Ionic Reactions between Formaldehyde and Hydrocarbons. H_2 Transfer as a Hydrogenation Mechanism in Astrochemistry

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Hydrogen transfer is a major channel in the ionized $C_2H_2^+$/H_2CO and H_2CO^+/C_2H_2 reaction systems, producing $C_2H_4^+ + CO$. Similarly, H_2 transfer from H_2CO is observed in reactions of the ions $C_3H_3^+$ (linear), CH_3CCH^+, $H_2CCCH_2^+$, $C_3H_5^+$, and $HCCCCH^+$ with formaldehyde, resulting in hydrogenated hydrocarbon ions. The energetics of these reactions allow a two-step mechanism of H^+ or H transfer forming a distonic ($BH^+\cdot HCO$) complex, followed by H transfer to form BH_2^+. Ab initio calculations on the acetylene/formaldehyde system show that the reaction can proceed through a stable cyclic adduct, dissociating to yield $C_2H_4^+$ that contains carbon atoms from both acetylene and formaldehyde. Both experiment and theory show that H_2CO^+ does not react with hydrogen, making it a stable reactant ion in interstellar chemistry. The reactions where either H_2^+ or H_2 is transferred can provide significant pathways for the hydrogenation of unsaturated hydrocarbons in interstellar clouds. The reactions of three $C_2H_x^+$ ($x = 0$, 1, or 2) species with acetaldehyde are also reported.

1. Introduction

The advent of selected ion flow tube (SIFT) mass spectrometry and complementary methods has resulted in much research in ion−molecule chemistry, including the ion chemistry of interstellar gas clouds. More than 120 different molecules have been detected in both dense and diffuse interstellar clouds. Formaldehyde is an important interstellar species in a large number of interstellar clouds,[1] as it is observed by the microwave spectra of both the *ortho*- and *para*-formaldehyde as well as by absorption for the ^{13}C isotope of *ortho*-formaldehyde.[2] Both ionized and neutral forms of the formaldehyde molecule have been observed in diffuse (particle density 10−1000 cm^{-3}) and dense (particle density 10^3−10^6 cm^{-3}) interstellar clouds.[3] Formaldehyde can play significant roles in the chemistry of these clouds and in gas planets, both as a neutral reactant and in its ionized form as H_2CO^+, providing it does not react with H_2 and He that are the major gases in these environments.

In the present work, we shall examine ion−molecule reactions that occur between formaldehyde and several hydrocarbons that are known or are expected to be present in extraterrestrial environments. In particular, we are interested in reactions in the acetylene/formaldehyde system, because acetylene is expected to be a major reactive hydrocarbon in astrochemical environments. Acetylene is present in the atmospheres of gas planets, has been detected in protoplanetary nebulae,[4] and is expected in interstellar clouds, although it is undetected so far by microwave spectroscopy, because it lacks a dipole moment. Here, we examine reactions of acetylene and its fragment ions with neutral H_2CO, and also ion−molecule reactions in systems containing H_2CO^+ (or H_2COH^+) and acetylene or other small unsaturated hydrocarbons.

2. Experimental Section

The SIFT apparatus has been described previously in detail.[5,6] Ions are formed by a flow of helium gas, at a pressure of ∼0.5 Torr through a microwave discharge in the flowing afterglow ion source, and react with a neutral reagent to create the desired ion precursor.[7] These ions are then focused and mass-selected by a quadrupole mass spectrometer before being injected through a Venturi orifice into the flow tube. Here, they react with neutral reactants added downstream from the Venturi orifice, typically in a total pressure of helium carrier gas of 0.45 Torr. The neutral reactants are introduced into the helium flow through one of two ports. In this study, the upstream port is generally used to form the reactant ion of interest, which can then react with the neutral reagents that enter through the downstream port. A tiny fraction of the ions exiting at the downstream end of the flow-tube are sampled through a small orifice into a second quadrupole mass spectrometer, where they are mass-identified and quantified using pulse counting.

Rate coefficients for reactions are determined from a semilogarithmic plot of ion counts per second against the flow rate for the neutral reactant.[5] The example in Figure 1 shows a semilogarithmic plot with an initial linear range at low reactant flows for the reaction between H_2CO^+ and C_2H_2. The branching ratios for the reaction channels are obtained by extrapolating the observed ratios of product ions to zero neutral reactant flow.

