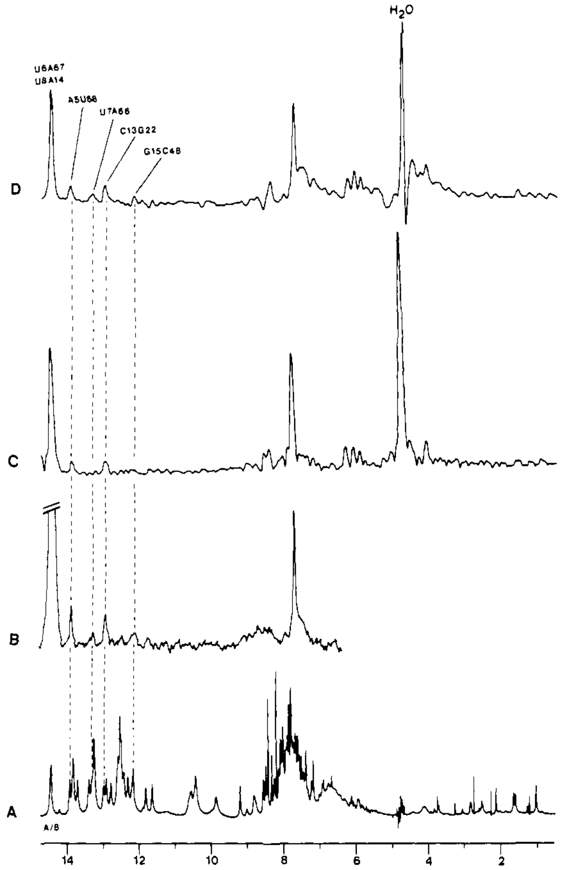

Figure 2. Comparison of NOE results obtained for the A/B imino proton resonance of yeast tRNA^{Phe} using different techniques. The assignments of the imino protons of adjacent Watson–Crick base pairs are indicated. The large NOE observed at 7.7 ppm is from the A14H8 and the A67H2 proton resonances, which at this temperature coincide. (A) Reference spectrum (same as in Figure 1). (B) 1D-NOE spectrum recorded with a "Redfield 2-1-4" pulse in combination with ADA.[1,7] (C) Cross section (parallel to ω_1) through the contour plot given in Figure 1 taken for a value of ω_2 corresponding to the position of resonance A/B. (D) Same cross section as in (C), however, after "phase sensitive" Fourier transformation in both dimensions.

combination with DSA[7]) is presented above the contour plot.

The peaks along the diagonal of the contour plot in Figure 1 represent the normal 1D-NMR spectrum, while the cross peaks depict the transfer of magnetization that occurs between several resonances during the mixing period τ_m. As explained elsewhere[7] the 2D spectrum is not symmetrical with respect to the diagonal due to the use of a semiselective observation pulse in combination with the DSA technique.

A detailed analysis of all the cross peaks observed in the 2D-NOE spectrum is clearly beyond the scope of the present communication; however, one general feature merits further discussion. In Figure 2C a cross section along the f_1 axis of the 2D spectrum is shown, which was taken at the f_2 position coinciding with the resonance at 14.4 ppm marked A/B in the 1D spectrum (Figure 2A). The latter resonance was shown[1] to originate from two imino protons of the tRNA^{Phe}: base pair U6A67 and the (tertiary) base pair U8A14. Using 1D-NOE techniques (Figure 2B), the resonances arising from the base pairs adjacent to these U6A67 and U8A14 pairs were identified[1,2] as indicated in Figure 2.

When the 1D-NOE difference spectrum (Figure 2B) is compared with the aforementioned cross section in Figure 2C, it is seen that not all interimino proton NOE's detected in the 1D-experiment have counterparts in the analogous 2D experiment. The reason for this fact must be sought in the method of 2D-data processing. In general, 2D spectra are presented in absolute value mode (as is the case in Figures 1 and 2C) in order to avoid phase correction in two dimensions. However, as absolute value mode signals normally display line shapes with long "tails" on both sides, 2D spectra must be heavily resolution enhanced (e.g., by multiplying the FID's with a sine-bell window[11]) in order to remove these "tails" from the spectrum.[12] The loss in sensitivity introduced by this type of resolution procedures is considerable and in the case at hand it even leads to an intolerable loss of information (cf. Figure 2, B and C). The solution for this problem is found in a "phase sensitive" 2D-FT procedure. Recently, States et al.[13] have shown that pure absorption phase 2D spectra have a much better intrinsic resolution, thus abolishing the need for resolution enhancement digital filtering. In fact, it is possible to enhance the signal-to-noise ratio by applying line-broadening digital filters without significant loss in resolution. This is shown in Figure 2D, which depicts the same cross section as given in Figure 2C, but now after the (same) 2D data file was Fourier transformed after applying a Gaussian line-broadening filter in both dimensions. It is seen that all four expected interimino proton NOEs are present in the spectrum (Figure 2D). The magnitude of these NOE's depends somewhat on the position where the cross section is chosen, because the A/B imino proton resonances are not coinciding exactly. The spectrum represents a compromise in the sense that for the given cross section all four NOE's are visible.

