$$\Delta_{0,q}(\mathbf{r}) = \sum_s \sum_t \chi^*_s(\mathbf{r}) \chi_t(\mathbf{r}) P_{st}^q \qquad (A9)$$

with

$$P_{st}^q = \sum_{\alpha m} \sum_{\beta n} \{C_{sm} C_{tn} \delta_{\alpha\beta} - C_{s\alpha} C_{t\beta} \delta_{mn}\} \Xi_{\alpha m, \beta n}^q \qquad (A10)$$

Use of the Mulliken approximation (eq A4) yields the population analysis expression

$$\Delta_{0,q}(\mathbf{r}) = \sum_s \chi_s^2(\mathbf{r}) \gamma_{s,q} \qquad (A11)$$

where

$$\gamma_{s,q} = P_{ss}^q + \sum_{t \neq s} S_{st} P_{st}^q \qquad (A12)$$

is the rearrangement population in orbital s. The gross atomic rearrangement population on atom A is obtained by summing eq A13 over all orbitals on A, i.e.,

$$\Gamma_{A,q} = \sum_s^A \gamma_{s,q} \qquad (A13)$$

It follows from eq 16 that

$$\sum_s \gamma_{s,q} = \sum_A \Gamma_{A,q} = 0 \qquad (A14)$$

Computationally, the orbital populations (eq A6 and A13) provide useful information about which parts of the atomic orbital basis are particularly involved in a given set of excitations, and they can hence guide the search for optimal basis sets. Moreover, since they incorporate the entire sum over configurations $\alpha \rightarrow m$, they can often clarify the nature of the excitation and of possible IVO descriptions.

Note Added in Proof. After this paper was accepted, a theoretical study appeared of the CD spectrum of (3R)-3-methyl-cyclobutene (MCB),[72] resulting in spectral assignments that differ from those originally proposed.[73] Since the chiroptical properties of MCB fit naturally into the present context, we have calculated them in our basis B, using the MINDO-optimized geometry of ref 72. The resulting RPA calculations encompassed 728 particle–hole excitations.

Our results for the lowest five excitations are as follows: $\Delta E = 6.70$ eV ($\pi \rightarrow 3s$), $f^{r\nabla} = 0.029$, $R^\nabla = -2.3$; $\Delta E = 7.09$ eV ($\pi \rightarrow \pi^*$), $f^{r\nabla} = 0.209$, $R^\nabla = -30.9$; $\Delta E = 7.25$ eV ($\pi \rightarrow 3p$), $f^{r\nabla} = 0.017$, $R^\nabla = 6.7$; $\Delta E = 7.31$ eV ($\pi \rightarrow 3p$), $f^{r\nabla} = 0.020$, $R^\nabla = 12.1$; $\Delta E = 7.25$ eV ($\pi \rightarrow 3p$), $f^{r\nabla} = 0.14$, $R^\nabla = 16.9$ In addition, ring strain destabilizes the σ orbitals, so that the $\sigma_y \rightarrow \pi^*$ excitation (no. 9) drops down to 8.48 eV ($R^\nabla = 12.6$) in MCB. Another valence excitation, $\sigma_{CC} \rightarrow \pi^*$, is computed to lie at 9.20 eV, as the twelfth excitation.

MCB shows a strong negative CD band at 6.49 eV, with $\Delta\epsilon = -10.4$ (corrected to 100% optical purity), and a shoulder at 6.42 eV with $\Delta\epsilon = -7.6$. These features were assigned as $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3s$, respectively.[73] In ref 72, however, a *positive* $\pi \rightarrow \pi^*$ rotatory strength was obtained in a variety of basis sets. Their largest calculation ("DZD") placed the $\pi \rightarrow 3s$ at 7.14 eV with $f_{av} = 0.012$ and $R_{av} = -3.65$, and $\pi \rightarrow \pi^*$ as the third excitation at 8.18 eV with $f_{av} = 0.037$ and $R_{av} = +3.4$. The present calculations are thus consistent with the experimental data and original assignments[73] but differ markedly from the calculations recently reported.[72]

Registry No. (3R)-3-Methylcyclopentene, 39750-38-4; (–)-*trans*-cyclooctene, 931-89-5.

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Stable Hydrogen-Bonded Isomers of Covalent Ions. Association of Carbonium Ions with n-Donors

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Abstract: Addition reactions of carbonium ions R^+ with n-donors such as H_2O can produce covalent condensation products ROH_2^+, or cluster adducts $H_2O\cdots R^+$. While $\Delta S^\circ_{condensation}$ is −35 to −40 cal mol^{-1} K^{-1}, the measured values for several reactions are only −20 to −24 cal mol^{-1} K^{-1}, which indicates cluster formation. A review of thermochemical data of 15 addition reactions suggests that in eight reactions a cluster involving $XH^+\cdots Y$ or $CH^{\delta+}\cdots X$ hydrogen bonding is favored over a covalent condensation product. This may result from enthalpy factors, or, when ΔH° for condensation and clustering is comparable, from the more favorable entropy of the loose cluster product. Such thermochemical factors apply to the addition of H_2O and CH_3OH to the oxocarbonium ions $CH_3CH^+OCH_3$ and $(CH_3)_2C^+OCH_3$, where the incipient covalent bond is weakened due to the stabilization of the ions. The adducts are cluster ions rather than protonated acetals and hemiacetals; nevertheless, limits on the ΔH_f° of the protonated acetals and hemiacetals, and on the proton affinities of these compounds, in the range of 202–207 kcal mol^{-1}, can be derived. In other addition reactions of carbonium ions, we find that the collisional dissociation spectra of the adducts of CH_3^+, $C_2H_5^+$, i-$C_3H_8^+$, and t-$C_4H_9^+$ with H_2O are identical with those of protonated alcohols and amines, except for i-$C_3H_7^+\cdot H_2O$ and t-$C_4H_9^+\cdot H_2O$, where another structure, presumably a cluster ion, is formed. These results are consistent with thermochemical predictions. The possibility of clustering must be considered in the thermochemical uses of association data, and in the contribution of ion-molecule association to atmospheric synthesis.

The formation and subsequent condensation of carbonium ions occurs in numerous organic reactions. In the gas phase, the association of carbonium ions with n-donors may contribute to organic synthesis in ionized atmospheres. Such reactions are, for example, the association of CH_3^+, $C_2H_5^+$, sec-$C_3H_7^+$, and t-$C_4H_9^+$ with H_2O,[1] NH_3 or alkylamines,[2] and HCN or CH_3CN.[3] The structures of the association products are of interest, because the empirical formulas of the products are identical with those of protonated alcohols, amines, and cyanides or isocyanides. For

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this reason, Hiraoka and Kebarle[1] investigated the association of t-$C_4H_9^+$ with H_2O and found that the *enthalpy* change is consistent with the formation of the protonated alcohol t-$C_4H_9OH_2^+$. Similarly, the heats of formation of the association products of sec-$C_3H_7^+$ and t-$C_4H_9^+$ with HCN were examined in this context.[3] Also, the gas-phase acidities of i-$C_3H_7^+\cdot NH_3$ and t-$C_4H_9^+\cdot NH_3$ were found to be consistent with the i-$C_3H_7NH_3^+$ and t-$C_4H_9NH_3^+$ protonated amine structures.[2]

Nevertheless, the experimental *entropy* changes for some of the association reactions are substantially too small to account for condensation processes. This also applies to association reactions of oxocarbonium ions such as $CH_3CH^+OCH_3$ with n-donors, which were measured in the present study. We shall argue that the association products in these cases may be clusters bonded by unconventional, $CH^{\delta+}\cdots O$ interactions, which were shown recently[4] to be as strong as 9–15 kcal mol⁻¹. These hydrogen-bonded clusters are favored over the covalently bonded isomers by entropy factors. Thus, the entropy factors may be both the physical reason for clustering vs. condensation as well as the diagnostic tool to identify the formation of cluster products.

