bilayers undergo at least a 4% increase in the in-plane packing density with pressurization from 1 bar to 1.9 kbar. This is consistent with a reduction in the lateral compressibility of the lipid and a decrease in the number of defects that are potential conduits for translocation. A model for translocation involving tandomly formed defects on the donor and acceptor leaflets, respectively, is consistent with other data. Small molecules should flip-flop faster than large ones; Homan and Pownall[8] reported that translocation rates decrease with increasing acyl chain length and with the size of the headgroup. Although other effects, such as hydration and headgroup conformation, also affect the rate of translocation, these are probably superimposed on a mechanism involving the tandem defect formation described above. This mechanism could be operative in a native cell membrane wherein the defects are formed at the interface between lipids and integral membrane proteins.

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Hydroxyethylidene ($\mathrm{CH_3{-}C{-}OH}$), but Not Ethenol, Tautomerizes to Ethanal

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Although the unimolecular tautomerization of gaseous ethenol to ethanal, $\mathrm{CH_2{=}CH{-}OH \rightarrow CH_3CH{=}O}$, has been the subject of numerous theoretical investigations,[1-5] no experimental data exist for this reaction, probably due to the inaccessibility of *pure* ethenol. For a century it was suggested as an intermediate in various reactions[6] but was first identified directly in 1973.[7] It has since been prepared by gas-phase pyrolysis[8-12] and identified by using microwave,[8] photoelectron,[10] and mass[11,12] spectra and ionization energy.[9] We report here on the stability and unimolecular reactions of the isomers $\mathrm{CH_3{-}CH{=}O}$, $\mathrm{CH_2{=}CH{-}OH}$, and $\mathrm{CH_3{-}C{-}OH}$ (ΔH_f, Figure 1)[13b,9,14a] produced by neutralization[15,16] of the corresponding ions[17,18] and characterized by collisionally activated dissociation (CAD) and product reionization.[15e-h,j]

To obtain neutralization–reionization (NR) mass spectra[15] (Figure 2), mass-selected 10 keV $\mathrm{C_2H_4O^{\bullet+}}$ ions are neutralized by Hg (90% transmittance).[15d] Residual ions are deflected, and the resulting beam of fast neutrals is ionized by collision with He at transmittance values of 90% and 30% (maximum sensitivity), corresponding to ~1 and ~2 collisions, respectively, of the affected species.[19] The additional collision at 30% transmittance can dissociate the primary neutrals prior to reionization.[15j] Consistent with their expected stability, the extent of collisional dissociation of the $\mathrm{CH_3{-}CH{=}O}$ neutrals and ions is small, relative to scattering; the higher He pressure has little effect on the NR spectra (parts A and D of Figure 2) mainly increasing *m/z* 28, $\mathrm{CO^{\bullet+}}$. This should arise from CO or $\mathrm{{}^{\bullet}CHO}$ produced by CAD of neutral, not reionized, $\mathrm{CH_3{-}CH{=}O}$ (Figure 1), as

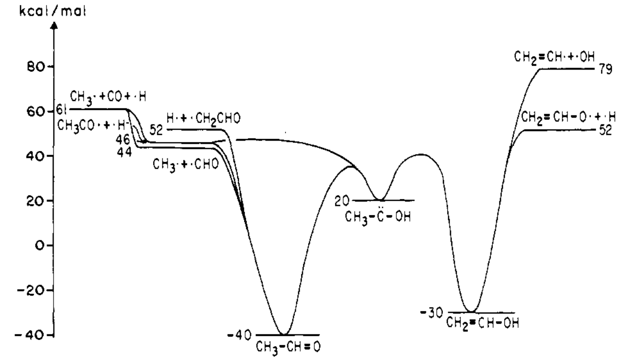

Figure 1. Proposed energy profile for the $\mathrm{C_2H_4O}$ neutral tautomers.[9,13,14]