Because the process of injecting H_2CO^+ ions formed in the ion source directly into the flow tube resulted in substantial fragmentation, even at the lowest injection energies, it was necessary to generate these ions in the SIFT flow tube. This was achieved by first injecting mass-selected O_2^+ ions into the SIFT flow tube and allowing them to react by charge transfer with H_2CO introduced through the upstream inlet. The H_2CO^+ product ions from this reaction can then react further with neutrals (Bs) introduced through the downstream inlet. There are some complications arising from this procedure. One complication is that any unreacted O_2^+ ions can react with neutrals (Bs) added through the downstream inlet, giving products that complicate product analysis. This complication can be minimized by increasing the flow of H_2CO through the

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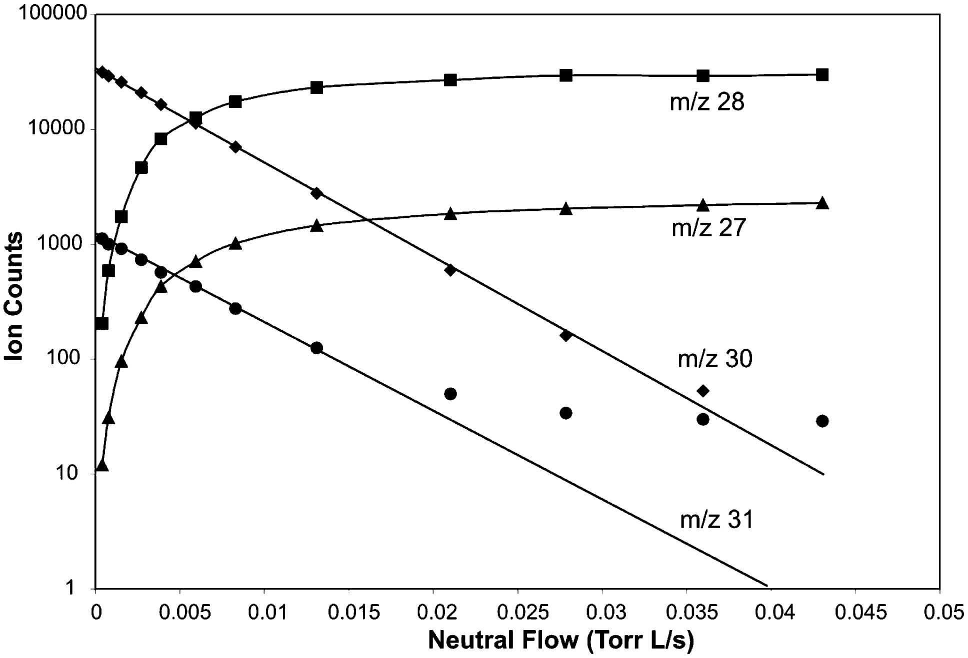

Figure 1. Semilogarithmic plots of ion intensities in the reaction of H_2CO^+ with C_2H_2 in a typical reaction system.

