Ion Cyclotron Resonance Mass Spectrometric and ab Initio Studies of the Structure and Mechanism of Formation of Protonated Dimers in Simple Carbonyl Compounds XYCO (X or Y = H or F)

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Abstract: A combination of experimental mass spectrometric and theoretical ab initio calculations was applied to the study of the formation and structure of protonated dimers in simple carbonyl compounds. The formation of protonated dimers in formaldehyde, formyl fluoride, and carbonyl fluoride and binary mixtures of formaldehyde with the latter two has been studied by ion cyclotron resonance mass spectrometric techniques. In addition to the symmetric protonated dimers $(H_2CO)_2H^+$ and $(HFCO)_2H^+$, two asymmetric ions were observed, $(H_2CO\text{-}HFCO)H^+$ and $(H_2CO\text{-}F_2CO)H^+$. The latter two were formed only when a large excess of the fluoride was present in the mixture. Ab initio calculations, using a minimal STO-4G basis set, were used to determine the most stable conformation, which was found to be a proton-bridged dimer. The equilibrium conformations of the four protonated dimers were then calculated with an extended 4-31G basis set. The geometric parameters which affected the stability of the protonated dimers, namely, the length of the O—H and C═O bonds and the HOC angles, were optimized in this basis set. Electron difference density plots of the proton bridged dimers were constructed. The presence of a three-center bond along the O-H-O axis was evident in the symmetric ions, while in the asymmetric ones this feature was not as pronounced. The heats of reaction for the dimerization processes were calculated, and the relative stabilities of the protonated dimers were estimated. A correlation between the measured reaction rates and the calculated heats of reaction was found.

Introduction

The question of the structure and mechanism of formation of protonated dimers in simple carbonyl compounds instigated an extensive theoretical ab initio study on the neutral[2a] and protonated[2b] monomers and protonated dimers of these compounds. The former two topics were dealt with in previous papers.[2] In this paper the experimental observations and theoretical calculations on the protonated dimers are described and discussed.

Protonated dimers of carbonyl compounds in general,[3-7] and of formaldehyde[3] and formyl fluoride[4] in particular, have been observed experimentally by mass spectrometric techniques. In ion cyclotron resonance (ICR) studies of formaldehyde (H_2CO)[3] and of formyl fluoride (HFCO)[4] an association reaction between a neutral and protonated molecule was observed:

$$HYCOH^+ + HYCO \rightarrow (HYCO)_2H^+ \qquad (1)$$

where Y = H or F. However, in preliminary experiments with a binary mixture of formaldehyde with carbonyl fluoride (F_2CO) the latter was not observed to participate in protonated dimer formation.[4] In order to understand these phenomena on the molecular level, ab initio studies were carried out. These studies indicated that the experimentally observed symmetric protonated dimers, $(H_2CO)_2H^+$ and $(HFCO)_2H^+$, as well as the hitherto unobserved asymmetric ones, $(H_2CO\text{-}HFCO)H^+$ and $(H_2CO\text{-}F_2CO)H^+$, should all have considerable stabilization energies. Furthermore, some indication of the experimental conditions appropriate for formation of the asymmetric protonated dimers could be derived from the calculations. In further ICR experiments, the asymmetric protonated dimers were indeed observed, as reported below.

Ab initio studies, using a minimal STO-3G basis set, on neutral formaldehyde dimers[8] and on other hydrogen-bonded dimers containing formaldehyde[9] were reported by Del Bene et al. The stabilization energy of the protonated dimers is an order of magnitude larger than that of the neutral dimers, as indicated by the calculations carried out here. In this work, minimal STO-4G basis set calculations were used as a preliminary step toward determining which plausible conformation of protonated formaldehyde dimers was the most stable. Once this question was settled, the extended 4-31G basis set was used to optimize the major geometrical parameters and to study the four experimentally observed protonated dimers, namely, $(H_2CO)_2H^+$, $(H_2CO\text{-}HFCO)H^+$, $(HFCO)_2H^+$, and $(H_2CO\text{-}F_2CO)H^+$.

Experimental Section

The experiments were performed with a commercial Varian V-5900 ion cyclotron resonance (ICR) mass spectrometer. The instrument and the experimental techniques used in this work were described in detail earlier.[3,4] Formaldehyde[3] and formyl fluoride[4] were synthesized by methods previously described. Carbonyl fluoride was purchased from PCR, Inc., Gainsville, Fla., and purified by several freeze-pump-thaw cycles.