In summary, we have demonstrated that 2D-NOE spectroscopy is indeed possible for tRNA molecules having a molecular weight of ~28 000 even when large dynamic range problems are involved. Moreover, it is shown that, using this experimental technique, NOEs between imino protons of adjacent Watson–Crick base pairs are detectable, but full information can only be extracted after a "phase sensitive" 2D Fourier transformation of the data.

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Methyleneoxonium and Hydroxymethylene Dications: Dicationic Analogues of Ethylene and Acetylene

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There has been considerable recent theoretical and experimental interest in the methyleneoxonium ($CH_2OH_2^{+\cdot}$)[1-4] and hydroxymethylene ($HCOH^{+\cdot}$)[4-8] radical cations. The methyleneoxonium

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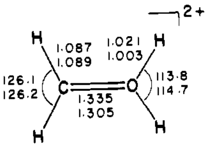
radical cation is found to lie substantially lower in energy than its more conventional isomer, the radical cation of methanol ($CH_3OH^{+}\cdot$), while $HCOH^{+}\cdot$ lies only marginally higher in energy than formaldehyde radical cation ($CH_2O^{+}\cdot$). Thus, in both these cases, ionization leads to a strong relative stabilization of structures (CH_2OH_2 and HCOH) that lie high in energy for the parent neutrals. It is intriguing to ask what would be the effect of removal of a second electron in these systems. This is the question that is addressed here with the aid of ab initio molecular orbital calculations. In the light of recent experimental[9] and theoretical[9e,i,10] interest in dications, additional impetus for the present study comes from the recognition that $CH_2OH_2^{2+}$ and $HCOH^{2+}$ are dicationic analogues of ethylene and acetylene, respectively.

Ab initio calculations were carried out for CH_3OH^{2+}, $CH_2OH_2^{2+}$, CH_2O^{2+}, $HCOH^{2+}$, the transition structures for various dissociative processes, and for various dissociation fragments.[11] Optimized geometries were obtained[14] with the 3-21G[15] and 6-31G*[16] basis sets. In order to obtain improved energy comparisons, electron correlation was incorporated at the MP2 and MP3 levels[17] with the 6-31G** basis set.[16] Vibrational frequencies[18] (3-21G//3-21G) were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPVE's). Optimized structures are displayed within the text[19] and relative energies given in Table I. Structural parameters, unless otherwise noted, refer to 6-31G* values[20] while relative energies quoted within the text and the figure refer to MP3/6-31G**//6-31G* values, corrected for zero-point vibration.[21]



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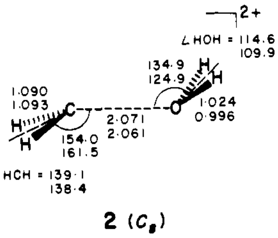

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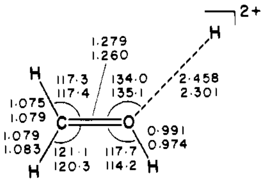

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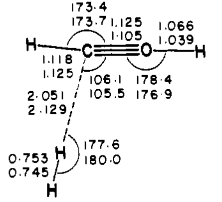
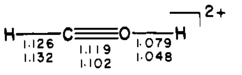
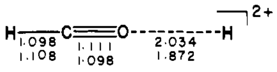


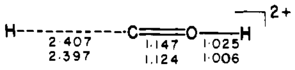
4 (C_s)



5 ($C_{\infty v}$)



6 ($C_{\infty v}$)



7 ($C_{\infty v}$)

The methyleneoxonium dication ($CH_2OH_2^{2+}$, **1**), isoelectronic with ethylene, is found to be planar with C_{2v} symmetry. The C–O bond is quite short with a length (1.305 Å) between that of a normal C–O single bond (e.g., 1.399 Å in methanol) and a C–O double bond (e.g., 1.184 Å in formaldehyde). The C—O length is similar to that of the ethylenic C=C double bond (1.317 Å). Calculations on $CH_2OH_2^{2+}$ but without geometry optimization have been reported previously.[10h,o]

$CH_2OH_2^{2+}$ lies 33 kJ mol^{-1} above $CH_2^{+}\cdot + OH_2^{+}\cdot$ and 103 kJ mol^{-1} above $CH_2OH^{+} + H^{+}$.[22,23] However, it is separated from each of these possible pairs of fragment products by large barriers (Figure 1a) and the transition structures **2** and **3**, respectively. The lower energy decomposition pathway, i.e., via **3** to give $CH_2OH^{+} + H^{+}$, requires 252 kJ mol^{-1}.