One use of equilibrium studies of addition reactions is to obtain thermochemical data on the adduct. This is especially useful if the adduct ions or their neutral precursors are unstable and cannot be produced in other ways. For example, Kebarle[5] used the addition of $C_2H_5^+$ and CH_4 to obtain $\Delta H_f^\circ(C_3H_9^+)$. In the present study we attempt to use the association of the carbonium ions $CH_3CH^+OCH_3$ and $(CH_3)_2C^+OCH_3$ with H_2O and CH_3OH to obtain ΔH_f° of protonated acetals and hemiacetals. These species cannot be obtained otherwise, since the hemiacetal precursors are unstable and the acetals decompose upon protonation. An application of thermochemical arguments to the association products suggests, however, that in these cases too the products are cluster ions. Nevertheless, the thermochemistry can be used to derive limiting values for ΔH_f° of protonated acetals and hemiacetals.

The structural predictions from thermochemistry cannot be tested with the pulsed mass spectrometer which was used for equilibrium studies. However, structural information can be obtained from collisional dissociation mass spectrometry of adduct ions. We use this method to test the structure of the adducts of CH_3^+, $C_2H_5^+$, i-$C_3H_7^+$, and t-$C_4H_9^+$ with H_2O and NH_3. Of special interest is the structure of i-$C_3H_7^+\cdot H_2O$ and t-$C_4H_9^+\cdot H_2O$, where the thermochemistry suggests that the stabilities of the covalent and cluster adducts may be comparable.

Experimental Section

Equilibrium measurements were done with the NBS pulsed high-pressure mass spectrometer and standard techniques.[6] Reaction mixtures consisted of neat H_2O, 20% H_2O in CH_4, or 10% CH_3OH in CH_4, plus 0.01–1% of the sample compounds CH_2CHOCH_3, $CH_2C(CH_3)OCH_3$, and $CH_3C(O)OCHCH_2$. One-millisecond pulses of 1000-eV electrons start the reaction sequences that yield the carbonium ions R^+, which in turn react with neutrals B, where B = H_2O, CH_3OH, or the neutral sample compound. The formation of adducts $R^+\cdot B$ is observed for 2–4 ms following the pulse, during which time a constant equilibrium ratio of ion intensities $[R^+\cdot B]/[R^+]$ is established.

The equilibrium constants are calculated from (1), where P_B is the partial pressure of compound B in the ion source. The collision spectra

$$K = \frac{[R^+\cdot B]}{[R^+]} \frac{1}{P_B} \text{ atm}^{-1} \tag{1}$$

of adduct ions and protonated reference compounds were obtained on a reverse-geometry double-focusing mass spectrometer.[7,8] Ion–molecule reactions were used to produce protonated or adduct ions in a chemical ionization source at pressures of about 1 torr at ≈300 K. Reagent grade

chemicals were used in the ion/molecule collision spectroscopy studies. High-resolution mass spectrometry was used to verify the identities of the reaction products.

In the studies of $CH_3OH_2^+$ and $C_2H_5OH_2^+$, a minor problem arose in that ions of the same composition also result from the addition of CH_3^+ or $C_2H_5^+$ to water impurity in the methane. However, the contribution of these reaction product ion abundances was less than 1% of the ion abundance of the reference ions generated by protonating methyl or ethyl alcohol.

The mass-analyzed ion kinetic energy spectra reported are a result of the computer average of at least 10 spectra. The studies reported were repeated on three different days to verify reproducibility.

Results and Discussion

1. The Thermochemistry of Condensation and of Clustering Reactions. An objective of the present experimental equilibrium studies is to examine whether the association of carbonium and oxocarbonium ions with H_2O produces covalent adducts. In the case of oxocarbonium ions, we shall use thermochemistry as a test. Preceding these special cases, we shall first review the available literature data on ion–molecule addition reactions where the product may be either a covalent product or a cluster ion.

In the reaction of carbonium ions with n-donors it would seem facile for the electrophilic carbon centers of the ions to attack the lone pair of the n-donor base to form a
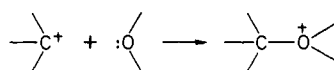
covalently bonded condensation product. The thermochemistry of such condensation reactions can be calculated or estimated from available data.

a. Enthalpies. The enthalpies of condensation reactions can be calculated from known heats of formation[9] of the reactants and products for all the reactions except 4–6 and 15 in Table I. These values are reliable to within ±2 kcal mol⁻¹.

For reactions 4–6, we use ΔH_f° of the oxocarbonium ions as obtained from the PAs of olefinic ethers[9]: $CH_3CH^+OCH_3$, ΔH_f° = 134, and $(CH_3)_2C^+OCH_3$, ΔH_f° = 117 kcal mol⁻¹. The ΔH_f° of the products, which would be protonated acetals and hemiacetals, is not available. To estimate these values, we use the following ΔH_f° and PA values: $CH_3CH(OCH_3)_2$, −93,[16] 199; $CH_3CH(OH)OCH_3$, −98,[11] 198; $(CH_3)_2C(OH)OCH_3$, −111,[11] 200. These PAs are estimated on the basis of PAs of comparable ethers, and assuming that the O–C–O grouping does not affect the PAs significantly, since the PAs of tetrahydropyran and 1,3-dioxane are similar, and also the PAs of $CH_3OC(O)C_2H_5$ and $(CH_3O)_2$ CO are similar.[9] Because of the uncertainties in these estimates, the estimated ΔH values are reliable only to about ±4 kcal mol⁻¹.

b. Entropies. ΔS°_{300} for all of the condensation reactions can be estimated reliably, since third-law S°_{300} values change regularly with structure and S°_{300} of isoelectronic molecules are usually similar.[12] For example, substitution of an $-CH_2CH_3$ group by an $-OCH_3$ group decreases S°_{300} by 1.3 ± 0.5 cal mol⁻¹ K⁻¹, and substitution of an n-butyl group by a *tert*-butyl group decreases S°_{300} by 5–7 cal mol⁻¹ K⁻¹. Such relations can be used to estimate S°_{300} of the protonated acetals and hemiacetals in Table I from analogous ethers and hydrocarbons (see footnotes to Table I).

For the S°_{300} of the carbonium ions in reactions 1–11 and 15 the corresponding radicals are good models, since both are planar at the C or C^+ center. For C_2H_5, sec-C_3H_7, and t-C_4H_9, $S^\circ_{300}(R^+)$ = $S^\circ_{300}(R\cdot)$ − 1.4 cal mol⁻¹ K⁻¹, the latter correction being due to the term $S_{electronic} = R \ln 2$ which applies only in the odd-electron