The molecular orbital calculations were carried out, as in the previous papers,[2] using the GAUSSIAN 70 program.[10] All degrees of freedom of the three proposed conformations of protonated formaldehyde were optimized, using the STO-4G basis set.[10b] The proton-bridged conformation of the protonated formaldehyde dimer was then fully optimized with the 4-31G basis set[10c] with the only constraint being that the ion was assumed to be planar. In all the other protonated dimers, the length of the C═O and O—H bonds and the HOC angles were optimized, using the 4-31G basis set. In all optimizations the final geometric parameters were interpolated, so that the precision is better than 0.005 Å in the bond lengths and 0.5° in the angles.

The electronic difference density maps were constructed by subtracting the electron density of the superposed spherical atoms from the molecular density as calculated from the molecular wave function. The method has been explained in detail previously.[11] No electron density was ascribed to the isolated proton, so nothing was subtracted from the total density for this atom.

Results

Mass Spectrometric Results. The formation of protonated dimers in pure formaldehyde[3] and in pure formyl fluoride[4] has been described earlier. Association reactions between protonated and neutral molecules lead to the formation of protonated dimers. In formaldehyde

$$H_2COH^+ + H_2CO \rightarrow (H_2CO)_2H^+ \qquad (2)$$

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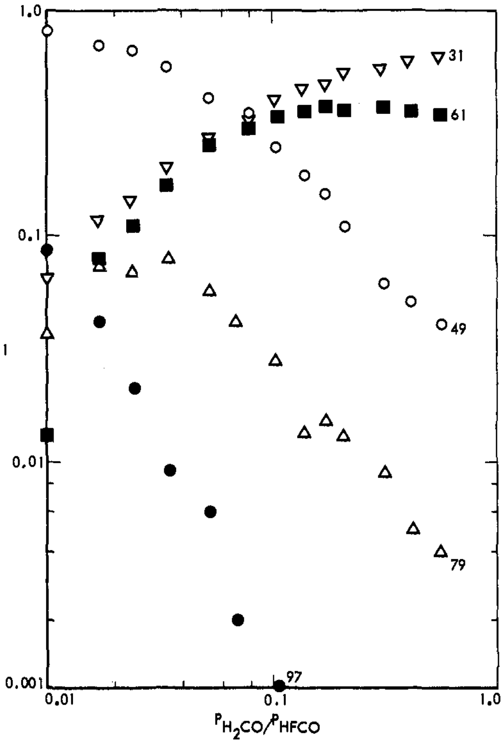


Figure 1. The fractional intensity of the protonated species in a binary mixture of formaldehyde and formyl fluoride as a function of the pressure ratio of the neutral reactants: (○) $HFCOH^+$, (▽) (H_2COH^+), (△) (H_2CO-$HFCO)H^+$, (■) $(H_2CO)_2H^+$, and (●) $(HFCO)_2H^+$.

and in formyl fluoride

$$HFCOH^+ + HFCO \rightarrow (HFCO)_2H^+ \qquad (3)$$

The heats of formation of the protonated dimers were not measured experimentally, so that the exothermicity of reactions 2 and 3 could not be determined from the available thermodynamic data. However, according to the ab initio calculations both reactions are exothermic by over 1 eV (see below). As no particle is released in the association reactions, the excess energy must be stored in the product ion as internal energy. The excited protonated dimer can either be collisionally stabilized (channel 4a) or dissociate according to channels 4b-d.

$$\begin{array}{llll} & & \rightarrow (HYCO)_2H^+ & (4a) \\ HYCOH^+ & & & \\ & \overset{(4)}{\rightleftarrows} [(HYCO)_2H^+]^* & \rightarrow C_2H_2Y_2O_2^+ + H & (4b) \\ + & & \rightarrow C_2H_3Y_2O^+ + O & (4c) \\ HYCO & & & \\ & & \rightarrow C_2H_3YO_2^+ + Y & (4d) \end{array}$$

All these channels were experimentally observed in pure formaldehyde[3] and pure formyl fluoride.[4] Reaction 4 is reversible, in which case no signal will be detected.

In a binary mixture of formaldehyde and formyl fluoride, two reactions leading to the formation of the asymmetric protonated dimer, $(H_2CO$-$HFCO)H^+$, were observed. They were verified by ion cyclotron double resonance (ICDR) and pressure-dependence techniques. Of the two reactions

$$HFCOH^+ + H_2CO \rightarrow (H_2CO\text{-}HFCO)H^+ \qquad (5)$$

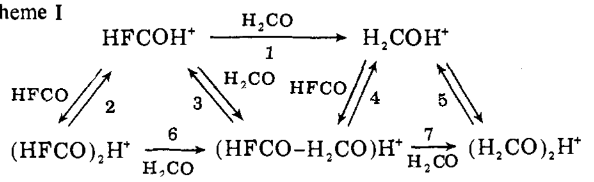
and

$$H_2COH^+ + HFCO \rightarrow (H_2CO\text{-}HFCO)H^+ \qquad (6)$$

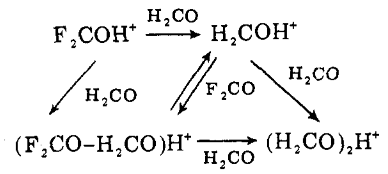
the former is an order of magnitude faster than the latter.

