ ΣI for 1-alkanol |
|-----------------------------|---|
| 3 | 2.7 |
| 5 | 4.2 |
| 6 | 4.5 |
| 7 | 3.9 |
| 8 | 4.0 |

that the ratio of the total ionization for the 2-alkanols to that for 1-alkanols is approximately four. Total ionization ratios have been calculated for other isomeric alcohols with the same number of carbon atoms, but no generalizations can be made. However, it appears that the total ionizations for the doubly branched heptanols are greater than that of 2-heptanol by a factor of about 1.6. The total ionization for 3-alkanols seems to be somewhat less than that for 2-alkanols, but the behavior is not very consistent.

One can offer speculative explanations for some of the observed behavior. The formation of R^+ ions does not occur for alcohols smaller than the pentanols, but in the pentanols and higher alcohols R^+ is very much the most intense ion. Methanol, ethanol, and the propanol cannot form tertiary carbonium ions, and thus the formation of R^+ by either reaction 1, (3), or (4) is endothermic. Thus for 2-propanol we have



We attribute the failure to produce the R^+ ions from the alkanols smaller than pentanols to the existence of these endothermicities. The heats of reaction for the formation of the alkyl ions from the pentanols and higher primary and secondary alkanols will be equal to or greater than that of reaction 7 assuming that the R^+ ions formed have primary or secondary structures. The extensive formation of the R^+ ions from the pentanols and the higher primary and secondary alkanols then suggests that rearrangement occurs in the course of the formation of the ions to produce tertiary carbonium

ions, since the formation of such ions with $t-C_4H_9^+$ as reactant will be approximately thermoneutral. The significantly smaller R^+ intensities observed with the 1-alkanols can be rationalized as resulting from the fact that a more extensive rearrangement is required to produce tertiary carbonium ions from primary alcohols than from secondary and tertiary alcohols.

The relative intensities of the $(M + 57)^+$ ions in alcohols of different structures can be rationalized in terms of some combination of proton affinity considerations and steric hindrance consideration, although problems with this rationalization exist. It is fairly obvious that steric hindrance in forming the $(M + 57)^+$ ions decreases in the order 1-alkanols > 2-alkanols > 3-alkanols, and thus this may be at least a partial explanation for the fact that the intensities of $(M + 57)^+$ decrease in this same order. However, proton affinity considerations may also play a role. We have reason to believe^{7,8} that $t-C_4H_9^+$ acts as a Brønsted acid to form $(M + 1)^+$ ions with relatively strong bases, but it tends to act as a Lewis acid to form $(M + 57)^+$ ions with weaker bases. For example, the most intense ion in the spectrum of benzyl acetate is the $(M + 1)^+$ ion,² but in *p*-nitrobenzyl acetate,⁷ which is doubtless a weaker base, the most intense ion under similar conditions is $(M + 57)^+$. Arnett⁹ has reviewed the subject of weak organic bases and he states that in solution the few data available indicate that the order of basicity of alcohols follows that to be expected from inductive electron release, *i.e.*, tertiary alcohols most basic and primary alcohols least basic. Brauman and Blair¹⁰ report that in gas phase the acidities of alcohols are in the order *t*-butyl > isopropyl > ethyl > methyl, and this suggests (although it does not demand) that the basicities of the alcohols be in the opposite direction, which conflicts with the solution results. The ionization potential of 2-propanol¹¹ is slightly lower than that of 1-propanol,¹¹ and since ionization potentials might be expected to be inverse to proton affinities, the ionization potential values suggest proton affinities of secondary alcohols greater than those of primary alcohols. Clearly uncertainties in this matter exist, but our results are in accord with a postulate that the proton affinities of primary alcohols are less than those of the corresponding secondary alcohols; that is, in the somewhat less basic primary alcohols the $(M + 57)^+$ ion is more favored than in the secondary alcohol. $(M + 57)^+$ ions are not observed with the tertiary alcohols studied nor with the secondary alcohols which have branched carbon chains. Presumably the reason for this is that these alcohols can form tertiary R^+ ions so easily that neither $(M + 57)^+$, $(M + 39)^+$, nor $(M + 1)^+$ ions exist long enough to be observed. $(M + 57)^+$ ions are not observed with methanol and ethanol, and their absence is not understandable.