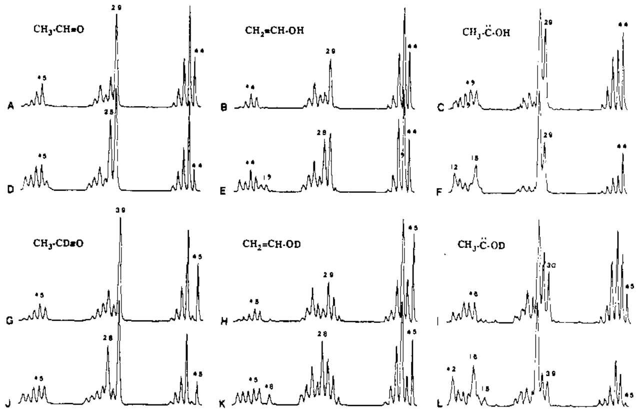

Figure 2. Hg/He NR spectra of $\mathrm{CH_3{-}CH{=}O^{\bullet+}}$ (A, D), $\mathrm{CH_3{-}CD{=}O^{\bullet+}}$ (G, J), $\mathrm{CH_2{=}CH{-}OH^{\bullet+}}$ from cyclobutanol[17] (B, E), $\mathrm{CH_2{=}CH{-}OD^{\bullet+}}$ from cyclobutanol-O-*d* (H, K), $\mathrm{CH_3{-}C{-}OH^{\bullet+}}$ from pyruvic acid[18] (C, F), and $\mathrm{CH_3{-}C{-}OD^{\bullet+}}$ from pyruvic acid-O-*d* (I, L): He transmittances of the neutral beam: 90% (A, B, C, G, H. I) and 30% (D, E, F, J, K, L); *m/z* values beside peaks. Absolute abundances (percent) from identical neutral fluxes: *m/z* 44, A and B, 0.016; C, 0.0095; D, 0.035; E, 0.032; F, 0.029; *m/z* 45, G, 0.012; H, 0.014; I, 0.0033; J, 0.028; K, 0.040; and L, 0.0014. Neutralization yields: $\mathrm{CH_3{-}CH{=}O^{\bullet+}}$, 9.3%, $\mathrm{CH_2{=}CH{-}OH^{\bullet+}}$, 6.0%; $\mathrm{CH_3{-}C{-}OH^{\bullet+}}$, 4.2%, unaffected by isotopic substitution.

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$[CO^{\bullet+}]$ is negligible in the CAD spectra of these $C_2H_4O^{\bullet+}$ tautomers.[17,18] The lowest energy fragmentations of $CH_3{-}CH{=}O$ lead to ${}^{\bullet}CHO$ or $CH_3CO^{\bullet}$ radicals that easily yield[13] CO[15d,i] and to ${}^{\bullet}CH_2{-}CH{=}O \leftrightarrow CH_2{=}CH{-}O^{\bullet}$ radicals. The reionization efficiency for producing $CO^{\bullet+}$ from ${}^{\bullet}CHO$ is nearly as great as from CO, but the reionization efficiencies of the other radicals are at best a few percent of that of CO.[20,23]