The dependence of the intensities of all the protonated species (the protonated monomers $HFCOH^+$ and H_2COH^+ and the protonated dimers $(HFCO)_2H^+$, $(H_2CO$-$HFCO)H^+$, and $(H_2CO)_2H^+$) on the ratio of the neutral reactants pressure, P_{H_2CO}/P_{HFCO}, is shown in Figure 1. The mass spectrum is dominated by the protonated formyl fluoride monomer and dimer before the addition of formaldehyde. The intensities of these two ions decrease upon formaldehyde addition and three new protonated species begin to form, namely, the protonated formaldehyde monomer and dimer and the asymmetric protonated dimer, $(H_2CO$-$HFCO)H^+$. This latter ion reaches its maximum intensity when the pressure ratio $P_{H_2CO}/P_{HFCO} \cong 0.03$. Further formaldehyde addition leads to a decrease in the intensity of all the ions that contain formyl fluoride. Formaldehyde monomers and dimers dominate the mass spectrum when the neutral formaldehyde pressure is above one-tenth of the total pressure. On the basis of the experiments described above, the following reaction scheme could be formulated.[13]

Scheme I



Scheme II



Owing to the fact that formaldehyde has a higher proton affinity than formyl fluoride, the reverse reactions (1), (6), and (7) in Scheme I are neglected. Addition of formaldehyde shifts the reaction to the right in the above scheme.

The ab initio calculations indicated that, in the formaldehyde–carbonyl fluoride mixture, an even larger excess of the latter would be needed if the asymmetric protonated dimer, $(H_2CO$-$F_2CO)H^+$, was to be obtained. In recent ICR experiments the ion was observed to be formed by the reactions

$$F_2COH^+ + H_2CO \rightarrow (H_2CO\text{-}F_2CO)H^+ \qquad (7)$$

and

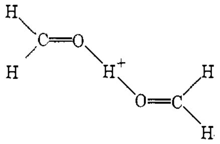
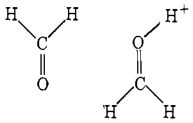
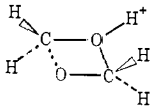
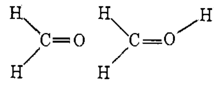
$$H_2COH^+ + F_2CO \rightarrow (H_2CO\text{-}F_2CO)H^+ \qquad (8)$$

Pressure-dependence measurements indicated that reaction 7 is two orders of magnitude faster than reaction 8. Double-resonance experiments confirmed the reaction channels.

The failure to observe $(H_2CO$-$F_2CO)H^+$ in the earlier ICR experiments[4] in this mixture was due to an insufficient excess of carbonyl fluoride. The ion reached its maximum fractional intensity when the pressure ratio was as low as $P_{H_2CO}/P_{F_2CO} \approx 0.02$. The reaction scheme of the protonated species in the formaldehyde–carbonyl fluoride mixture (Scheme II), is similar to the one formulated above. A protonated dimer of carbonyl fluoride, $(F_2CO)_2H^+$, was not observed, indicating that even at a density of $H_2CO/F_2CO < 0.01$, association of F_2COH^+ with formaldehyde (reaction 7) is preferred over condensation with F_2CO.

In a recent work, dealing with the measurement of equilibrium constants of protonated monomers and dimers by ICR techniques, Davidson et al.[13] proposed and solved analytically a reaction scheme quite similar to that described above. However, the assumptions made in that work in order to determine the equilibrium constant and the reaction rate constants are not necessarily valid for the H_2CO-YFCO systems (see Discussion).

Table I. Schematic Configuration of Protonated Formaldehyde Dimers, Their Total Energy, and Stabilization Energy (Minimal STO-4G Basis Set)

	schematic configuration	total energy, au	stabilization energy, kcal mol^{-1}
proton bridged		−226.7479	47.5
antiparallel		−226.6776	3.4
4-center nonplanar		−226.6760	2.4
separated reactants		−226.6722	0