(7) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 6334 (1969).

(8) D. P. Weeks and F. H. Field, submitted for publication.

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(10) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(11) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Standard Reference Data Series, NSRDS-NBS26, Washington, D. C., 1969.

At best a very speculative mechanism can be advanced for the behavior of the $(M + 39)^+$ ions; namely, the $C_3H_3^+$ ion can act only as a relatively weak Lewis acid, and as such it can form association complexes with the relatively basic 2-alkanols but not with the 1-alkanols. The lack of formation in the tertiary alkanols and in the branch chain secondary alkanols is again presumably the consequence of the ease of formation of R^+ from these alcohols. The lack of formation of the ion in 2-propanol is not understood. Note that steric hindrance consideration cannot be invoked to explain the trends observed in the behavior of this ion.

The higher intensities observed for the $(M + 1)^+$ ions in the secondary pentanols and hexanols as contrasted with those in the primary pentanols and hexanols may very loosely be rationalized in the same terms: more proton transfer occurs with the secondary alkanols, and not all of it results in the formation of R^+ ions by loss of water. The decreasing trend in the intensities of $(M + 1)^+$ as one goes to larger carbon chains probably results from the existence of more pathways for rearrangement to tertiary ions in the larger molecules and thus larger rate constants for the reactions consuming $(M + 1)^+$ ions. It is of interest that the intensities of the $(M + 57)^+$ ions in the 1-alkanols do not diminish as the length of the carbon chain increases.

Finally, the dependence of total additive ionization (ΣI) on alcohol structure is unexpected and interesting. The rate constants for ion-molecule reactions are usually represented in terms of an ion-induced dipole interaction for nonpolar molecules or a combination of an ion-induced dipole and ion-permanent dipole interaction for molecules containing a permanent dipole. One may write

$$k(g) = 2\pi e \left(\frac{\alpha}{\mu} \right)^{1/2} + (2\pi e \mu_D / g \mu) \quad (8)$$

where g = the velocity of the ion, $k(g)$ = the rate constant (a function of velocity), μ = the reduced mass of the ion and molecule, μ_D = the dipole moment, and α = polarizability. The dipole moments of 1-propanol and 2-propanol are essentially the same, and one would expect the dipole moments of analogous isomeric pairs of alcohols also to be the same. Similarly, one would expect the polarizabilities of alcohols con-

taining the same numbers of carbon atoms to be largely independent of structure, and thus on the basis of (8) the rate constants for the reaction of a given ion with isomeric alcohols would be expected to be the same. The dependence of the total ionizations on alcohol structure exhibited in Tables I and III demonstrate that chemical factors affect the occurrence of ion-molecule reactions. We think it reasonable to assume that the cross sections for the physical attraction of a $t-C_4H_9^+$ ion to 1-pentanol and 2-pentanol, for example, are identical, but this physical interaction results in a chemical reaction producing observable products four times less frequently in 1-pentanol than in 2-pentanol. The larger total ionizations in the secondary and tertiary alcohols doubtlessly result from the fact that R^+ ions are formed from these compounds with less rearrangement than the R^+ ions from primary alcohols, and thus the ion molecule complexes initially formed from the secondary and tertiary compounds decompose to carbonium ions more rapidly.

Analytical Applications

The chemical ionization spectra of alcohols are such as to suggest that this method can be of considerable utility in the analysis of alcohols. As is well known, the electron impact spectra of alcohols involve very extensive fragmentations, and ions in the molecular weight regions of alcohols larger than the simplest alcohols are for practical purposes nonexistent. Oxonium ions are formed in large abundance, and thus the electron impact spectra emphasize oxygen-containing fragments of the molecules. As may be seen from Table I, isobutane chemical ionization of the larger alcohols emphasizes the hydrocarbon fragments R^+ , and one may immediately conclude that for this class of compounds electron impact mass spectrometry and chemical ionization mass spectrometry complement each other very nicely. In addition, for primary and some secondary alcohols the $(M - 1)^+$ ion provides evidence for the molecular weight of the molecules. Finally, the dependence of the $(M + 39)$ and the $(M + 57)^+$ ions upon alcohol structure might be of some diagnostic value.

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