

Acid Catalysis in the Gas Phase: Dissociative Proton Transfer to Formic and Acetic Acid

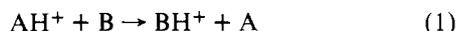
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Abstract: The flowing afterglow and selected ion flow tube techniques are employed in gas-phase measurements of the intrinsic kinetics of protonation of formic and acetic acid and of formyl and acetyl cation formation by dissociative proton transfer of the type $AH^+ + RCOOH \rightarrow RCOOH_2^+ + A$; $RCOOH_2^+ \rightarrow RCO^+ + H_2O$ with $R = H$ and CH_3 and $A = H_2, CH_4, CO$, and H_2O . Protonation by these acids, whose relative strengths span a range of 65 kcal mol⁻¹, is observed to proceed extremely rapidly with rate constants at 298 ± 2 K spanning the range $(1.8-6.8) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹. The fraction of dissociation which ensues in H_2 buffer gas between 0.26 and 0.46 Torr is observed to be dependent on the maximum excess energy available to $RCOOH_2^+$ in the form of reaction exothermicity and is discussed in terms of the sites of protonation and mechanisms of dissociation. The results of these measurements and others involving the deprotonation of these two cations also provide a likely explanation for the continuing failure to observe the formyl cation in highly acidic liquid media, in contrast to the success which has been reported for the observation in these media of other acylium ions.

Introduction

In gas-phase proton-transfer reactions of the type



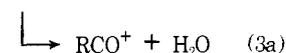
in which the neutral molecules A and B have widely different proton affinities (PA), enough internal energy may appear in the products, in particular the cation, to bring about subsequent decomposition. The extent of this chemical activation may be altered purposely by choosing a variety of acids, AH^+ , to cover a range of PA(A) and therefore a range of reaction exothermicities, $\Delta H^\circ = \Delta PA(A,B)$. In principle this allows a systematic examination of the dependence of the extent and nature of the ensuing decomposition on the excess energy in the form of reaction exothermicity. The outcome of such studies and the insight which they provide about the factors which govern this fundamental process are of considerable interest in several diverse areas of chemistry including chemical ionization mass spectrometry and the physical organic chemistry of the liquid phase, in particular acid-catalyzed decompositions.^{1,2}

In practice such a study can be facilitated with the flowing afterglow technique which has been employed extensively in this laboratory to study the kinetics of proton transfer.³ In a flowing afterglow apparatus a large variety of ions, AH^+ , can be generated by preliminary ion chemistry external to the reaction region and allowed to thermalize by collisions with a buffer gas prior to reaction with B. For example, in a recent study with nitromethane,⁴ the kinetics for reactions of type 1 were determined with $A = H_2, D_2, N_2, CO_2, CH_4, N_2O, CO, H_2O, HCN, CH_3CHCH_2,$ and CH_3OH which cover a range of proton affinities and ΔH°_{298} of 80 kcal mol⁻¹. The stronger acids in this series appeared to react with nitromethane by dissociative proton transfer according to



and increasingly so with increasing acidity (standard enthalpy changes are given at 298 K in kcal mol⁻¹).

In the current study we have examined the dissociative proton transfer to formic and acetic acid as a function of excess energy. We were particularly interested in generating the acetyl and formyl cations by loss of water according to

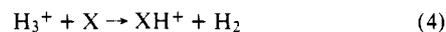


where $R = H$ and CH_3 . The acids $AH^+ = H_3^+, CH_3^+, HCO^+,$ and H_3O^+ which have proton affinities from 101 to 166 kcal mol⁻¹ were chosen to provide a wide range of reaction exothermicities including the minimum excess energy required for the production of the desired acylium ions. Although the acetyl ion has been fully characterized in the condensed phase, the formyl cation has never been detected in solution even in "favorable" superacid media at low temperatures.⁵⁻⁸