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Table I. Thermochemistry of Association Reactions of Carbonium Ions R^+ or Onium Ions BH^+ with Neutrals N

reaction no.	R^+ or BH^+	N	cluster	condensation product	$-\Delta H^\circ$ [a]			$-\Delta S^\circ$ [a]			$-\Delta G^\circ_{300}$ [a]		
					exptl	clus	cond	exptl	clus	cond	exptl	clus	cond
1	CH_3CO^+	H_2O	$O^+CCH_3\cdots OH_2$	$CH_3COOH_2^+$	24.6[b]	9–14[c]	27[b]	33[b]	22[c]	33[b]	14.7	2–7	17
2	$C_2H_5CO^+$	H_2O	$O^+CCH_2CH_3\cdots OH_2$	$C_2H_5COOH_2^+$	23.7[b]	9–14[c]	19[b]	35[b]	22[c]	33[b]	13.2	2–7	9
3	$t\text{-}C_4H_9^+$	H_2O	$(CH_3)_2C^+CH_3\cdots OH_2$	$(CH_3)_3COH_2^+$	11.2[d]	9–12[c]	11[e]	22[d]	22[c]	35[d,f]	4.6	2–5	0
4	$CH_3CH^+OCH_3$	H_2O	$CH_3CH^+OCH_3\cdots OH_2$	$CH_3C(OCH_3H^+)$-(OH)H	11.2[g]	9±3[c]	7[e]	19[h]	22[c]	31[f]	5.5	2±3	-2[h]
5	$CH_3CH^+OCH_3$	CH_3OH	$CH_3CH^+OCH_3\cdots O(CH_3)H$	$CH_3C(OCH_3H^+)$-(OCH_3)H	13.1[g]	10±3[c]	14[e]	21[h]	25[c]	40[f]	6.7	3±3	2
6	$(CH_3)_2C^+OCH_3$	H_2O	$CH_3OC^+(CH_3)_2\cdots OH_2$	$(CH_3)_2C(OCH_3H^+)$-(OH)	10.8[g]	9±3[c]	4[e,h]	23[h]	22[c]	31[f]	3.9	2±3	-5[h]
7a	$i\text{-}C_3H_7^+$	HCN	$(CH_3)_2CH^+\cdots NCH$	$(CH_3)_2CHCNH^+$	30.8[i]	14[j]	46[e]	32[i]	24[j]	36[f]	21.2	7	35
7b	$i\text{-}C_3H_7^+$	HCN		$(CH_3)_2CNCH^+$			38[s]			36[f]			27
8a	$t\text{-}C_4H_9^+$	HCN	$(CH_3)C^+(CH_3)_2\cdots NCH$	$(CH_3)_3CCNH^+$	16.3[i]	14[j]	31[e]	25[i]	24[j]	36[f]	8.8	7	20
8b				$(CH_3)_3CNCH^+$			22[s]			36[f]			11
9	$t\text{-}C_4H_9^+$	C_6H_6	$(CH_3)C^+(CH_3)_2\cdots Bz$	$t\text{-}C_4H_9C_6H_5H^+$	22[r]	9[j]	19[e]	49	20[j]	34[f]	7.3	3	9
10	NH_4^+	C_2H_4	$H_3NH^+\cdots\|$	$C_2H_5NH_3^+$		10[k]	26[e]		20[c]	30[f]		4	17
11	NH_4^+	C_6H_6	$H_3NH^+\cdots Bz$	$c\text{-}C_6H_7NH_3^+$	19.3[k]	16[k]	-8[e,h]	23	22[c]	34[f]	12.4	9	-18[h]
12	$CH_3NH_3^+$	CO_2	$CH_3NH_3^+\cdots O_2C$	$H_2C(NH_3)^+COOH$ (glycine H⁺)	13.2[l]	9[m]	-9[e,h]	21[l]	22[m]	30[f]	6.9	2	-18[h]
13	$C_2H_5NH_3^+$	CO_2	$C_2H_5NH_3^+\cdots O_2C$	$CH_3CH(NH_3^+)COOH$ (alanine H⁺)	11.2[l]	8[m]	-9[e,h]	21[l]	22[m]	32[f]	4.9	1	-18[h]
14	HCO^+	H_2	$OCH^+\cdots H_2$	CH_3O^+	3.9[n]	<9[o]	2±4[o]	21[n]	≈15[t]	22[p]	0.8[t]	<7[t]	1±4[t]
15	$C_2H_5^+$	CH_4	$CH_3CH_2^+\cdots CH_4$	$C_3H_9^+$	6.6[n]			23[n]	20–25[c]	28[q]			

[a] ΔH°, ΔG° in kcal mol⁻¹; ΔS° in cal mol⁻¹ K⁻¹. [b] Experimental results and calculated ΔS° values from ref 21. $\Delta H_f^\circ(CH_3CO^+)$ = 157 kcal mol⁻¹ (ref 22) and $\Delta H_f^\circ(C_2H_5CO^+)$ = 144 kcal mol⁻¹ (ref 23); $\Delta H_f^\circ(CH_3COOH_2^+)$ = 72 kcal·mol⁻¹ and $\Delta H_f^\circ(C_2H_5COOH_2^+)$ = 67 kcal mol⁻¹, ref 9. [c] Estimated on the basis of $N(CH_3)_4^+\cdots O$ complexes, ref 4. [d] Reference 1. [e] Calculated by using enthalpy data from ref 9 and/or ref 10 except for hemiacetals, where ΔH_f° was used as in footnote e, Table II, and PA's estimated from ethers as follows: $CH_3CH(OH)OCH_3$, 198; $CH_3CH(OCH_3)_2$, 199; and $(CH_3)_2C(OH)OCH_3$, 200 kcal mol⁻¹. For reaction 8, $PA(t\text{-}C_4H_9CN) \approx PA(i\text{-}C_3H_7CN)$ + $PA(t\text{-}C_4H_9OH) - PA(i\text{-}C_3H_7OH)$ = 197 is used to estimate $\Delta H_f^\circ(t\text{-}C_4H_9CNH^+)$ = 167 kcal mol⁻¹. [f] Third-law entropies calculated from data of ref 12. For ions see text. For acetal and hemiacetals by $-OCH_3$ or $-OH$ substitution on ethers, e.g., $S^\circ_{300}(CH_3CH(OH)OCH_3) \approx S^\circ_{300}(CH_3CH_2OCH_3)$ + $S^\circ_{300}(CH_3CHOHCH_3) - S^\circ_{300}(CH_3CH_2CH_3)$ = 87 cal mol⁻¹ K⁻¹. Similarly substitutions are used when S° is not given in ref 12. For example: $S^\circ_{300}(t\text{-}C_4H_9CN) = S^\circ_{300}(n\text{-}C_4H_9CN)$ + $S^\circ_{300}(t\text{-}C_4H_9CH_2CH_3) - S^\circ_{300}(n\text{-}C_4H_9CH_2CH_3)$ = 78 cal mol⁻¹ K⁻¹; $S^\circ_{300}(t\text{-}C_4H_9C_6H_5) = S^\circ_{300}(i\text{-}C_3H_7C_6H_5)$ + $S^\circ_{300}(t\text{-}C_4H_9OCH_3) - S^\circ_{300}(i\text{-}C_3H_7OCH_3)$ = 98 cal mol⁻¹ K⁻¹, $S^\circ_{300}(CH_2(NH_2)COOH) = S^\circ_{300}(CH_3COOH)$ + $S^\circ_{300}(CH_2(NH_2)CH_2CH_3) - S^\circ_{300}(CH_3CH_2CH_3)$ = 80 cal mol⁻¹ K⁻¹. [g] Present work. [h] Note that negative values indicate endothermic or endoergic reactions. [i] Reference 3. [j] Estimted on the basis of $N(CH_3)_4^+\cdot(CH_3)_2CO$, C_6H_6, and NH_3 as models for $-CH^{\delta+}\cdots HCN$, C_6H_6, or NH_3 complexes, ref 4. [k] Reference 4. [l] Reference 16. [m] On the basis of correlations and trends in $NH^+\cdots O$ clusters, ref 18. [n] Reference 5. [o] On the basis of $\Delta H_f^\circ(CH_3O^+) \approx$ 195 kcal mol⁻¹ (ref 24). For the clustering reaction, it is assumed that $\Delta H^\circ_D(OCH^+\cdots H_2) < \Delta H^\circ_D(H_3^+\cdots H_2)$ (ref 5). [p] $S^\circ_{300}(HCO^+) \approx S^\circ_{300}(HCN)$ = 48.3; $S^\circ_{300}(H_3CO^+) \approx S^\circ_{300}(CH_3OH) - S^\circ_{rot}(OH)$ = 52.5 cal mol⁻¹ K⁻¹, where $S^\circ_{rot}(OH)$ = 4.6 cal mol⁻¹ K⁻¹ (ref 11b), and other values from ref 24. ΔS° value quoted in the table is corrected by $-\tfrac{5}{2}R \ln (300/150)$ to represent ΔS°_{150}, since experimental data were measured near 150 K. [q] $S^\circ_{300}(C_2H_5^+) \approx S^\circ_{300}(C_2H_4)$ + 2.4 = 54.9 cal mol⁻¹ K⁻¹ (ref 9a), assuming a nonclassical, bridged structure of $C_2H_5^+$. $S^\circ_{300}(C_3H_9^+) \approx S^\circ_{300}(C_3H_8)$. ΔS° values corrected by $-3R \ln (300/150)$ to represent ΔS°_{150}, since experimental data were measured near 150 K. [r] Reference 15. [s] On the basis of $PA(i\text{-}C_3H_7NC)$ = 205.5 kcal/mol and $PA(t\text{-}C_4H_9NC)$ = 207.5 kcal/mol, and $\Delta H_f^\circ(i\text{-}C_3H_7NC) \approx$ 25 kcal/mol and $\Delta H_f^\circ(t\text{-}C_4H_9NC) \approx$ 19 kcal/mol. Proton affinities from Meot-Ner (Mautner) and Karpas, unpublished data; heats of formation from the respective nitriles, estimating $\Delta H^\circ(RCN \rightarrow RNC) \approx$ 20 kcal/mol. Heats of formation of the nitriles from ref 27. [t] T = 150 K.