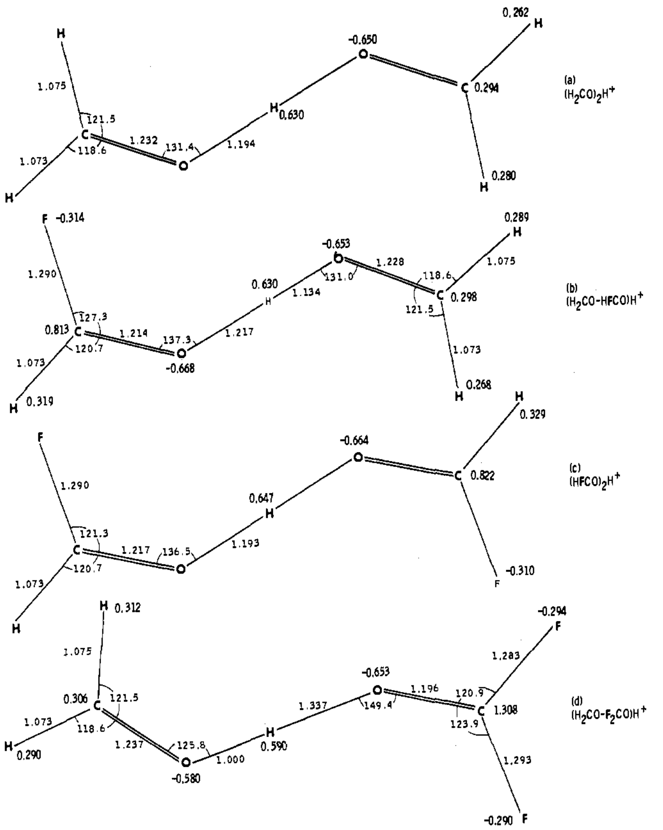


Figure 2. The optimized equilibrium conformations and Mulliken populations, calculated with the 4-31G basis set, of the proton-bridged dimers: (a) $(H_2CO)_2H^+$, (b) $(H_2CO\text{-}HFCO)H^+$, (c) $(HFCO)_2H^+$, and (d) $(H_2CO\text{-}F_2CO)H^+$. Note the proton position and HOC angle in the asymmetric ions.

Ab Initio Calculations. In order to determine the structure of protonated dimers in these simple carbonyl compounds, the protonated formaldehyde dimer was optimized initially with the minimal STO-4G basis set.[10b] The three basic configurations which were considered, their total energy, and their stabilization energy (relative to the separated reactants) are shown in Table I.

As evident from Table I, the proton-bridged configuration is by far the most stable. For this reason this was assumed to be the initial structure for the carbonyl protonated dimers, and will be discussed in detail below. In the antiparallel configuration only little charge redistribution takes place, and the relatively low stabilization energy arises mainly from the weak dipole-dipole interactions between the two reactants. The four-center nonplanar configuration involves considerable rearrangement. Although it is the least stable structure studied, despite the strain it is still lower in energy than the separated reactants. Such a model may account for oxygen ejection as discussed below.

Ab Initio Calculations of Proton-Bridged Dimers. The four protonated dimers formed in the association reactions 2-3 and 5-8, namely, $(H_2CO)_2H^+$, $(H_2CO\text{-}HFCO)H^+$, $(HFCO)_2H^+$, and $(H_2CO\text{-}F_2CO)H^+$, were studied by extended basis set calculations. A planar proton bridged conformation was assumed. The protonated formaldehyde dimer was fully optimized, and it was seen that the total energy of the ion was insensitive to small changes in the methylene (H_2C) parts of the ion. Hence, in order to save computer time, only the structural variables of the ion containing or adjacent to the proton were optimized, namely, the O-H and C-O bond lengths and the HOC angles. The results, including the total energy, the stabilization energy, as well as the experimental relative reaction rates of formation, are given in Table II. The geometrical parameters of the ions and the Mulliken atomic populations are schematically presented in Figure 2.

Protonated Formaldehyde Dimer, $(H_2CO)_2H^+$. The deformation density map of this ion is shown in Figure 3. The proton "bridges" the two oxygen atoms in what is apparently a three-center bond (Figure 3). The length of the carbonyl bond in the protonated dimer (1.232 Å) is slightly shorter than in the protonated monomer (1.244 Å) but considerably longer than in the neutral molecule (1.206 Å). The negative charge on the oxygen atom is larger than in the protonated monomer, while the proton in the protonated dimer has a larger positive charge than in the protonated monomer[2b] (Figure 2). Relatively small changes in the charge distribution take place in the methylene groups. It is of interest to note the 7° increase in the HOC angle in the protonated dimer (131.4°) relative to the protonated monomer (124.5°).[2] The stabilization energy calculated with the extended basis set, 34.7 kcal mol^{-1}, is considerably lower than that obtained with the minimal basis