Experimental Section

The majority of the measurements were carried out using a conventional flowing plasma mass spectrometer (flowing afterglow) system which has been described previously.⁹ A few of the measurements were carried out with the apparatus in the selected ion flow tube (SIFT) configuration modeled after the original design reported by Adams and Smith.¹⁰ In this configuration a differentially pumped quadrupole mass filter was interposed between the ion production and reaction regions. Ions were extracted from the ion production region through a 1 mm diameter orifice into the quadrupole mass filter which communicated with the flow tube through a 5 mm diameter gas-entrainment orifice. The ions were injected into the flow tube at ca. 40 eV and allowed to thermalize by collision at 298 ± 2 K before they entered the reaction region 106 cm farther downstream. This procedure eliminated ion types other than the reagent ion and the neutral reagent and buffer gas molecules from the reaction region.

The ions were produced in hydrogen carrier gas in the usual manner according to reactions of the type



with $k = (2.4 \pm 0.5) \times 10^{-9}, (2.0 \pm 0.4) \times 10^{-9},$ and $(4.3 \pm 1.1) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ for $X = CH_4, CO,$ and $H_2O,$ respectively.¹¹⁻¹³ We have shown elsewhere that the protonation of CO accomplished in this manner establishes the HCO^+ and not the COH^+ isomer.¹²

The carboxylic acids were added into the reaction region as vapors diluted to ca. 2% in helium. The determination of their flows required separate viscosity measurements¹⁴ and a correction for dimerization, as has been described.¹² Reagent and product ions were monitored as a function of addition of carboxylic acid vapor in the range from 5×10^{-5} to 5×10^{-3} mTorr, at total pressures between 0.26 and 0.46 Torr, and a reaction time of ca. 5 ms. Rate constants were determined in the usual manner.⁹

The gases used were hydrogen (Linde, very dry grade, 99.95% H_2), methane (Matheson, ultra high purity, 99.9% CH_4) and carbon monoxide (Matheson, CP grade, 99.5% CO). The liquids used were

Table I. Rate Constants and Product Distributions for Proton Transfer to Formic and Acetic Acid at 298 ± 2 K

reaction	PD ^a	k^b	k_{ADO}^c	ΔH°_{298}
$\text{H}_3^+ + \text{HCOOH} \rightarrow \text{HCOOH}_2^+ + \text{H}_2$	0.0	6.1 ± 1.8 (3)	3.92	-77 ± 3
→ $\text{HCO}^+ + \text{H}_2\text{O}$	0.7			$+42 \pm 3$
→ $\text{H}_3\text{O}^+ + \text{CO}$	0.3			$+18 \pm 4$
$\text{CH}_5^+ + \text{HCOOH} \rightarrow \text{HCOOH}_2^+ + \text{CH}_4$	1.0	2.9 ± 0.9 (3)	1.87	-47 ± 3
$\text{HCO}^+ + \text{HCOOH} \rightarrow \text{HCOOH}_2^+ + \text{CO}$	1.0	1.8 ± 0.5 (3)	1.56	-35 ± 3
$\text{H}_3\text{O}^+ + \text{HCOOH} \rightarrow \text{HCOOH}_2^+ + \text{H}_2\text{O}$	1.0	2.7 ± 0.8 (12)	1.80	-12 ± 5
$\text{H}_3^+ + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH}_2^+ + \text{H}_2$	0.0	6.8 ± 2.0 (4)	4.88	-86 ± 3
→ $\text{CH}_3\text{CO}^+ + \text{H}_2\text{O}$	1.0			$+27 \pm 3$
$\text{HCO}^+ + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH}_2^+ + \text{CO}$	0.8	2.5 ± 0.8 (2)	1.86	-44 ± 3
→ $\text{CH}_3\text{CO}^+ + \text{H}_2\text{O}$	0.2			$+27 \pm 3$
$\text{H}_3\text{O}^+ + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOH}_2^+ + \text{H}_2\text{O}$	0.95	3.0 ± 0.9	2.17	-21 ± 5
→ $\text{CH}_3\text{CO}^+ + \text{H}_2\text{O}$	0.05			$+27 \pm 3$