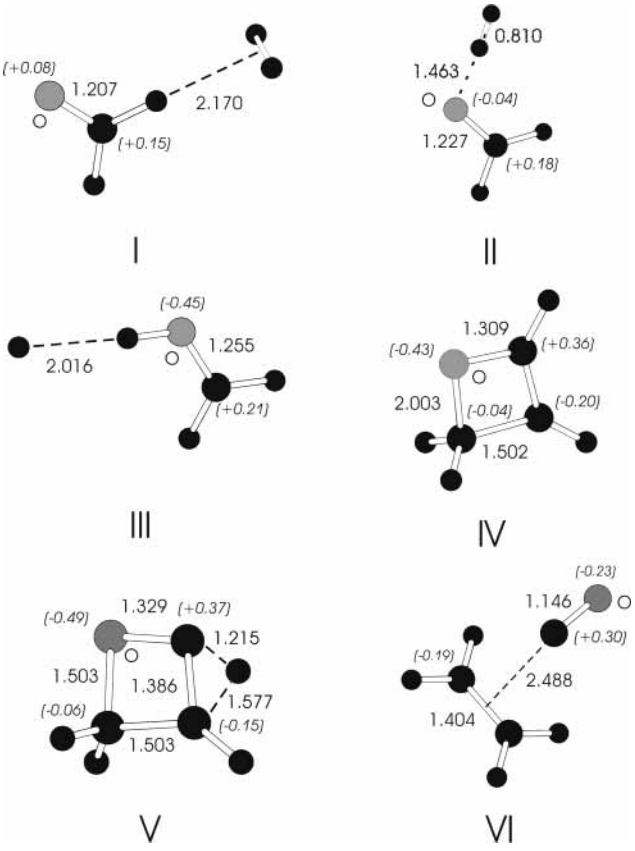

Figure 2. Structures of intermediates and transition state structures in the $H_2CO^+ + H_2$ and $H_2CO^+ + C_2H_2$ systems. All distances shown are in angstroms. Partial charges are shown in parentheses.

upstream inlet. However, H_2CO^+ reacts with H_2CO, in competition with its reaction with B, and the H_2COH^+ product of this reaction may react further with hydrocarbons that have higher proton affinities. In addition, the products of these reactions of B can react further with H_2CO to yield secondary products. To lessen these effects, the flow rate of H_2CO was minimized. The conflicting requirements of a high H_2CO flow rate, to minimize the injected O_2^+ ions, and of a low H_2CO flow, to avoid secondary reactions, means that the conditions cannot be fully optimized and complicating reactions are always present. These complications can often be accounted for by monitoring the product distribution at various reactant flow rates. Nevertheless, in some cases, we could not determine accurate branching ratios because of these effects.

All quantum calculations were performed using the *Gaussian 98* program[8] and the G2(MP2) procedure.[9] The calculated energies are given in Table 3. The structures of some important intermediates are shown in Figure 2.

3. Results

The measured rate coefficients and branching ratios are listed in Tables 1 and 2. Table 1 contains data for reactions of H_2CO^+ and H_2COH^+ with hydrocarbons as well as results for two additional reactions of H_2CO^+ where H_2 transfer is reported taken from the literature. (These additional reactions are unnumbered.) Table 2 contains results for the reactions of various ions with neutral H_2CO as well as several reactions involving CH_3CHO. For ease of discussion, the particles transferred in each reaction are also listed in both tables.

Table 1 considers the reactions of H_2CO^+ with a series of hydrocarbons. As noted already, because of the difficulty in injecting sufficient H_2CO^+ directly into the flow tube, O_2^+ was injected as the reactant ion and H_2CO was admitted via the upstream port. Along with H_2CO^+, other ions present include some residual O_2^+ plus some small amounts of the ions HCO^+, H_3CO^+, and H_3O^+ (from water impurities). In many cases, these ions also underwent reaction with the neutral reagent. These side reactions caused difficulties in the identification of the products resulting from the reactions of H_2CO^+ and in the calculation of the branching ratios. For allene (C_3H_4), propyne, and diacetylene (C_4H_2), these effects were significant enough that the products could not be quantified in the reactions of H_2CO^+.

4. Discussion

In the reactions of H_2CO^+ with the hydrocarbons in Table 1, products from three types of reaction were observed: charge