Table II. Total Energy, Stabilization Energy, and Relative Reaction Rates of Formation of the Protonated Dimers $(H_2CO)_2H^+$, $(H_2CO\text{-}HFCO)H^+$, $(HFCO)_2H^+$, and $(H_2CO\text{-}F_2CO)H^+$ (Extended 4-31G Basis Set Calculations)

	total energy, au	total energy of reactants, au		stabilization energy, kcal mol^{-1}, and relative reaction rates[a]	
		$H_2COH^+ + YFCO$	$YFCOH^+ + H_2CO$	$H_2COH^+ + YFCO$	$YFOCH^+ + H_2CO$
$(H_2CO)_2H^+$	−227.7292	−227.6739		−34.7 (2.6)	
$(H_2CO\text{-}HFCO)H^+$	−326.4631	−326.4269	−326.3948	−22.7 (0.055)	−42.9 (1.4)
$(HFCO)_2H^+$	−425.1948	−425.1478		−29.5 (1)	
$(H_2CO\text{-}F_2CO)H^+$	−425.1851	−425.1597	−425.0978	−15.9 (0.054)	−54.8 (5)

[a] The relative reaction rates are given in parentheses alongside the corresponding stabilization energy.

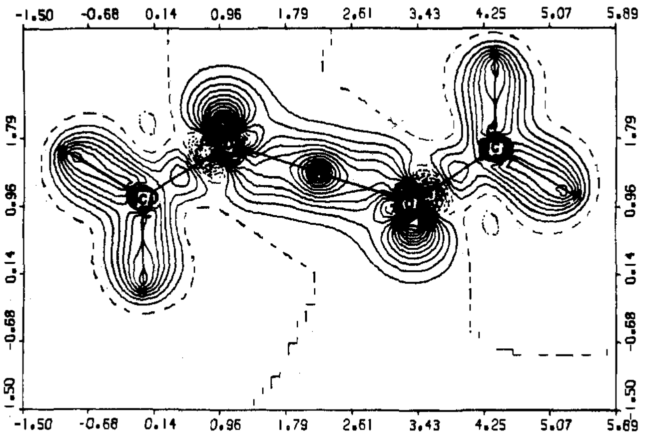


Figure 3. The electron deformation density map of a formaldehyde proton bridged dimer in the molecular plane. Solid, dashed, and dotted lines denote positive, zero, and negative difference densities, respectively. Contours are at 0.1 e/Å^3 intervals. Note the density along the O-H-O bond.

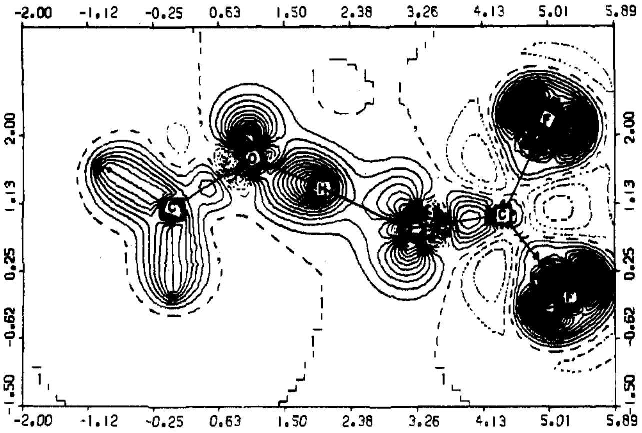


Figure 4. The electron deformation density map of the protonated asymmetric dimer $(H_2CO\text{-}F_2CO)H^+$ in the molecular plane. Contours as in Figure 3. Note the density along the O-H-O bond, the HOC angles, and the oxygen lone pair orientation.

set, 47.5 kcal mol^{-1}. This is consistent with the trend of the smaller basis set to overestimate the proton affinities of these compounds, as pointed out previously.[2b,12]

Formaldehyde-Formyl Fluoride Protonated Dimer, $(H_2CO\text{-}HFCO)H^+$. This ion is schematically represented in Figure 2b. Experimentally, the ion could be formed by two reaction channels, (5) and (6). The extended basis set calculations indicate that the former is more exothermic by ~20 kcal mol^{-1} than the latter (see Table II). This correlates with the experimental observation that reaction 5 is an order of magnitude faster than reaction 6 (see Table II). The most outstanding geometric feature of this ion is the position of the proton. It is not equidistant from the two oxygen atoms, but rather closer to the formaldehyde molecule. This is to be expected, as the proton is more strongly attracted to the stronger base and the proton affinity of formyl fluoride is lower than that of formaldehyde.[2b] Another interesting feature is the HOC angles. The angle of the proton with the formaldehyde carbonyl bond is almost equal to that angle in the formaldehyde protonated dimer, while the angle of the proton with the formyl fluoride carbonyl bond is similar to that angle in $(HFCO)_2H^+$, and is over 10° larger than in the protonated formyl fluoride monomer (126.8°).[2b] The significance of these features will be discussed below. The trends in charge distribution mentioned above occur here too, as seen in Figure 2.