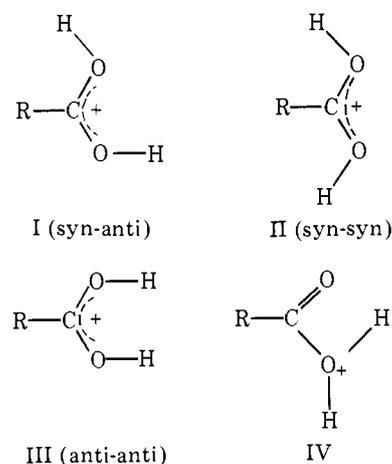
^a Product distributions ($\pm 20\%$) observed in H_2 between 0.26 and 0.46 Torr. ^b In units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The number of measurements is given in parentheses. ^c The collision rate constant in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ calculated using the average dipole orientation theory (the $\cos \theta$ model).¹⁵ Permanent dipole moments were taken from R. D. Nelson, D. R. Lide, and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 10* (1967). Mean polarizabilities of 3.09 \AA^3 for HCOOH and 5.03 \AA^3 for CH_3COOH were calculated from bond and group polarizabilities taken from E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964). ^d Standard enthalpy change in kcal mol^{-1} . PA's for H_2 , CH_4 , CO , and H_2O are 101 ± 1 , 131.5 ± 2.2 , 143 ± 1 , and $166.4 \pm 2.4 \text{ kcal mol}^{-1}$, respectively.¹² PA's for HCOOH and CH_3COOH are 178.1 ± 2 and $187.4 \pm 2 \text{ kcal mol}^{-1}$ taken from P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977). $\Delta H_f^\circ_{298}(\text{CH}_3\text{CO}^+)$ taken from P. Ausloos and S. G. Lias, *Chem. Phys. Lett.*, **51**, 53 (1977). Auxiliary thermodynamic data were taken from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6** (1977).

distilled water, formic acid (BDH chemicals, analytical reagent grade), and acetic acid (Anachemia Chemicals, glacial, 99.7%).

Results and Discussion

Kinetics of Proton Transfer. The rate constants measured in this study for the reactions of H_3^+ , CH_5^+ , HCO^+ , and H_3O^+ with formic acid and of H_3^+ , HCO^+ , and H_3O^+ with acetic acid are given in Table I. All of these reactions were observed to be quite rapid, the rate constants spanning a range of $(1.8\text{--}6.8) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The values are close to, but systematically higher than, the values of the collision rate constants derived from the average dipole orientation (ADO) theory¹⁵ which are included in Table I. The deviations are similar to those observed previously in our laboratory for other proton-transfer reactions, for which the implications have been discussed elsewhere.¹⁶ Deuteron transfer between DCO^+ and formic acid has been observed previously in the ion source of a medium-pressure mass spectrometer by Pritchard, Thynne, and Harrison,¹⁷ who reported a rate constant of $(1.32 \pm 0.1) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at approximately 373 K and an ion exit energy of 2.4 eV.

Site(s) of Protonation. The exothermicities quoted in Table I should refer to the lowest energy route of protonation, i.e., the protonation of the atom of the molecule which has the highest proton affinity, since they are based on stepwise equilibrium measurements for series of nearly thermoneutral reactions. They should therefore be a measure of the maximum excess energy potentially available in the initial protonation and thus provide an indication of the accessibility of higher energy sites of protonation, given the proton affinities of the latter. The protonation of formic acid has been investigated by Hopkinson et al.¹⁸ using ab initio LCAO-MO-SCF calculations with medium-sized uncontracted Gaussian basis sets. These calculations indicated that protonation of the carbonyl group of formic acid can give rise to three conformers ($\text{R} = \text{H}$) only 7 kcal mol^{-1} apart in energy, and all are considerably more stable than the hydroxy protonated isomer (IV) (IV is 25 kcal mol^{-1} above I). Conformers II and III lie 5.67 and $7.11 \text{ kcal mol}^{-1}$, respectively, above the lowest energy conformer