The methanol dication (CH_3OH^{2+}) is found to fall apart on both the 3-21G and 6-31G* surfaces. It yields a weak complex

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(19) Structural parameters correspond to 3-21G (upper) and 6-31G* (lower) values. Throughout this paper, bond lengths are in angstroms and bond angles in degrees.

(20) Structural parameters (6-31G* values) for reference molecules taken from: Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University: Pittsburgh, PA, 1981.

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Table I. Calculated Relative Energies (kJ mol^{-1}) for the Methyleneoxonium Dication ($CH_2OH_2^{2+}$), the Hydroxymethylene Dication ($HCOH^{2+}$), and Related Species

		3-21G// 3-21G	6-31G*// 6-31G*	6-31G**// 6-31G*	MP2/ 6-31G**// 6-31G*	MP3/ 6-31G**// 6-31G*	MP3/ 6-31G**// 6-31G*^{a}
$CH_2OH_2^{2+}$	1	0^b	0^b	0^b	0^b	0^b	0^b
$CH_2^{+}\cdot + OH_2^{+}\cdot$		−116	−137	−135	41	8	−33
$CH_2OH^+ + H^+$		−8	−71	−51	−78	−69	−103
TS ($1 \rightarrow CH_2^{+}\cdot + OH_2^{+}\cdot$)	2	309	312	315	426	400	375
TS ($1 \rightarrow CH_2OH^+ + H^+$)	3	309	265	284	262	273	252
$HCOH\cdots H_2^{2+}$	4	380	345	360	320	343	312
$HCOH^{2+} + H_2$		405	366	377	343	366	326
$HCOH^{2+}$	5	0^c	0^c	0^c	0^c	0^c	0
$HCO^+ + H^+$		−229	−270	−251	−287	−272	−289
$COH^+ + H^+$		−143	−134	−128	−108	−122	−147
TS ($5 \rightarrow HCO^+ + H^+$)	6	112	99	116	95	107	92
TS ($5 \rightarrow H^+ + COH^+$)	7	195	206	212	221	215	194

[a] Including zero-point contribution (see text). [b] Total energies (hartrees) are, respectively, −113.511 22, −114.129 33, −114.147 53, −114.438 78, and −114.454 62. [c] Total energies (hartrees) are, respectively, −112.234 09, −112.863 21, −112.872 51, −113.150 45, and −113.152 07.

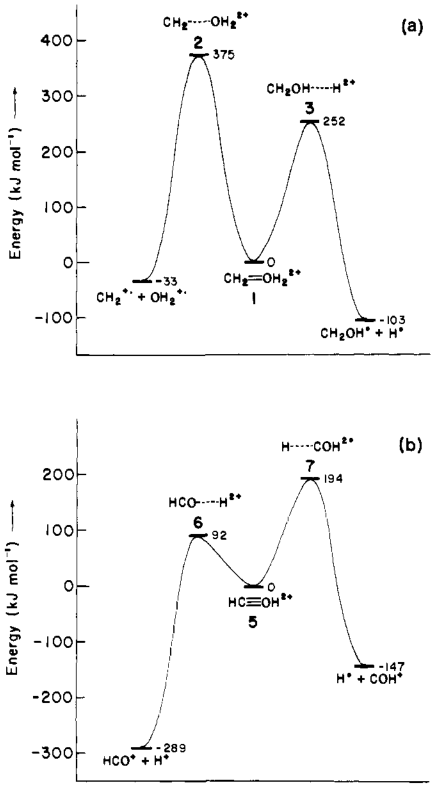

Figure 1. Schematic potential energy profile for dissociative processes in (a) the methyleneoxonium dication (**1**) and (b) the hydroxymethylene dication (**5**).

(**4**) of $HCOH^{2+}$ (see below) and H_2, with a calculated binding energy of 14 kJ mol^{-1}. The complex 4 lies substantially higher in energy (by 312 kJ mol^{-1}) than the methyleneoxonium dication (**1**).