Protonated Formyl Fluoride Dimer, $(HFCO)_2H^+$. The geometric parameters of this symmetric protonated dimer are schematically represented in Figure 2c. The proton is equidistant from both oxygen atoms, as would be expected from symmetry. The length of the O-H bond is essentially the same as in $(H_2CO)_2H^+$, but the HOC angle is considerably larger in $(HFCO)_2H^+$ than in either $(H_2CO)_2H^+$ or in the protonated formyl fluoride monomer.[2b] The trends in charge distribution mentioned above, i.e., the oxygen becomes more negative while the proton becomes more positive in the protonated dimer than in the monomer, again occur here. The stabilization energy of this ion is 29.5 kcal mol^{-1}, as calculated with the extended basis set, which is slightly less than that of the protonated formaldehyde dimer.

Formaldehyde-Carbonyl Fluoride Protonated Dimer, $(H_2CO\text{-}F_2CO)H^+$. The geometric parameters of this "asymmetric" ion are schematically represented in Figure 2d, and its electron deformation density map is shown in Figure 4. As in the other "asymmetric" protonated dimer described above, the most interesting geometric feature is the position of the proton. The proton is closer to the formaldehyde part of the molecule, so much so that the calculated O-H bond length (1.000 Å) and the HOC angle (125.8°) are almost the same as in protonated formaldehyde monomer (0.966 Å and 124.5°, respectively). On the other hand, the carbonyl fluoride O-H bond length is large for such a bond (1.337 Å) and the HOC angle of 149.4° is much larger than in the protonated monomer (126.9°).[2b] The length of the carbonyl bonds in the ion also indicates that it is structurally close to a protonated formaldehyde molecule and a neutral carbonyl fluoride molecule. This implies that $(H_2CO\text{-}F_2CO)H^+$ ions would have a tendency to dissociate, as in the reverse reaction (8). The difference density map of the ion (Figure 4) shows that density along the two O-H bonds is mainly concentrated on the formaldehyde side, in support of the assumption that the ion will tend to dissociate to $H_2COH^+ + F_2CO$. Of the two reaction channels through which the ion can be formed, reaction 7 is more exothermic by 38.9 kcal mol^{-1} according to the calculations (Table II). This correlates with the experimental observation that reaction 7 is some two orders of magnitude faster than reaction 8.

Discussion

A tentative picture of the structure and mechanism of formation of protonated dimers in simple carbonyl compounds seems to be emerging through the combination of the experimental ICR mass spectrometric results with the results of ab initio calculations. The experimental observation of $(H_2CO\text{-}F_2CO)H^+$ alters one of the fundamental assumptions upon which an earlier proposed mechanism of formation and structure of protonated dimers was based.[4] According to the experimental data available at that time, carbonyl fluoride did not participate in protonated dimer formation. Thus, in view of the additional experimental data and the results of the ab initio studies, a somewhat different model is proposed here. The formation of protonated dimers in binary mixtures of formaldehyde with formyl fluoride or carbonyl fluoride can be explained in terms of competition of the neutral reactants for the available protons. The more acidic fluoride molecules are displaced by formaldehyde from their protonated species. This is evident in the protonated dimers as well as in protonated monomers. Ab initio calculations show that the displacement of formyl fluoride by formaldehyde in reactions 9 and 10 is exothermic by 13.4 and 12.0 kcal mol^{-1}, respectively.

$$(HFCO)_2H^+ + H_2CO \rightarrow (HFCO\text{-}H_2CO)H^+ + HFCO \quad (9)$$

$$(HFCO\text{-}H_2CO)H^+ + H_2CO \rightarrow (H_2CO)_2H^+ + HFCO \quad (10)$$

In the carbonyl fluoride-formaldehyde mixture, displacement of carbonyl fluoride by formaldehyde is even more exothermic than the displacement of formyl fluoride described above. Reaction 11 is exothermic by 18.7 kcal mol^{-1} according to the ab initio calculations:

$$(F_2CO\text{-}H_2CO)H^+ + H_2CO \rightarrow (H_2CO)_2H^+ + F_2CO \quad (11)$$

Thus, a large excess of carbonyl fluoride is needed to drive reaction 11 to the left and to get the asymmetric protonated dimer. In the preliminary experiment[4] this was not clearly appreciated and it was for this reason that the initial attempts to form the "mixed" protonated species failed.