(I). Experimental evidence¹⁹ for the low-energy structures (I) and (II) can be derived from the NMR spectrum of formic acid in $\text{FSO}_3\text{H-SbF}_5$ solution and in HF-BF_3 solution at low temperatures with conformer I predominating by a factor of about 2. Conformer II was observed to be present to an extent of only about 5% in protonated acetic acid ($\text{R} = \text{CH}_3$) under the same conditions. Conformer III was not observed in either case nor was the higher energy tautomer corresponding to protonation at the hydroxy oxygen atom. Both the molecular orbital calculations (25 kcal mol^{-1}) and the experimental ionization energy correlations of Benoit and Harrison²⁰ ($26 \pm 3 \text{ kcal mol}^{-1}$) show the proton affinity of the hydroxy group to be considerably lower than that of the carbonyl group. Benoit and Harrison²⁰ also provide an energy difference of $27 \pm 3 \text{ kcal mol}^{-1}$ between the corresponding tautomers of acetic acid. From these predictions and the exothermicities given in Table I, we have inferred that the higher energy protonation at the hydroxy oxygen atom in formic and acetic acid is thermodynamically feasible in the gas phase with the stronger acids H_3^+ , CH_5^+ , and HCO^+ but not with H_3O^+ for which the protonation would be 14 ± 8 and $6 \pm 8 \text{ kcal mol}^{-1}$ endothermic.

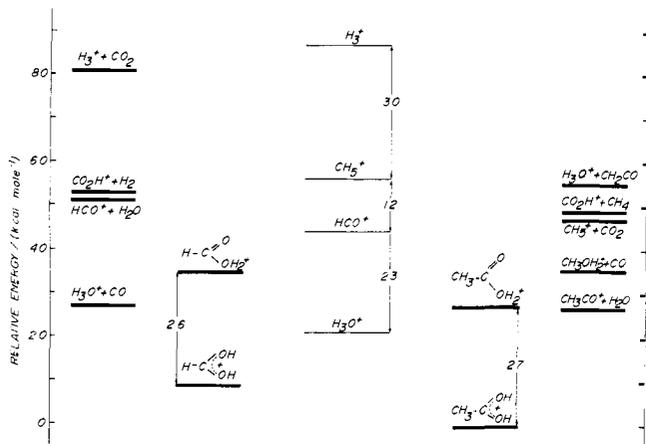


Figure 1. Relative energies of the acids H_3^+ , CH_5^+ , HCO^+ , and H_3O^+ , the two tautomers of protonated formic and acetic acid, and possible dissociation products of the protonated carboxylic acids.

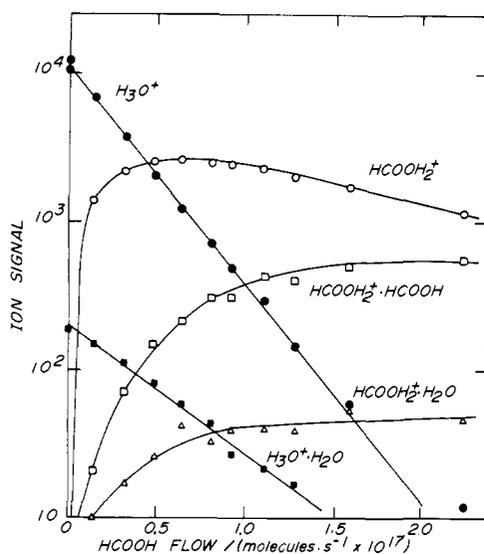


Figure 2. The variation of the major positive ions observed upon the addition of formic acid vapor into a flowing $\text{H}_2\text{O}-\text{H}_2$ plasma in which H_3O^+ is initially a dominant ion. This decay of the H_3O^+ signal provides a rate constant of $2.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. $T = 298 \text{ K}$, $P = 0.414 \text{ Torr}$, $\bar{v} = 8.0 \times 10^3 \text{ cm s}^{-1}$, and $L = 85 \text{ cm}$.

mic, respectively. As regards the three conformers which may result from the carbonyl protonation of formic acid, they are all energetically accessible to all of the four acids.