radicals. Thus we obtain for $C_2H_5^+$, i-$C_3H_7^+$, and t-$C_4H_9^+$ $S°_{300}$ = 58.6, 65.6, and 73.2 cal mol^{-1} K^{-1} from the values for the corresponding radicals;[11b] the latter is in good agreement with the experimental value[9b] of 71.3 cal mol^{-1} K^{-1}, which is used for the present purposes.

For the carbonium ions in 1, 2, and 4–6, $S°_{300}$ is obtained by using the difference method estimates of O'Neal and Benson[11b] and the values of the ref 10 for the corresponding molecules. As applied to the present case, these estimates suggest that the only significant $S°_{300}$ changes between the ions and parent molecules are the $R \ln 2$ terms, a change of 0 to -1 cal mol^{-1} K^{-1} due to S_{vib}, and a term due to the change in rotational barriers whose magnitude is ±2 cal mol^{-1} K^{-1} and which cannot be estimated with higher certainty. Similar considerations apply to ions obtained by protonation, except that the vibrational term is 0 to $+1$ cal mol^{-1} K^{-1}.

We also note that the experimental temperature for most measurements in Table I lies between 300 and 500 K. The entropies of the reactions vary as 6 ln (T_1/T_2), resulting in a variation of 2.5 cal mol^{-1} K^{-1} over this temperature range.[13]

Altogether, the $\Delta S°$ of condensation reactions can be estimated to within ±3 cal mol^{-1} K^{-1}.

c. Thermochemical Criteria for Condensation Reactions. In comparing the calculated condensation thermochemistry with the experimental results, the uncertainty in the calculated $\Delta H°$ and estimated $\Delta S°(300)$ values must be combined with the usual experimental error of ±1 kcal mol^{-1} for $\Delta H°$ and ±2 cal mol^{-1} K^{-1} for $\Delta S°$. Consequently, the experimental values and the calculated values of $\Delta H°$ for condensation reactions should agree within ±3 kcal mol^{-1} (±5 kcal mol^{-1} for acetal and hemiacetal formation), and $\Delta S°$ values should agree within ±5 cal mol^{-1} K^{-1}, to confirm a condensation reaction on the basis of thermochemistry. As we shall observe, the differences of interest here, i.e., the differences between $\Delta S°_{experimental}$ and $\Delta S°_{condensation}$, often substantially exceed these uncertainty limits.

2. Thermochemistry of the Association of Carbonium Ions with n-Donors and the Structures of the Products. Of all the reactions in Table I, only the condensation of acylium ions CH_3CO^+ and $C_2H_5CO^+$ with H_2O satisfies the required criteria for condensation. In contrast, the thermochemistry of the carbonium ion reactions 3–6 is significantly different from the expected values. The difference is evident in the $\Delta S°_D$ values, which are smaller by 8–19 kcal mol^{-1} K^{-1} than those expected for covalent condensation. Indeed, the actual small experimental values of 19–23 cal mol^{-1} K^{-1} are typical for the formation of hydrogen-bonded clusters. For example, $\Delta°S_D$ for the hydrogen-bonded complexes of N-$(CH_3)_4^+$ with H_2O, CH_3OH, and $(CH_3)_2CO$ are 22, 24, and 25 cal mol^{-1} K^{-1}, respectively.[4] The $\Delta S°_D$ values for the adducts of the carbonium ion t-$C_4H_9^+$, and of the oxocarbonium ions $CH_3CH^+OCH_3$ and $(CH_3)_2C^+OCH_3$ with oxygen n-donors, therefore suggests that the adducts are cluster ions.

One possible structure of the clusters may be a noncovalent >C^+···OH_2 bond. However, such a cluster would probably rearrange to the covalent structure; indeed, ab initio calculations[14] show that there is no minimum on the potential surface for an extended C^+–OH_2 bond. The more likely structure of the cluster ions would be hydrogen-bonded structures. Since the ions in reactions 3–6 lack protonated heteroatoms, these hydrogen bonds would have to be of the unconventional $-C$—$H^{\delta+}$···O type. Recently, the strengths of such hydrogen bonds were measured in complexes of $(CH_3)_4N^+$ with H_2O, CH_3OH, and $(CH_3)_2CO$. Association energies of 9.0, 9.8, and 14.6 kcal mol^{-1}, respectively, were measured.[4] Theoretical calculations[4] showed that in the $(CH_3)_4N^+$···OR_2 complex 1 the oxygen lies in a cavity created by three partially positively charged hydrogen atoms of three methyl groups, to which the ligands bond electrostatically. In analogy, theoretical 4-31B//3-21G ab initio calculations[14] on the adduct of t-$C_4H_9^+$ with H_2O, i.e., H_2O···$(H_3C)_3C^+$, show a bonding

energy of 13 kcal mol^{-1}, in good agreement with the experimental energy of 11 kcal mol^{-1}. The most stable hydrogen-bonded interaction is one where H_2O interacts with two hydrogens from different methyl groups as in ion 2. A similar geometry may be possible in the $CH_3CH^+OCH_3$···OH_2 complex as in ion 3. Here

1

2

3
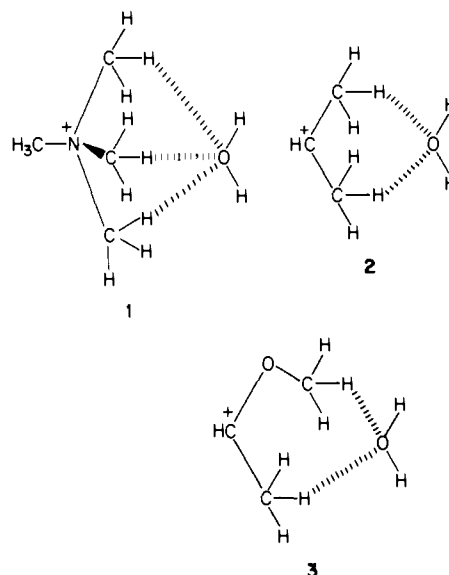
two hydrogen atoms from one methyl group and another hydrogen atom from another methyl group can create a cavity on the exterior of the planar $(CH_3)_3C^+$ ion or of $CH_3CH^+OCH_3$ and $(CH_3)_2C^+OCH_3$, into which fits the oxygen atom of H_2O or CH_3OH. These may be termed "two-methyl cavity", unconventional hydrogen bonded complexes.