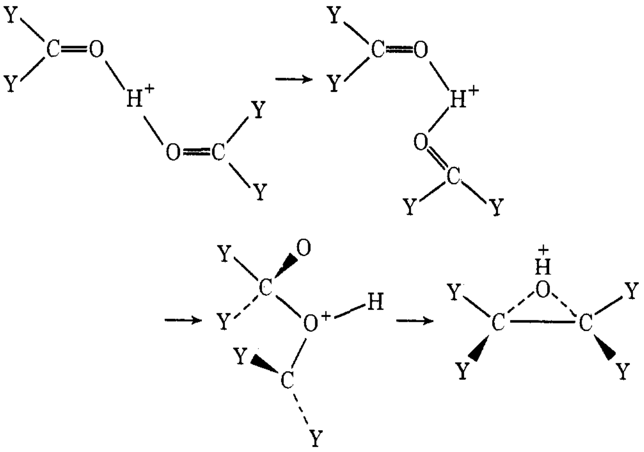
In a recent work, Davidson et al.[13] determined the equilibrium constants and free energies in systems in which protonated dimer formation competes with proton transfer. They noted that the equilibrium constants depended on the relative rates of the dimerization and proton transfer reactions and on the total and relative pressure of the neutral reactants.[13] This appears to be the case in these systems as well. Although we were not concerned with the measurement of the equilibrium constants, the dependence of the fractional intensities of the ion signals on the ratio of the neutral reactants density, shown in Figure 1, demonstrates these points. The H_2CO-HFCO reaction system shown in Scheme I is more complex than the reaction scheme solved by Davidson et al.[13] Some assumptions made in that work were found to be invalid for these carbonyl systems, namely: (1) the rate of formation of the asymmetric protonated dimers is not equal in both channels (reactions 5 and 7 are much faster than reactions 6 and 8), (2) the displacement reactions (9–11) should not be neglected, and (3) dissociation of the asymmetric protonated dimer to H_2COH^+ + YFCO is an important channel for the depletion of that species.

The excess energy, with which the protonated dimer is initially formed, is disposed of either by collisional relaxation processes or by the dissociation channels described above (reactions 4b-d). In the binary mixtures of formaldehyde with the fluoride molecules, the dissociation of the excited protonated dimer to a protonated formaldehyde ion and a neutral fluoride molecule is evident,[4] but could not be experimentally distinguished from direct proton transfer reactions. Thus, the proton-bridged dimer can be viewed as an intermediate in some proton-transfer reactions of simple carbonyl compounds.

Correlating theoretical structures of the protonated dimers with those obtained in the experiment was somewhat more problematic. The ab initio calculations strongly favored the proton-bridged conformation, as it was found to have a stabilization energy which was an order of magnitude larger than that of the square planar or the four-centered nonplanar conformations. This type of conformation can also explain the relative reactivity of formaldehyde, formyl fluoride, and carbonyl fluoride toward participation in the formation of protonated dimers. The reactivity can thus be correlated to their relative acidity. The major difficulty in accepting this conformation was that the ejection of an oxygen atom (channel 4c) would lead to breaking the link between the two carbon atoms. It would be difficult to visualize the formation of ions of the type $C_2H_3Y_2O^+$ (Y = H or F), which were observed in formaldehyde[3] and formyl fluoride, from this structure.[4] The process of oxygen atom ejection may take place through some concerted rearrangement of the excited protonated dimer and this requires further study. A possible rearrangement scheme would be Scheme III. Thus, based on the energetics, the proton-bridged dimers seem to be the most plausible initial conformations for these protonated dimers, followed by some type of rearrangement or dissociation. The latter may involve a proton transfer.

As mentioned above, the position of the proton, especially in the asymmetric protonated dimers, is of interest. In the symmetric ions, $(H_2CO)_2H^+$ and $(HFCO)_2H^*$, the proton is equidistant from the oxygen atoms in each ion, and the O-H bond length, 1.193 Å, is essentially equal in both these ions. The outstanding feature in these ions is the increase in the HOC angles, which are 7–10° larger than in the protonated monomers. This increase in the HOC angles is even more prominent in the asymmetric protonated dimers (see Figure 2). While in the protonated monomers, H_2COH^+, $HFCOH^+$, and F_2COH^+, the HOC angle is essentially constant,[2b] the HOC angles in the protonated dimers of these compounds vary strongly. The reason for this difference may be rationalized in terms of the relative contribution of the electrostatic and "covalent" contributions. In the protonated monomers the O-H bond is largely "covalent" and, as seen from the difference density maps of these ions,[2b] the HOC angle is close to the LOC angle (L is the "center" of the lone pair).[2b] In the protonated dimers, on the other hand, the O-H bond is not as covalent as in the protonated monomers. This is reflected in the longer O-H bond and the difference density maps of these ions (Figures 3 and 4). The electrostatic interaction becomes relatively more important and the HOC angle opens correspondingly (the electrostatic repulsion between the carbonyl carbon and the proton is minimal when HOC = 180°). This feature is most pronounced in the asymmetric ions, as shown in Figure 4. Thus, in $(F_2CO\text{-}H_2CO)H^+$, where the charge on the carbon atom of F_2CO is large (1.308 e), the HOC angle is also large (149°), while in $(HFCO\text{-}H_2CO)H^+$ where the charge on the HFCO carbon is 0.873 e, the HOC angle is 137.3°, and in $(H_2CO)_2H^+$, the charge is 0.294 and HOC = 131.4°. The stabilization energies of the protonated dimers were calculated with the 4-31G basis set (Table II). Both this basis set and the STO-4G basis set had a tendency to overestimate the proton affinities of simple carbonyl compounds (the former by only a few kilocalories per mole), while preserving the experimentally observed trends.[2b] Thus, the values obtained in this work for the stabilization energies of the protonated dimers, may be regarded as upper bounds for the dimerization energy.