Dissociative Proton Transfer. The energetics of the protonation and dissociation of formic and acetic acid are delineated in Figure 1 from which it is apparent that dissociative proton transfer is thermodynamically feasible with H_3^+ , CH_5^+ , and HCO^+ but not with H_3O^+ . The excess energies span a range from 12 ± 5 to $77 \pm 3 \text{ kcal mol}^{-1}$ and 21 ± 5 to $86 \pm 3 \text{ kcal mol}^{-1}$ in the case of formic and acetic acid, respectively.

Not only H_3O^+ but also HCO^+ and CH_5^+ were observed to react with formic acid by proton transfer without detectable dissociation ($<1\%$).²¹ Figure 2 presents results obtained with H_3O^+ . The only primary product ion observed was HCOOH_2^+ which reacted further by solvation to form the proton-bound formic acid dimer, $\text{HCOOH}_2^+ \cdot \text{HCOOH}$, presumably via three-body association according to the reaction

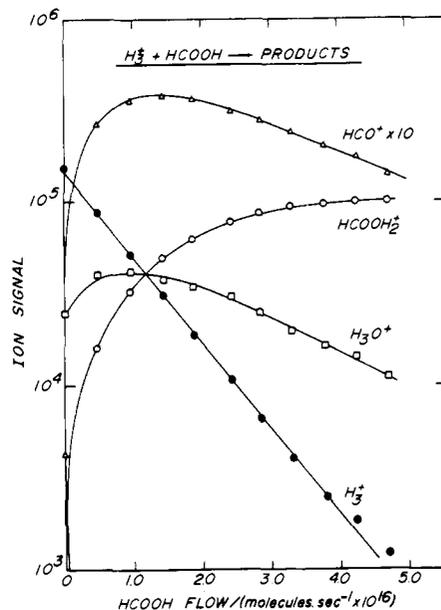


Figure 3. The observed variation of ion signals recorded upon the addition of formic acid vapor into a flowing H_2 plasma. $T = 298 \text{ K}$, $P = 0.361 \text{ Torr}$, $\bar{v} = 7.7 \times 10^3 \text{ cm s}^{-1}$, and $L = 85 \text{ cm}$.

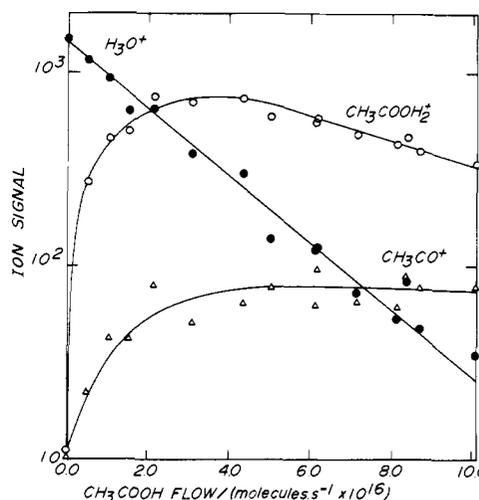


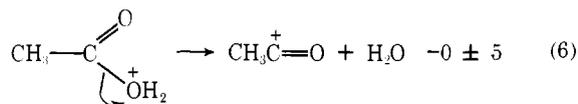
Figure 4. Variation of ion signals recorded upon the addition of acetic acid vapor into the reaction region in the SIFT configuration with H_3O^+ as the selected ion. Buffer gas = H_2 , $T = 299 \text{ K}$, $P = 0.358 \text{ Torr}$, $\bar{v} = 8.1 \times 10^3 \text{ cm s}^{-1}$, and $L = 59 \text{ cm}$.