It should be noted that in reactions 3–5 the small condensation energies that are calculated result from the stabilization of the carbonium ions. These energies are small enough to be comparable with weak hydrogen bonds.

An even more extreme case results with the highly stabilized $(CH_3)_2C^+OCH_3$ where condensation with H_2O (reaction 6) is predicted to be exothermic by only 4 kcal mol^{-1}, while the observed association is exothermic by 10.8 kcal mol^{-1}. In this case the hydrogen bond is stronger than the covalent bond.

In reactions 3 and 4 the expected enthalpy terms for condensation and clustering are comparable. In these cases, the determining factor in favor of clustering is the entropy term $-T\Delta S°_D$, which renders clustering more exoergic by 2 to 5 kcal mol^{-1} than condensation.

With respect to reaction 3, if the hydrogen-bonded cluster $C^+(CH_3)_3$···OH_2 product of (3) is indeed favored over t-$C_4H_9OH_2^+$, then the question arises whether the protonation of t-C_4H_9OH also yields this cluster ion. Alternatively, can the product of association reaction 3 and of protonation both be the covalently bonded ion t-$C_4H_9OH_2^+$, in which vibration of the loose covalent bond contributes $+15$ cal mol^{-1} K^{-1} to $S°_{300}$? This would imply $\Delta S° = 15$ cal mol^{-1} K^{-1} for the proton transfer equilibrium

(13) Due to translation plus rotational entropy terms of $3R \ln T + 3R \ln T$ for each reactant.

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Table II. Thermochemistry[a] of Association Reactions and Products

reaction no.	RH⁺ + N → PH⁺	$-\Delta H°$	$-\Delta S°$	$-\Delta G°$ (T)	$\Delta H°$-(O–H⁺···O)[b]	$-\Delta H°_{cond}$[c]	$\Delta H_f°$-(PH⁺)[d]	PA(P)[e]
16	CH₃CH⁺OCH₃ + H₂O → CH₃CH(OH)OCH₃H⁺	11.2	18.8		18	<15	>60	<207
17	CH₃CH⁺OCH₃ + CH₃OH → CH₃CH(OCH₃)₂H⁺	13.1	21.3		16	<19	>66	<206
18	(CH₃)₂CH⁺(OCH₃) + H₂O → (CH₃)₂C(OH)OCH₃H⁺	10.8	23.3		16	<13	>53	<202
19	CH₃CH⁺OCH₃ + CH₂CHOCH₃ → (CH₂CHOCH₃)₂H⁺	<27	<40[f]	<6.8 (520)	30			
20	[structure] + H₂O → [structure]·H₂O	<16	≤32[f]	4.2 (382)	24			
21	[structure] + [structure] → [structure]·[structure]	<19	≤32[f]	6.6 (382)	30			
22	[structure] + H₂O → [structure]·H₂O	<16	≤32[f]	4.9 (344)	19			
23	CH₃COOCHCH₂H⁺ + H₂O → CH₃COOCHCH₂H⁺·H₂O	18	(25)[g]	5.4 (492)	18[h]			
24	CH₃COOCHCH₂H⁺ + CH₃COOCHOH₂ → (CH₃COOCHCH₂)₂H⁺	25	(30)[g]	10.4 (492)	28[h]			

[a] $\Delta H°$ and $\Delta G°$ in kcal mol⁻¹ (=4.18 kJmol⁻¹); ΔS in cal mol⁻¹ K⁻¹ (=4.28 J mol⁻¹ K⁻¹). [b] From the correlation (ref 18); $\Delta H°_D = 30.4 - 0.30\Delta PA$ kcal mol⁻¹. For pyrroleH⁺·H₂O from the correlation for NH⁺···OH₂ bonds (ref 18): $\Delta H°_D = 30.0 - 0.26\Delta PA$ kcal mol⁻¹. [c] From eq 2, using $\Delta S°_{condensation}$ as in Table I. [d] From $\Delta H_f°(PH⁺) = \Delta H°_{cond} + \Delta H_f°(RH⁺) + \Delta H°(N)$, using $\Delta H°_{cond}$ from the preceding column and $\Delta H_f°(RH⁺)$ from ref 4. [e] From $-PA = \Delta H_f°(PH⁺) - \Delta H_f°(H⁺) - \Delta H_f°(P)$, using $\Delta H_f°(CH₃CH(OH)OCH₃) = -98$, $\Delta H_f°(CH₃CH(OCH₃)₂) = -93$ and $\Delta H_f°((CH₃)₂C(OH))CH₃ = -111$ kcal mol⁻¹ from group estimates (ref 11). [f] Estimated $\Delta S°$ for condensation, using data for homologous compounds from ref 12. For example, $\Delta S°_{cond} = S°(CH₃CHOHCH₂CH₃) - S°(CH₃CH₂CH₂CH₃) - S°(H₂O)$ for reactions 16 and 18; and $\Delta S°(cond) = S°(biphenyl) - 2S°(benzene)$ for reaction 21. [g] Estimated from $\Delta S°$ of analogous clustering reactions. [h] Estimated as in footnote b but considering 2 kcal mol⁻¹ cluster weakening in ethers (ref 25).

between t-C₄H₉OH and a rigid reference base B, i.e., BH⁺ + t-C₄H₉OH → t-C₄H₉OH₂⁺ + B, where $S°$ of B and BH⁺ are, as usual, comparable. In this case, the apparent PA of t-C₄H₉OH, determined from $\Delta G° \approx \Delta H°$ for proton transfer reactions at 300 K would be higher by 4.5 kcal mol⁻¹ than at 600 K. This, however, is not the case.[9] Therefore, the small entropy change in reaction 3 does not result from the formation of a loose covalent ion.

3. Clustering vs. Condensation in Other Systems. In view of the present results, it is of interest to review some other reactions where clustering may compete with condensation.

The association of carbonium ions R⁺ with HCN may lead by direct attack to protonated isonitriles RNCH⁺, or, with rearrangement, to the more stable protonated nitriles RCNH⁺, or to hydrogen-bonded clusters. With R = CH₃⁺, collisional dissociation results[26] indicate condensation with rearrangement, leading to CH₃CNH⁺. In this case, the rearrangement may be driven by the large exothermicity ($\Delta H° = -99$ kcal mol⁻¹) of the reaction. With R = i-C₃H₇⁺ (Table I, reactions 7a and 7b), the entropy change may be consistent with condensation. However, $\Delta H°$ is not consistent with the formation of either i-C₃H₇CNH⁺ or i-C₃H₇NCH. With R = t-C₄H₉⁺, $\Delta H°$ may be consistent with cluster formation to yield C⁺(CH₃)₃···NCH. Also, the observed $\Delta S°$ seems to be too small for condensation. The experimental data are similar to the clustering of N⁺(CH₃)₄ with the polar ligand (CH₃)₂CO, where $\Delta H° = -14.6$ kcal/mol and $\Delta S° = -24.7$ kcal/mol. Therefore, the thermochemistry suggests cluster formation. With respect to the alkylation of HCN we note recent results from our laboratory which show that alkyl transfer from ROH₂⁺ or RXR⁺ to HCN always yields RNCH⁺, i.e., the protonated isocyanide.