Scheme III



A correlation between the reaction rate constants, estimated from the ICR experiments, and the exothermicity of the reactions, calculated with the 4-31G basis set, was found. This is evident especially in cases where competing reaction channels yield the same product; the more exothermic reaction is faster, as in reactions 5 and 6 or reactions 7 and 8.

Microscopic reaction rate constants were not rigorously determined, as the complexity of the system was prohibitive. However, work to give a general solution for systems such as the one shown in Scheme I is underway.

Summary

The factors affecting the formation of protonated dimers in simple carbonyl compounds was studied by mass spectrometric methods and by ab initio calculations. The initial structure of the protonated dimers seems to be that of a proton-bridged conformation, in which the proton and the two carbonyl oxygen atom lone pairs form a "three-center bond". The symmetric dimers, in which the proton is equidistant from both oxygen atoms, are more stable toward dissociation to reactants than the asymmetric protonated dimers, in which the proton is further from one of the oxygen atoms forming a weaker O-H bond. The tendency of the neutral reactants to participate in the formation of protonated dimers was related to their proton affinity. Thus, in order for the acidic fluorides to form asymmetric protonated dimers with formaldehyde, a large excess of the former is needed. Electron deformation density maps were calculated. These also indicate that the three-center bond is strongest in the symmetric protonated dimers, while in the asymmetric ones, especially in (H_2CO-F_2CO)H^+, there is a tendency toward dissociation to protonated formaldehyde and a neutral fluoride molecule. Finally, the reactions rates were correlated with the exothermicities of the association reactions.

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Supplementary Material Available: Schematic conformations and the STO-4G charges (condensed to atoms) of protonated formaldehyde dimers (Figure S1), the electronic difference density map of a square planar protonated formaldehyde dimer in the molecular plane (Figure S2), the charge distribution, condensed to atoms, in proton-bridged dimers, calculated with the 4-31G basis set (Figure S3), the electronic difference density map of the proton-bridged asymmetric dimer (H_2CO-HFCO)H^+ in the molecular plane (Figure S4), the electronic difference map of a protonated formyl fluoride in the molecular plane (Figure S5), and the electronic difference density map of the protonated asymmetric dimer (H_2CO-F_2CO)H^+ in the molecular plane (Figure S6) (6 pages). Ordering information is given on any current masthead page.

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Communications to the Editor

A General Methodology for Pseudoguaiane Synthesis: Total Synthesis of (±)-Damsinic Acid and (±)-Confertin[1]

Sir:

The facile synthesis and further elaboration of functionalized bicyclo[5.3.0]decanes constitute an objective of considerable dimension in synthesis as suggested, in part, by the number and complexity of natural product families characterized by this subunit (e.g., pseudoguaiane, guaiane, daphnane, tigliane, ingenane, asebotoxin).[2] The significance of this objective is further amplified by the potent and varied biological activity and, in particular, significant antitumor[3] or cocarcinogenic activity[4] exhibited by various constituents of this series. In connection with these considerations, we describe herein an efficient synthesis of (±)-damsinic acid (**1**) and (±)-confertin (**2**)[5] which embodies a general methodology of potentially broad applicability to the synthesis of the above skeleta.

With respect to synthesis design, a convergent route to the previously noted families was expected to be derivable from methodology which would allow for the annelation of a seven-membered ring onto a preformed five-membered ring. Our studies on the development of such methodology in the specific context of pseudoguaiane synthesis were guided by two considerations which bear on the generality of an approach to this family. Specifically, the A-ring functionality of most pseudoguaianes is characterized by or could be derived from a C-4 carbonyl and the stereochemistry of those pseudoguaianes characterized by α-oriented hydrogens at B-ring stereocenters could be efficiently established by a single-step hydrogenation of unsaturated intermediates[6] such as **5** or **6** derivable from a common precursor such as dienone **7**. With respect to these considerations, we previously described a method for the preparation of divinylcyclopropanes which can be utilized to efficiently effect the requisite annelation (e.g., Scheme I: **8** + **9a** (and/or **10a**) → **11a** (and/or **12a**) → **13a**, 72% overall).[7,8] However the simple but crucial extension of

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