where M is a stabilizing third body which is primarily H_2 in these experiments. The rise in the hydrated ion $\text{HCOOH}_2^+ \cdot \text{H}_2\text{O}$ may be attributed primarily to the reaction of the hydrated H_3O^+ with HCOOH .²² Only with H_3^+ , the strongest acid in this series, was there any evidence for dissociation. In fact, in this case the dissociation appeared to proceed completely into $\text{HCO}^+ + \text{H}_2\text{O}$ and $\text{H}_3\text{O}^+ + \text{CO}$ in a ratio of about 2:1 (see Figure 3) with both HCO^+ and H_3O^+ reacting further by fast secondary proton transfer.

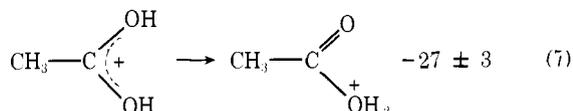
All of the reactions of H_3^+ , HCO^+ , and H_3O^+ with acetic acid were observed to be accompanied by a partial dissociation in this case only into $\text{CH}_3\text{CO}^+ + \text{H}_2\text{O}$. The extent of dissociation appeared to be sensitive to the magnitude of the excess energy in the form of proton-transfer exothermicity, increasing with increasing excess energy as summarized in Table I. Figure 4 shows the results obtained in the SIFT configuration for the weakest acid, H_3O^+ , for which the dissociative proton-transfer

channel is only 5%, albeit production of CH_3CO^+ is actually endothermic by $6 \pm 8 \text{ kcal mol}^{-1}$ in this case. Similar results were obtained with the flowing afterglow in the conventional mode with H_2O and $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ present in the reaction region as in the experiments with HCOOH (Figure 2). Figure 5 shows the dissociation proceeding with essentially unit probability with H_3^+ . The CH_3CO^+ and $\text{CH}_3\text{COOH}_2^+$ ions appeared to react further with CH_3COOH by solvation in a manner analogous to reaction 5.

Mechanisms of Dissociation. The observations of dissociative proton transfer are most reasonably understood in terms of the mechanism of unimolecular acyl oxygen fission, A_{Ac1} , commonly invoked for the cleavage of esters, amides, and carboxylic acids in concentrated acid solutions.²³ For acetic acid this mechanism is

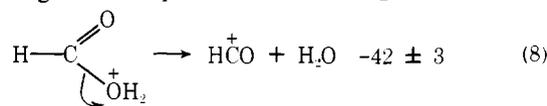


and requires protonation at the hydroxyl oxygen. Alternatively, this tautomer may be achieved indirectly through carbonyl protonation followed by a 1,3 hydrogen shift according to



However, this route seems more improbable as barriers to 1,3 hydrogen shifts in similar systems are known to be high.^{24,25} In either case a minimum of $27 \pm 3 \text{ kcal mol}^{-1}$ must appear as internal energy of $\text{CH}_3\text{COOH}_2^+$ which seems to be the case for only a small fraction of these ions with H_3O^+ as the protonating agent and essentially all of these ions in the case of H_3^+ .

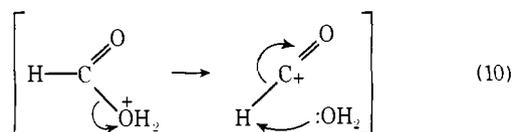
The analogous decomposition of HCOOH_2^+ , viz.



requires a minimum internal energy of $42 \pm 3 \text{ kcal mol}^{-1}$, or 16 kcal mol^{-1} more than the $26 \pm 3 \text{ kcal mol}^{-1}$ required to protonate at the hydroxy oxygen. This amount of internal energy is conceivably available only with CH_5^+ and H_3^+ as protonating agents for which the excess energies are 47 ± 3 and $77 \pm 3 \text{ kcal mol}^{-1}$, respectively. However, the measurements indicated formation of the formyl cation only in the case of H_3^+ . The second route of decomposition, again observed only with H_3^+ , viz.