In reaction 9, $\Delta H°$ is consistent with condensation in agreement with the conclusion of Sen-Sharma et al.[15] $\Delta S°$ is too large, however, even for condensation. There is no obvious reason for the large $\Delta S°$.

In reactions 10 and 11 the products are either NH⁺···Π type hydrogen-bonded clusters or protonated amines. In (10) the thermochemistry favors condensation and qualitative observations support this process.[14] Reaction 11 is interesting in that hydrogen bonding is expected to be exothermic, while condensation would be endothermic, due to the loss of benzene resonance. Here both $\Delta H°$ and $\Delta S°$ favor clustering over condensation.

The thermochemistry of reactions 12 and 13 also favors clustering over condensation. This occurs since in the condensation
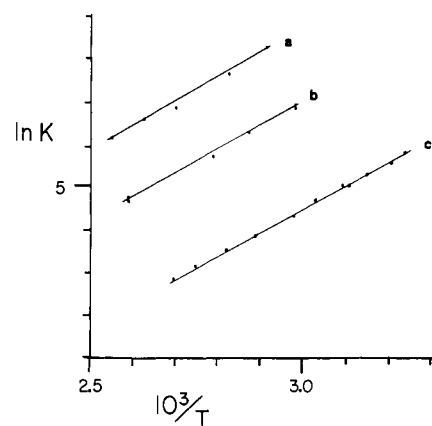
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Figure 1. Van't Hoff plots for association reactions: (a) CH₃CH⁺OCH₃ + CH₃OH; (b) CH₃CH⁺OCH₃ + H₂O; (c) (CH₃)₂C⁺OCH₃ + H₂O.

products the carboxyl group *destabilizes* the charge by intramolecular electron withdrawing effects, while in the cluster the charge is *stabilized* by intermolecular electrostatic interactions.[16]

In reaction 14 the observed $\Delta S°$ is consistent with condensation. The observed entropy values are consistent, however, also with those expected for clustering. Indeed, the small association energy of HCO⁺ with H₂ (reaction 14) may be consistent both with the formation of CH₃O⁺ and OCH⁺···H₂. Here again the loose structure of the hydrogen-bonded complex vs. the condensation product may lead to a more favorable entropy term for clustering, and thus to a $\Delta G°$ term that may favor clustering over condensation.

Unfortunately, for reaction 15 $\Delta H_f°(C₃H₉⁺)$ is not available independently, and therefore no $\Delta H°$ data exist to decide between condensation and clustering. However, the experimental $\Delta S°$ value is substantially smaller than that expected for condensation, indicating that the product ion is a C₂H₅⁺·CH₄ cluster rather than protonated propane C₃H₉⁺. In this case, using the experimental $\Delta H°$ value to obtain $\Delta H_f°$ of protonated propane is not valid.[5]

In summary, in 8 out of the 15 association reactions in Table I, the observed thermochemistry, in particular the small reaction entropies, suggests that the adducts are cluster ions rather than covalent products.
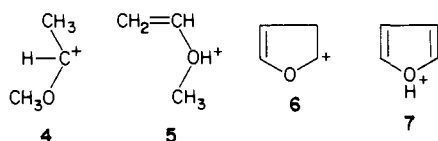
4. Association Thermochemistry of Oxocarbonium Ions. a. Implications Concerning the Structures of the Reactant Ions. The thermochemistry of association of CH₃CH⁺OCH₃ and (CH₃)₂C⁺OCH₃ with H₂O and CH₃OH and the implications
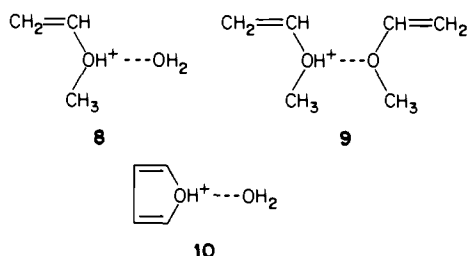
concerning the nature of the products were discussed above. In Table II and Figure 1 we present results on these association reactions and some related systems.

Besides the implications concerning the condensation products, these data are useful also as a probe of the nature of the reactant ions themselves. In particular, the reactant ions in the reactions in Table II may be carbonium ions such as **4** and **6**, or oxygen-protonated (or nitrogen-protonated, in reaction 22) onium ions such as **5** and **7**. For the ions in reactions 16–22, Table II, the
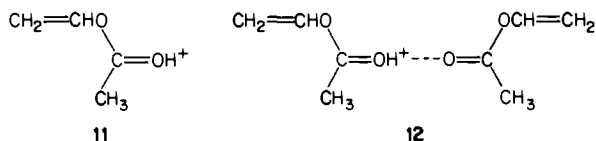
$$
\begin{array}{cccc}
\underset{\substack{\text{CH}_3 \\ | \\ \text{H}-\text{C}^+ \\ | \\ \text{CH}_3\text{O}}}{} & \underset{\substack{\text{CH}_2=\text{CH} \\ | \\ \text{OH}^+ \\ | \\ \text{CH}_3}}{} & \underset{\substack{\boxed{} \\ O}}{}^+ & \underset{\substack{\boxed{} \\ O^+ \\ H}}{} \\
\mathbf{4} & \mathbf{5} & \mathbf{6} & \mathbf{7}
\end{array}
$$

proton affinities of the respective olefinic ethers and of pyrrole suggest that the more stable isomers are the carbonium ions.[17] The association data support these conclusions, as follows.

We consider the expected hydrogen-bonding energies involving the hypothetical onium ions that would be formed from the unsaturated ethers by protonation on oxygen. In this case the structure of adducts **8–10** would involve an $>\text{OH}^+\cdots\text{O}$-type ionic hydrogen bond. The dissociation energies $\Delta H^\circ{}_\text{D}$ of such

$$
\begin{array}{ccc}
\underset{\substack{\text{CH}_2=\text{CH} \\ | \\ \text{OH}^+\cdots\text{OH}_2 \\ | \\ \text{CH}_3}}{} & & \underset{\substack{\text{CH}_2=\text{CH}\qquad\text{CH}=\text{CH}_2 \\ \quad|\qquad\qquad| \\ \text{OH}^+\cdots\text{O} \\ \quad|\qquad\qquad| \\ \text{CH}_3\qquad\quad\text{CH}_3}}{} \\
\mathbf{8} & & \mathbf{9}
\end{array}
$$

$$
\underset{\substack{\boxed{} \\ \text{OH}^+\cdots\text{OH}_2}}{}
$$
$$\mathbf{10}$$

$-\text{OH}^+\cdots\text{O}-$ and $-\text{NH}^+\cdots\text{O}-$ bonded adducts have been shown to correlate with the difference between the proton affinities of the components, ΔPA.[16] In the hydrates of the protonated unsaturated ethers, however, the experimental dissociation energies are substantially lower than the values expected for $-\text{OH}^+\cdots\text{O}-$hydrogen-bonded adducts. Indeed, the small experimental dissociation energies $\Delta H^\circ{}_\text{D}$ of the oxocarbonium ion hydrates are similar to that of $t\text{-}\text{C}_4\text{H}_9{}^+\cdot\text{H}_2\text{O}$. Similarly, the expected values of $\Delta H^\circ{}_\text{D}$ for the protonated dimers of $\text{CH}_2\text{CHOCH}_3$ and furan, and for the hydrates of furanH$^+$ and pyrroleH$^+$, are substantially lower than the value expected on the basis of $-\text{OH}^+\cdots\text{O}-$ and $-\text{NH}^+\cdots\text{O}$-type hydrogen bonds. These observations support the delocalized carbonium ion nature of these monomer ions.