TABLE 1: Reactions of $H_2CO^{+\cdot}$ and H_2COH^+ Ions with Neutral Reactants

	ion	neutral	products	particle transferred	branching ratio	$\Delta H^{\circ\,a}$	k^b	k_{col}^c
1	H_2CO^+	C_2H_2	$C_2H_4^+ + CO$	H_2^+	0.75	−189	1.2	1.2
			$C_2H_3^+ + HCO$	H^+	0.25	−29		
2	H_2CO^+	C_2H_4	$C_2H_4^+ + H_2CO$	charge	~0.8	−56	1.3	1.3
			$C_2H_5^+ + HCO$	H^+	~0.2	−69		
3	H_2CO^+	C_3H_4	$C_3H_4^+ + H_2CO$	charge	major	−143	1.3	1.4
		(allene)	$C_3H_5^+ + HCO$	H^+	minor	−164		
4	H_2CO^+	C_3H_4	$C_3H_4^+ + H_2CO$	charge	major	−78	1.3	1.6
		(propyne)	$C_3H_5^+ + HCO$	H^+	minor	−136		
			$C_3H_6^+ + CO$	H_2^+	minor	−293		
5	H_2CO^+	C_4H_2	$C_4H_2^+ + H_2CO$	charge	ratios not determined	−96	1.2	1.4
			$C_4H_3^+ + HCO$	H^+		−125		
			$C_4H_4^+ + CO$	H_2^+		−317		
6	H_2CO^+	C_6H_6 (benzene)	$C_6H_6^+ + H_2CO$	charge	1.00	−186	2.1	1.6
7	H_2CO^+	CH_2CHCN	$CH_2CHCNH^+ + HCO$	H^+	1.00	−173	4.4	4.4
8	H_2CO^+	H_2	$H_2COH^+ + H$	H		−43	<0.001	1.5
	H_2CO^+	O_2[d]	$HCO^+ + HO_2$	H	0.70	+34		0.75
			$H_2O_2^{+\cdot} + CO$[e]	H_2^+	0.30	−187		
	H_2CO^+	OCS[d]	$H_2S^+ + 2CO$	H_2^+	0.56	−55		1.5
			$HCOS^+ + HCO$	H^+	0.41	−17		
			$H_2COS^+ + CO$	S	0.03			
9	H_2COH^+	C_2H_2	$C_3H_3O^+ + H_2$	C_2 or HCO^+	1.00	−177	0.032	1.1
10	H_2COH^+	C_2H_4	$C_3H_7O^+$	adduct	0.80		0.20	1.3
			$C_3H_5^+ + H_2O$	CH^+	0.20	−29		
11	H_2COH^+	C_3H_4	$C_3H_5^+ + H_2CO$	H^+	0.45	−53	1.0	1.4
		(allene)	$C_3H_7^+ + CO$	$H^+ + H_2$	0.40	−202		
			or					
			$CH_3CO^+ + C_2H_4$	C		−221		
			$C_4H_5^+ + H_2O$	CH^+	0.15	−77		
12	H_2COH^+	C_3H_4	$C_3H_5^+ + H_2CO$	H^+	0.45	−57	1.0	1.7
		(propyne)	$C_3H_7^+ + CO$	$H^+ + H_2$	0.40	−197		
			or					
			$CH_3CO^+ + C_2H_4$	C		−217		
			$C_4H_5^+ + H_2O$	CH^+	0.15	−72		
13	H_2COH^+	C_4H_2	$C_4H_3^+ + H_2CO$	H^+	0.50	−24	1.1	1.4
			$C_5H_5O^+$	adduct	0.50			

[a] kJ mol^{-1}. Thermodynamic data from the NIST.[10] [b] In units of 10^{-9} cm^3 s^{-1}. Error estimate for rate coefficients and branching ratios is ±20% of the listed values. [c] Collision rates have been calculated using the parametrized trajectory calculation method of Su and Chesnavich[11] in units of 10^{-9} cm^3 s^{-1}, with dipole moments and polarizabilities from various sources.[12,13] [d] Reference 14. [e] The H_2^+ transfer channel was also confirmed in ref 15.

transfer, H^+ transfer, and H_2^+ transfer. The first two reaction types have been studied in many systems,[14,16,17] but H_2^+ transfer reactions are less common. In general, when exothermic proton transfer is available, it tends to be the major channel.[17] However, in reaction 1 (Table 1), where both H^+ and H_2^+ transfer channels are observed, the latter is much more exothermic and is a major pathway. In the other reactions of H_2CO^+ listed in Table 1, exothermic charge transfer is the major channel, while H^+ and H_2^+ transfer were either observed as minor channels or could not be observed or quantified because of the experimental problems discussed already.

Table 2 shows reactions of hydrocarbon ions with H_2CO. Of the 15 measured reactions, 10 proceed at a somewhat slower rate than the collision rate, which indicates that those reactions proceed through a complex that can dissociate back to the reactants. The reactions of $C_3H_4^+$ (allene, propyne) and $C_3H_5^+$ are particularly slow and probably form adducts consistent with the existence of a long-lived intermediate.

Exothermic charge transfer is the largest channel in the reaction of $C_2H_2^+$ and H_2CO, but H_2 transfer is still a significant channel. In most of the other reactions of hydrocarbon ions with H_2CO, charge transfer is endothermic and is not observed. The dominant channel is the strongly exothermic H_2 transfer from H_2CO for $C_3H_3^+$ (acyclic), $C_3H_4^+$ (allene, propyne), $C_3H_5^+$, and $C_4H_2^+$ ions. These H_2 transfer reactions are exothermic because of the formation of a stable triple bond in the leaving CO neutral entity. An H_2 transfer channel is observed also in the reaction of $C_6H_6^+$ with H_2CO, but this is a very slow reaction.