The NR spectra of $CH_2{=}CH{-}OH^{\bullet+}$ are consistent with its structure. Compared to parts A and D of Figure 2, parts B and E of Figure 2 show lower CH_3^+ and HCO^+ (m/z 15 and 29) and higher OH^+ (m/z 17; OD^+ from $CH_2{=}CH{-}OD^{\bullet+}$) and $CH_2O^{\bullet+}$ (also unique in its CAD spectrum)[18] absolute abundances. Neutralization and reionization of $CH_2{=}CH{-}OH^{\bullet+}$ appear to occur with $\ll$10% direct isomerization of $CH_2{=}CH{-}OH$ to $CH_3{-}CH{=}O$; the NR spectrum of $CH_2{=}CD{-}OH^{\bullet+}$ (not shown) indicates a dominant $H^{\bullet}$ loss (as does its CAD spectrum) with m/z [44]/[45] values of 1.6 and 1.9 for 90% and 30%T, while $CH_3{-}CD{=}O^{\bullet+}$ shows values of 0.11 and 0.13. Increasing CAD (part E vs. B of Figure 2) increases $[OH^+]$ via $CH_2{=}CH{-}OH \rightarrow CH_2{=}CH^{\bullet} + {}^{\bullet}OH$, as $CH_2{=}CH{-}OH^{\bullet+}$ ions do *not* yield OH^+ upon CAD;[17] the counterpart product, $C_2H_3^{\bullet}$, is reionized less efficiently than ${}^{\bullet}OH$.[20] The lowest energy dissociation of $CH_2{=}CH{-}OH$ leads to $CH_2{=}CH{-}O^{\bullet}$ (Figure 1)[22] which has a poor He reionization cross section;[20] it could contribute to the abundances of $C_2H_2O^{\bullet+}$ (m/z 42) and CHO^+ (m/z 29) in Figure 2E. The extra collision of part E vs. B of Figure 2 also increases $[CO^{\bullet+}]$; it must result from rearrangement, as formation of ${}^{\bullet}CHO$ or CO from $CH_2{=}CH{-}OH$ by simple bond cleavages would require >100 kcal/mol higher energy than $CH_2{=}CH{-}O^{\bullet}$ formation. The pathway of this rearrangement is indicated by isotope effects; determined separately under identical experimental conditions, the $[CO^{\bullet+}]$ increase is very similar (within 5%) for $CH_2{=}CH{-}OH$ and $CH_2{=}CH{-}OD$ but significantly (20% and 50%) smaller for $CH_2{=}CD{-}OH$ and $CH_3{-}CD{=}O$. For two-fifths of CO loss to proceed by $CH_2{=}CD{-}OH \rightarrow CH_3{-}CD{=}O$ would require that the major (three-fifths) rearrangement pathway shows no isotope effect, which is not likely for migration of the central hydrogen. Thus, the probable main pathway is the 1,2 H-migration $CH_2{=}CH{-}OH \rightarrow CH_3{-}C{-}OH$ (Figure 1).[24] However, appreciable amounts of nondissociating $CH_3{-}CH{=}O$ are *not* formed through this intermediate, according to the m/z [30]/[44] values of parts G vs. H and J vs. K of Figure 2.

This hydroxyethylidene intermediate has also been suggested in the photochemical decarboxylation and the pyrolysis of pyruvic acid.[14] The NR spectra (parts C and F of Figures 2) of stable $CH_3{-}C{-}OH^{\bullet+}$ ions are dominated by $CO^{\bullet+}$, which should *not* result from $CH_3{-}C{-}OH \rightarrow CH_4 + CO$, as little CH_3D is formed from $CH_3{-}C{-}OD$ (m/z 12-16 in part I vs. C of Figure 2).[20] The negligible peak at m/z 30 (31 in $CH_3{-}C{-}OD$) indicates little isomerization to $CH_2{=}CH{-}OH$. The spectra also exhibit abundant molecular ions, but a substantial part appears not to represent reionized $CH_3{-}C{-}OH$. The lowest energy dissociation of both $CH_3{-}C{-}OH$ and $CH_3{-}C{-}OH^{\bullet+}$ involves loss of the hydroxylic hydrogen atom,[13] so that its substitution with D should decrease its loss. However, in the NR spectrum of $CH_3{-}C{-}OD^{\bullet+}$ the $C_2H_2(H,D)O^+$ signal is increased and $C_2H_3DO^{\bullet+}$ decreased (parts I,L vs. C,F of Figure 2). Assuming that the yield for reionization to stable molecular ions is lower for hydroxyethylidene than for ethanal,[15h] the $[C_2H_3DO^{\bullet+}]$ decrease suggests that D-substitution slows the isomerization of $CH_3{-}C{-}OD$ to $CH_3{-}CD{=}O$. The much lower stability of hydroxyethylidene would account for the collisional reduction in the *absolute* abundance of the molecular ion of $CH_3{-}C{-}OD$ (m/z 45 in parts I and L of Figure 2), while the tripling of the absolute abundance for $CH_3{-}C{-}OH$ (m/z 44, parts C and F of Figure 2) is consistent with the presence of the stable $CH_3{-}CH{=}O$ isomer.