is energetically accessible to HCO^+ as well as CH_5^+ and H_3^+ . This route can also be viewed as an A_{Ac1} cleavage, but in this instance accompanied by the synchronous or near-synchronous transfer of a proton from the carbon atom to the developing water molecule:



The analogous route with acetic acid, viz.



requires at least 55 kcal mol^{-1} of excess energy which is conceivably available only in the case of CH_5^+ and H_3^+ . The results, shown in Figure 5, allow an upper limit of $\sim 1\%$ to be set on the occurrence of this channel under our operating conditions.

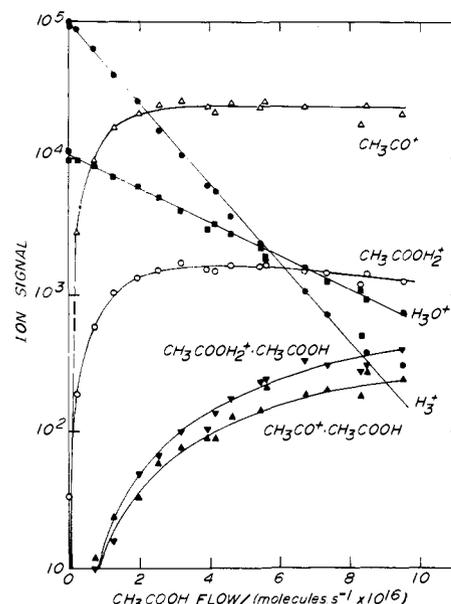


Figure 5. The observed variation of ion signals recorded upon the addition of acetic acid vapor into a flowing H_2 plasma. $T = 300 \text{ K}$, $P = 0.203 \text{ Torr}$, $\bar{v} = 7.8 \times 10^3 \text{ cm s}^{-1}$, and $L = 58 \text{ cm}$.

Observation of the Formyl Cation. Protonated carboxylic acids²⁶⁻²⁸ and acylium ions,⁵⁻⁸ RCO^+ , produced by A_{Ac1} fission of the corresponding protonated carboxylic acids, have been fully characterized in highly acidic solvents. Also the acetyl ion, CH_3CO^+ , has been isolated in a crystalline salt $\text{CH}_3\text{CO}^+\text{SbF}_6^-$ and this was sufficiently stable to have permitted an X-ray structure determination.²⁹ However, the formyl cation, HCO^+ , one of the cations produced here in the gas phase from formic acid, has never been detected in solution. This ion has been implicated as the intermediate in the dehydration of formic acid by H_2SO_4 or P_2O_5 , in the A_{Ac1} decomposition of formate esters,³⁰ in the acid-catalyzed decomposition of formic anhydride,⁸ and in the Gatterman-Koch hydroformylation of aromatic molecules. Olah has made a determined effort to observe this ion by using high pressures of CO (50 atm) over a superacid solution but even at 143 K the formyl cation was not detected.⁸ Similarly, attempts to observe this ion at low temperatures in the acid-catalyzed decomposition of formic acid and a variety of formyl derivatives have all failed.

The gas-phase measurements reported here indicate that not only the acetyl cation but also the formyl cation can be generated from the corresponding protonated carboxylic acid if sufficient excess energy is available from the initial protonation. However, the excess energy threshold appears to be distinctly higher for the production of the formyl cation from HCOOH_2^+ which suggests that the acetyl ion may be formed much more readily than the formyl cation from analogous reactions proceeding in solution. Furthermore, and perhaps more significantly, the formyl cation is intrinsically a much stronger acid. This is evidenced by the very brief chemical lifetime of HCO^+ under the experimental conditions operative in Figure 5 and has also been borne out in separate gas-phase experiments performed in this laboratory¹² which have demonstrated that HCO^+ also transfers a proton rapidly ($k > 1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K) to CH_3COOH , H_2O , alcohols (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$), aldehydes (H_2CO , CH_3CHO), ethers (CH_3OCH_3), ketones (CH_3COCH_3), esters (HCOOCH_3), cyanides (HCN , CH_3CN), C_2H_2 , CH_3NO_2 , and CH_2CO . Thus HCO^+ is a much stronger acid than CH_3CO^+ (and presumably also the higher homologous acylium ions) which is the weakest acid of all the conjugate acids of the aforementioned species. Consequently the gas-phase