The theoretical results for $CH_2OH_2^{2+}$ and CH_3OH^{2+} show pleasing agreement with the experimental observations of Holmes et al.[3] They found, in charge-stripping mass spectrometry experiments, an intense peak corresponding to $[CH_4O]^{2+}$ in the spectrum of $CH_2OH_2^{+}\cdot$. In contrast, no $[CH_4O]^{2+}$ was observed by charge stripping from $CH_3OH^{+}\cdot$. Our calculations, in addition to indicating in general terms the stability of $CH_2OH_2^{2+}$ and the instability of CH_3OH^{2+}, *demonstrate specifically the stability of* $CH_2OH_2^{2+}$ *when formed from* $CH_2OH_2^{+}\cdot$ *in charge-stripping experiments*. Thus, vertical ionization from $CH_2OH_2^{+}\cdot$[26] yields a $CH_2OH_2^{2+}$ dication lying 108 kJ mol^{-1} (MP3/6-31G**//6-31G* without zero-point correction) above the equilibrium structure of $CH_2OH_2^{2+}$, i.e., comfortably within the potential well shown in Figure 1a. This contrasts with our corresponding results (see below) for $HCOH^{2+}$.

The hydroxymethylene dication ($HCOH^{2+}$, **5**) is isoelectronic with acetylene. It has been examined previously by Summers and Tyrrell[10d] and by Cremaschi and Simonetta[10e] who obtained results similar to those reported here. It has a linear structure with a C–O bond length (1.102 Å) close to that of carbon monoxide (1.114 Å) and somewhat shorter than the C≡C triple bond of acetylene (1.185 Å).

The hydroxymethylene dication lies substantially higher in energy than the fragmentation products $HCO^+ + H^+$ (by 289 kJ mol^{-1}) and $H^+ + COH^+$ (by 147 kJ mol^{-1}) (see Figure 1b).[27] However, there are again significant barriers to such decompositions although the barrier heights are considerably smaller than in the case of $CH_2OH_2^{2+}$ above. Fragmentation to $HCO^+ + H^+$ requires 92 kJ mol^{-1} via transition structure **6** while fragmentation to $H^+ + COH^+$ requires 194 kJ mol^{-1} via transition structure **7**.

The "conventional" isomer, formaldehyde dication (CH_2O^{2+}), is again unstable. In this case, we find decomposition without a barrier to give $HCO^+ + H^+$.

Very recent attempts by Holmes and co-workers to observe $HCOH^{2+}$ in charge-stripping experiments have been unsuccessful.[28] Our calculations provide a plausible rationalization. Vertical ionization from $HCOH^{+}\cdot$ yields an $HCOH^{2+}$ dication lying 195 kJ mol^{-1} (MP3/6-31G**//6-31G* without zero-point contribution) above that of the equilibrium $HCOH^{2+}$ structure.[29] Examination of Figure 1b then shows that dissociation from this vertically ionized structure to give $HCO^+ + H^+$ would be a facile and highly exothermic process; i.e., *$HCOH^{2+}$ is unlikely to be observable in charge-stripping experiments from $HCOH^{+}\cdot$*. This contrasts with our results above for $CH_2OH_2^{2+}$. Alternative procedures for synthesizing $HCOH^{2+}$ must therefore be devised.

In summary, we find that the greatly enhanced stability of $CH_2OH_2^{+}\cdot$ (vs. $CH_3OH^{+}\cdot$) and of $HCOH^{+}\cdot$ (vs. $CH_2O^{+}\cdot$) compared with the parent neutrals is further accentuated following removal of a second electron. Thus, whereas CH_3OH^{2+} and CH_2O^{2+} are unstable, $CH_2OH_2^{2+}$ and $HCOH^{2+}$ are well-bound species. The latter pair are undoubtedly stabilized in part by favorable electronic effects associated with their isoelectronic relationship to ethylene and acetylene, respectively.

Registry No. Methyleneoxonium dication, 83584-97-8; hydroxymethylene dication, 63541-95-7.

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(26) The 6-31G* structure of $CH_2OH_2^{+}\cdot$ has been reported in: Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1982**, *17*, 340.

(27) For a detailed study of the HOC^+/HCO^+ system, see: Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1.

(28) Holmes, J. L., personal communication. We are indebted to Professor Holmes for bringing this observation to our attention and for suggesting that we examine the vertical ionization process.

(29) The UHF/6-31G* structure for $HCOH^{+}\cdot$ has C–O = 1.210, C–H = 1.084, and O–H = 0.972 Å and ∠HCO = 125.3°, ∠COH = 118.8°, and ∠HCOH = 180.0°.