In contrast to the above ions, $\Delta H^\circ{}_\text{D}$ for the hydrate and dimer of protonated vinyl acetate are close to that expected for $-\text{OH}^+\cdots\text{O}-$ interactions (Table II). This result supports the conclusion from PA data[17] that vinyl acetate is indeed protonated on the carbonyl group as in ions **11** and **12**. The considerations above illustrate the use of association thermochemistry in ion structure determination.

$$
\begin{array}{cc}
\underset{\substack{\text{CH}_2=\text{CHO} \\ \quad\searrow \\ \quad\text{C}=\text{OH}^+ \\ \quad| \\ \quad\text{CH}_3}}{} & \underset{\substack{\text{CH}_2=\text{CHO}\qquad\qquad\text{OCH}=\text{CH}_2 \\ \quad\searrow\qquad\qquad\qquad\swarrow \\ \quad\text{C}=\text{OH}^+\cdots\text{O}=\text{C} \\ \quad|\qquad\qquad\qquad\quad| \\ \quad\text{CH}_3\qquad\qquad\qquad\text{CH}_3}}{} \\
\mathbf{11} & \mathbf{12}
\end{array}
$$

b. The Thermochemistry of Protonated Hemiacetals and Acetals.

If reactions such as 3–5 in Table I were condensation reactions, then the measured ΔH° could be used directly to calculate $\Delta H_f{}^\circ$ for the product protonated acetals and hemiacetals. However, the entropy considerations suggest that the adducts are clusters, and therefore their $\Delta H_f{}^\circ$ is not that of the covalent products. Nevertheless, we can still obtain limits on these values. For example, for reaction 4, clustering is favored over condensation by a ΔS° term of 9 cal mol^{-1} K^{-1}, or, at 300 K, by a $\Delta G^\circ = -T\Delta S^\circ$ term of 2.7 kcal mol^{-1}. This term would be overcome if $\Delta H^\circ{}_\text{D}$ for the condensation product was larger than the observed 11.2 kcal mol^{-1} by more than 2.7 kcal mol^{-1}. Therefore, a lower limit is

is imposed on $\Delta H^\circ{}_\text{D}$ of the covalent condensation product as in eq 2. From this we obtain a lower limit for $\Delta H_f{}^\circ$ of the condensation product ion and an upper limit for the proton affinity of the corresponding neutral. The results obtained from reactions 4–6 are shown in Table II.

$$\Delta H^\circ{}_\text{D}(\text{condensation product}) \geq \Delta H^\circ{}_\text{D}(\text{experimental}) +$$
$$T\Delta S^\circ{}_\text{D}(\text{condensation product}) - T\Delta S^\circ{}_\text{D}(\text{experimental}) \quad (2)$$

The limits obtained are consistent with PA estimates from homologous ethers which suggest PA's of 198–202 kcal mol^{-1} for the acetals and hemiacetals.

It should be noted that eq 2 can be applied only when condensation vs. clustering is determined solely by thermochemistry. If kinetics prevents condensation, the formation of a cluster does not imply that its free energy is favored over that of the condensation product. This reservation must be kept in mind considering the limiting values in Table II.

5. Collision Spectroscopy of Adduct Ions.

Tandem mass spectroscopy methods[7] employing collisional activation or collision-induced dissociation can be used to differentiate isomers of ions. The use of a collision spectrum from a reference compound of known structure for comparison with the spectrum of a compound of unknown structure is the preferred method to identify unknowns.[8,19,20] In the present study, the mass-analyzed ion kinetic energy spectrometry (MIKES) method was used to determine the nature (cluster vs. condensation) of several carbonium ion/n-donor reaction products.

Two series of carbonium ion/n-donor reactions were studied by collision spectroscopy. The $\text{CH}_3{}^+$, $\text{C}_2\text{H}_5{}^+$, $sec\text{-}\text{C}_3\text{H}_7{}^+$, and $t\text{-}\text{C}_4\text{H}_9{}^+$ ions (generated by ionization of methane, isopropane, or isobutane) were reacted with water or ammonia in a chemical ionization source. For comparison, reference ions corresponding to the expected condensation products were generated also in a chemical ionization source by ion/molecule proton transfer reactions of appropriate protonating reactants ($\text{CH}_5{}^+$, $\text{C}_2\text{H}_5{}^+$, $sec\text{-}\text{C}_3\text{H}_7{}^+$, or $t\text{-}\text{C}_4\text{H}_9{}^+$) with alcohols (methanol, ethanol, isopropyl alcohol, or *tert*-butyl alcohol) or alkylamines (methylamine, ethylamine, *sec*-propylamine, or *tert*-butylamine). The reagent ions were selected so as to assure the least exothermic protonation. For example, $i\text{-}\text{C}_3\text{H}_7{}^+$ was used to protonate CH_3OH, $\text{C}_2\text{H}_5\text{OH}$, and $i\text{-}\text{C}_3\text{H}_7\text{OH}$, and $t\text{-}\text{C}_4\text{H}_9{}^+$ was used to protonate $t\text{-}\text{C}_4\text{H}_9\text{OH}$, in reactions that are exothermic by only 0–10 kcal mol^{-1}. The protonated species, as well as the products of the addition reactions, are expected to be thermalized by collisions in the ion source, and should therefore be free of excess internal energy. The lack of internal energy effects was shown by protonating CH_3OH, $\text{C}_2\text{-}\text{H}_5\text{OH}$, and $i\text{-}\text{C}_3\text{H}_7\text{OH}$ both by $i\text{-}\text{C}_3\text{H}_7{}^+$ and $t\text{-}\text{C}_4\text{H}_9{}^+$ and $t\text{-}\text{C}_4\text{H}_9\text{OH}$ by $\text{CH}_5{}^+ + \text{C}_2\text{H}_5{}^+$ and by $t\text{-}\text{C}_4\text{H}_9{}^+$. A spread of up to 70 kcal/mol in these processes did not affect the collision spectra of the protonated alcohols. The collision spectra of the reference ions were compared with the collision spectra of the carbonium ion/n-donor adducts. Pairs of collision spectra (reference ion spectrum vs. adduct spectrum) that are similar are indicative that the adduct is a condensation reaction product, while spectra that are different indicate a different structure, which, considering the thermochemical arguments, is probably a cluster ion.

The results of this study are summarized in Table III, and the collision spectra for the first series of reactions (carbonium ions with water) and reference ions are shown in Figure 2. The top two pairs of collision spectra (Figure 2) show excellent agreement and similarity between the reference (condensation product) ions (A) $\text{CH}_3\text{OH}_2{}^+$ and (C) $\text{C}_2\text{H}_5\text{OH}_2{}^+$, their reaction product counterparts (B) $\text{CH}_3{}^+$ and H_2O, and (D) $\text{C}_2\text{H}_5{}^+$ and H_2O. This is in agreement with the thermodynamic criteria (Table III), which indicate that reactions B and D will yield condensation products. In contrast, the two bottom pairs of collision spectra (Figure 2) do not show very good agreement although there are similarities. For example, the product ions of reactions (F) $(\text{CH}_3)_2\text{C}^+\text{H} + \text{H}_2\text{O}$ and (H) $(\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O}$ show abundant losses of one and two hydrogens from the reaction products. The corresponding reference spectra (E) $(\text{CH}_3)_2\text{CHOH}_2{}^+$ and (G) $(\text{CH}_3)_3\text{COH}_2{}^+$ do not show daughter ions corresponding to the successive loss of