Formation of undissociated $CH_3{-}CH{=}O$ from $CH_3{-}C{-}OH$ (Figure 1) requires that the transition-state energy for the isomerization $CH_3{-}C{-}OH \rightarrow CH_3{-}CH{=}O$ must lie well below 44 kcal/mol (ΔH_f of $CH_3^{\bullet} + {}^{\bullet}CHO$), possibly ~35 kcal/mol. This is also a lower limit for the transition-state energy of the isomerization $CH_2{=}CH{-}OH \rightarrow CH_3{-}C{-}OH$ leading to the observed $CO^{\bullet+}$, as $CH_3{-}C{-}OH$ forms a negligible amount of $CH_2{=}CH{-}OH$ (vide supra). This transition-state energy for the tight complex $CH_2{=}CH{-}OH \rightarrow CH_3{-}C{-}OH$ isomerization must also be substantially below that[22] for the loose-complex loss of ${}^{\bullet}H$ or possibly ~40 kcal/mol (Figure 1). The direct 1,3 H-rearrangement $CH_2{=}CH{-}OH \rightarrow CH_3{-}CH{=}O$ is not observed; the predicted transition-state energies of the latter are 36[5]-64 kcal/mol for the symmetry allowed entropically unfavorable antarafacial and 65-75 kcal/mol for the symmetry-forbidden suprafacial isomerization.[1-3]

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(20) Relative reionization efficiencies were determined for 5 keV CO, $OH^{\bullet}$, $CH_3^{\bullet}$, CH_4, ${}^{\bullet}CHO$, $C_2H_3^{\bullet}$, $CH_3{-}CH{=}O$, $CH_2{=}CH{-}OH$, $CH_3CO^{\bullet}$, and $CH_2{=}CH{-}O^{\bullet}$.[15e] The first eight molecules were prepared by charge exchange neutralization from the respective cations while the last two were formed by dissociation from $CH_3COCOCH_3^{\bullet+}$ and $CH_3CO_2CH{=}CH_2^{\bullet+}$, respectively.[21,22] He (90% transmittance) reionization of identical abundances of the above neutral species produces molecular ions (and total ions) with the following intensities relative to the values of CO: CO, 1.0 (1.1 vs. $[28^{\bullet+}]$); $OH^{\bullet}$, 0.60 (1.0); $CH_3^{\bullet}$, 0.48 (1.7); CH_4, 0.015 (1.4); $C_2H_3^{\bullet}$, 0.035 (0.32); $CH_3{-}CH{=}O$, 0.032 (0.45); $CH_2{=}CH{-}OH$, 0.025 (0.26); $CH_3CO^{\bullet}$, 0.012 (0.061); $CH_2{=}CH{-}O^{\bullet}$, 0.00073 (0.035); ${}^{\bullet}CHO$, 0.069 (1.3, from which 1.0 is $[CO^{\bullet+}]$; note, however, that Franck-Condon factors can increase the extent of fragmentation for species formed by vertical neutralization).[15j]

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(23) In parts G and J of Figure 2 the significant fragments at m/z 16, presumably CH_2D^+, must originate from dissociation of $CH_3{-}CD{=}O^{\bullet+}$, as the complementary reionized product CHO^+ is of minor importance, and the CAD spectrum of $CH_3{-}CD{=}O^{\bullet+}$ shows a similar m/z 16 peak.

(24) An unfavorble isotope effect would be expected for the isomerization $CH_2{=}CH{-}OD \rightarrow {}^{\bullet}CH_2{-}CHD{-}O^{\bullet} \rightarrow CH_3{-}CD{=}O$ discussed by Splitter et al.[4]

Kinetically Stable Complexes of Alkali Cations with Rigidified Calix[4]arenes. X-ray Structure of a Calixspherand Sodium Picrate Complex

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In this communication we describe the synthesis of a novel class of highly preorganized host molecules in which the structural features of the calix[4]arenes and spherands are combined (calixspherand **2d**), together with the complexation with alkali cations.

The hexa-anisyl spherand **1** represents a macrocyclic host with an enforced cavity in which Li^+ or Na^+ cations are complexed with a very high *thermodynamic* stability.[1] Cram and co-workers have shown that these complexes of **1** with Li^+ and Na^+ are also *kinetically* very stable. However, the scope of complexation is

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