deprotonation of the formyl cation can be expected to be much more extensive at equilibrium than that for the other acylium ions, just as has been observed in solution.

Acknowledgment. We thank the National Research Council of Canada for financial support and the referees for helpful comments.

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Calculations of Proton Shieldings in Conjugated Hydrocarbons

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Abstract: In this paper a theory for the calculation of ^1H chemical shifts of planar conjugated hydrocarbons with sp^2 - and sp -hybridized atoms is given. All nonlocal ring current (RC) and local anisotropic (LA) contributions are calculated in the framework of an extended π theory using the coupled Hartree-Fock perturbation theory. The σ core is approximated by localized two-center bonds. Therefore, it gives only LA contributions which are calculated by applying the uncoupled Hartree-Fock perturbation theory. The method can be successfully applied to cyclic and noncyclic conjugated hydrocarbons containing double and triple bonds. The anisotropic long-range shielding of the double and the triple bond is discussed.

In recent years the ring-current concept^{1,2} has been used extensively to calculate ^1H chemical shifts of cyclic conjugated hydrocarbons. These ring currents (RC) can be obtained quantum mechanically by using the Pople³ and McWeeny⁴ modifications of the London² theory or their extensions to the SCF method.^{5,6} Also a classical formulation of ring currents has been applied to account for the deshielding of the protons in polycyclic hydrocarbons.⁷ It was shown,^{8,9} however, that the RC contributes only about 50% to the observed deshielding in benzene. The remaining part has to be attributed to local anisotropic (LA) shielding effects. Only a consideration of the combined LA and RC effects provides a useful explanation of the chemical shifts of the inner and outer protons of annulenes.^{9,10}

All mentioned theoretical methods can only be applied to cyclic conjugated hydrocarbons which consist only of sp^2 -hybridized carbon atoms. Most of the known annulenes contain, however, sp -hybridized atoms in triple or in cumulated double bonds. The conformational mobility in these dehydroannulenes is considerably reduced against the annulenes. This fact facilitates the comparison of experimental and theoretical

shifts. Therefore, a quantum mechanical method is presented in this study at which all local and nonlocal contributions to the shielding of any conjugated planar hydrocarbon can be calculated. The size of the studied molecules forces one to adopt the π -electron approximation in order to derive the wave function.

Quantum Mechanical Formulation

A. π -SCF Procedure. Hell¹¹ proposed a modified PPP method¹² which allows the study of conjugated molecules with sp^2 - and sp -hybridized carbon atoms. For the benefit of the reader we shall review this method. The atomic orbital basis set consists of the $2p_{z_A}$ functions on each carbon atom A as in ordinary PPP theory. On each sp -hybridized atom A we have an additional $2p_{y_A}$ function defined as linear combination of $2p_{x_A}$ and $2p_{y_A}$ functions: $2p_{y_A} = a_A 2p_{x_A} + b_A 2p_{y_A}$. The coefficients a and b are defined as $a_A = a_B = (y_A - y_B)r_{AB}^{-1}$ and $b_A = b_B = (x_B - x_A)r_{AB}^{-1}$. A and B are two adjacent sp -hybridized atoms with internuclear separation r_{AB} . Bond angles on sp -hybridized atoms are always taken as 180° . The Hartree-Fock operator F^0 is defined as in ordinary PPP theory.