Table III. Thermochemistry[a] and Collisional Spectroscopy Results for Clustering vs. Condensation of Carbonium Ion–n-Donor Additions

carbonium ion/n-donor	condensation product/ref Ion	$-\Delta H°$		$-\Delta S°$		$-\Delta G°_{300}$		collisional spectra	
		clus	cond[b]	clus[c]	cond[d]	clus	cond	clus[e]	cond[e]
$CH_3^+ + H_2O$	$CH_3OH_2^+$	21[f]	68	22	33	14	58		+
$C_2H_5^+ + H_2O$	$C_2H_5OH_2^+$	18[f]	37	22	34	11	27		+
$i\text{-}C_3H_7^+ + H_2O$	$i\text{-}C_3H_7OH_2^+$	16[f]	21	22	34	9	11	+	
$t\text{-}C_4H_9^+ + H_2O$	$t\text{-}C_4H_9OH_2^+$	11[g]	11	22	35	4	0	+	
$CH_3^+ + NH_3$	$CH_3NH_3^+$	20[h]	105	22	34	14	95		+
$C_2H_5^+ + NH_3$	$C_2H_5NH_3^+$	19[h]	68	22	34	12	58		+
$i\text{-}C_3H_7^+ + NH_3$	$i\text{-}C_3H_7NH_3^+$	15[h]	53	22	34	8	43		+
$t\text{-}C_4H_9^+ + NH_3$	$t\text{-}C_4H_9NH_3^+$	10[h]	39	22	32	3	29		+

[a] $\Delta H°$, $\Delta G°$ in kcal mol^{-1}; $\Delta S°$ in cal mol^{-1} K^{-1}. [b] Calculated using thermochemical data in ref 9. [c] Estimated on the basis of observed values for reactions 3, 4, and 6, Table I. [d] Estimated by using methods as in Table I. [e] See text. [f] Theoretical values (ref 14). The quoted values are 2 kcal mol^{-1} smaller than the actual calculated values, based on the difference between calculated and experimental values for $t\text{-}C_4H_9^+ \cdot H_2O$. [g] Experimental value, interpreted as clustering product. [h] $\Delta H°_D$ for the $R^+ \cdot NH_3$ clusters is estimated to be smaller by 2 kcal mol^{-1} than $\Delta H°_D(R^+ \cdot H_2O)$, on the basis of observed difference between $\Delta H°_D(CH_3)_4N^+ \cdot NH_3$ and $(CH_3)_4N^+ \cdot H_2O$ (ref 4).
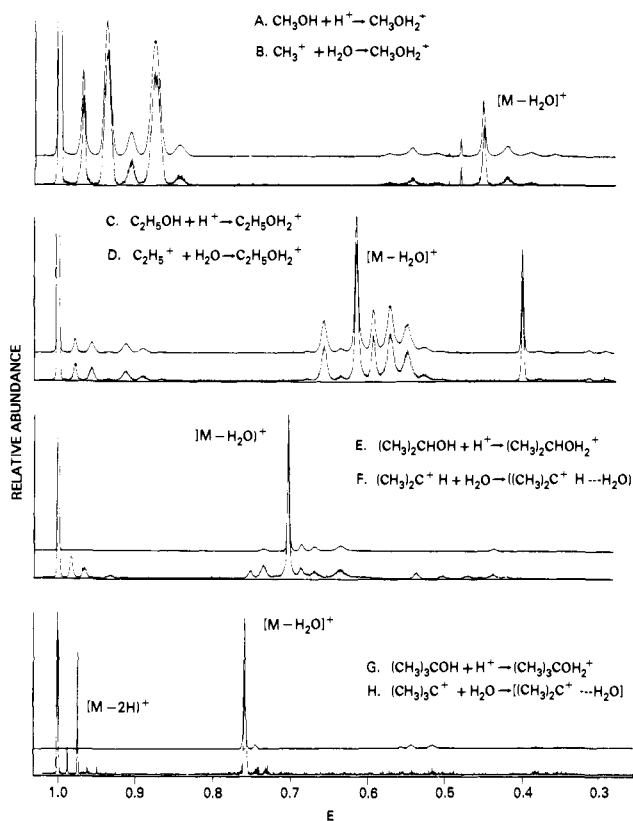
Figure 2. Collision spectra of a series of protonated alcohols ((A) methyl, (C) ethyl, (E) isopropyl, (G) *tert*-butyl) compared with collision spectra of corresponding product ions from the reaction of a series of alkyl carbonium ions ((B) CH_3^+, (D) $C_2H_5^+$, (F) $i\text{-}C_3H_7^+$, (H) $t\text{-}C_4H_9^+$) with H_2O.

hydrogens. These major differences and several other subtle differences in these pairs of collision spectra are indicative of different isomers (or a mixture of isomers). That is, the reaction products are not exclusively condensation products. This is in agreement with the $\Delta G°$ values in Table III which indicate that, within the accuracy of the present estimates, the cluster should be thermodynamically comparable or favored to the condensation products.

All of the product ion collision spectra shown in Figure 1 give abundant losses of H_2O from the molecular species. This fragmentation might seem to imply the dominance of a cluster product ion. However, this loss is also abundant in the collision spectra of the model protonated alcohols. This observation emphasizes

the requirement for reference spectra of model compounds when this technique is used, because fragmentation patterns alone are not always indicative of isomeric structure.

The second series of reactions, alkyl carbonium ions with ammonia, gave collision spectra that were in agreement with their corresponding reference ion collision spectra. These results indicate that the products are condensation products rather than clusters (Table III), which is also is accord with the thermodynamic predictions.

Conclusions

Several types of ion–molecule association reactions produce hydrogen-bonded clusters even though covalent condensation is also possible. Cluster formation is indicated by the thermochemistry, especially the small reaction entropies. In the case of $i\text{-}C_3H_7^+ \cdot H_2O$ and $t\text{-}C_4H_9^+ \cdot H_2O$, the thermochemical predictions are supported by collisional spectroscopy. Cluster formation may be preferred for several reasons:

1. The cluster ion is more stable than the condensation product. This may occur when the condensation would eliminate resonance stabilization of the reactants, such as in $c\text{-}C_6H_7NH_3^+$ vs. $NH_4^+ \cdot C_6H_6$, or when the condensation product may be destabilized by intramolecular interactions, such as in $CH_3(NH_3^+)COOH$ vs. $CH_3NH_3^+ \cdot CO_2$.

2. The condensation products would be more stable, but condensation requires prohibitively large rearrangement energies. Possible examples include the reactions $i\text{-}C_3H_7^+$ or $t\text{-}C_4H_9^+$ + $HCN \rightarrow i\text{-}C_3H_7CNH^+$ or $t\text{-}C_4H_9CNH^+$, and maybe $C_2H_5^+$ + $CH_4 \rightarrow C_3H_9^+$, as well as the association of $CH_3NH_3^+$ and $C_2H_5NH_3^+$ with CO_2 which would form protonated amino acids.

3. In cases where $\Delta H°$ for condensation and clustering are comparable, the looser structure of the cluster can result in entropy terms that render $\Delta G°$ for clustering more negative. The association of carbonium ions with H_2O and CH_3OH and of $t\text{-}C_4H_9^+$ with HCN may fall into this class.

The entropies of the association reactions may therefore serve both as the factor that determines the thermochemically favored product as well as the tool whereby the nature of the product can be identified.

The possibility of cluster formation must be considered when association thermochemistry is used to determine the thermochemistry of the supposedly covalent adducts. The collisional spectra of adduct ions confirms that the association of CH_3^+ and $C_2H_5^+$ with H_2O, and of carbonium ions in general with NH_3 and amines, can contribute to atmospheric synthesis. However, in general, if an association reaction is to contribute to prebiotic synthesis, condensation must occur preferentially to clustering.