It is the loss of the stable CO molecule which provides the common mechanistic thread for the hydrogenation reactions of the types $H_2CO^+ + B$ and $B^+ + H_2CO$, where B is an unsaturated hydrocarbon molecule. In the first case, H_2^+ is transferred, and in the second, H_2 is transferred. Presumably, the first step in both cases is the formation of a $(B{\cdot}H_2CO)^+$ collision complex. This complex can dissociate back to the reactants, with or without charge transfer, or can undergo further rearrangement. The H_2 or H_2^+ transfer mechanism can occur within the collision complex as two successive H transfer steps or as a concerted rearrangement where the carbon monoxide molecule is formed by the linking of a carbon atom and an oxygen atom from the two separate reactant moieties. The two-step mechanism for H_2 or H_2^+ transfer is energetically plausible because the first H^+ or H transfer step is exothermic in all cases (at least for the separated reactants).

As an alternative to the two-step mechanism, ab initio results for the $H_2CO^+ + HCCH$ potential energy surface (as summarized in Table 3 and Figure 2) show that these reactants can form stable cyclic intermediate IV (−255.5 kJ mol^{-1}). This intermediate can lead to the observed products by a hydrogen shift through transition state V (−5.1 kJ mol^{-1}) from the

TABLE 2: Reactions of Ions with Formaldehyde and Acetaldehyde

	ion	neutral	products	particle transferred	branching ratio	ΔH^a	k^b	$k_{col}{}^c$
14	C_2^+	H_2CO	$H_2CO^+ + C_2$	charge	1.00	−22	2.4	3.1
15	C_2H^+	H_2CO	$C_2H_2^+ + HCO$	H	0.65	−111	2.4	3.1
			$H_2CO^+ + C_2H$	charge	0.35	−42		
16	$C_2H_2^+$	H_2CO	$H_2CO^+ + C_2H_2$	charge	0.50	−27	2.4	3.1
			$C_2H_4^+ + CO$	H_2	0.45	−248		
			$C_3H_3O^+ + H$	C_2H^+ or HCO	0.05	−242		
17	$C_2H_3^+$	H_2CO	$H_2COH^+ + C_2H_2$	H^+	1.00	−77	3.0	3.0
18	$C_3H_3^+$ (cyclic)	H_2CO	no reaction					
19	$C_3H_3^+$ (acyclic)	H_2CO	$C_3H_5^+ + CO$	H_2	0.95	−202	1.0	2.8
			$H_2COH^+ + C_3H_2$	H^+	0.05			
20	$C_3H_4^+$ (allene)	H_2CO	$C_3H_6^+ + CO$	H_2	0.95	−156	0.3	2.8
			$C_4H_6O^+$	adduct	0.05			
21	$C_3H_4^+$ propyne	H_2CO	$C_3H_6^+ + CO$	H_2	0.95	−214	0.3	2.8
			$C_4H_6O^+$	adduct	0.05			
22	$C_3H_5^+$	H_2CO	$C_3H_7^+ + CO$	H_2	0.95	−163	0.3	2.8
			$C_4H_7O^+$	adduct	0.05			
23	$C_4H_2^+$	H_2CO	$C_4H_4^+ + CO$	H_2	0.75	−222	1.2	2.6
			$C_4H_3^+ + HCO$	H	0.25	−30		
24	$C_4H_3^+$	H_2CO	$C_5H_7O^+$	adduct			$\sim k_{coll}$	2.6
25	$C_6H_5^+$ (reactive isomer)[d]	H_2CO	$C_6H_5OCH_2^+$?	adduct	1.00		1.0	2.5
26	$C_6H_6^+$	H_2CO	$C_6H_8^+ + CO$	H_2	1.00	−69	<0.003	
27	O_2^+	H_2CO	$H_2CO^+ + O_2$	charge	1.00	−87	1.8	2.9
28	C_2^+	CH_3CHO	$CH_3CHO^+ + C_2$	charge	0.55	−113	2.8	3.4
			$CH_3CO^+ + C_2H$	H^-	0.45	−627		
29	C_2H^+	CH_3CHO	$CH_3CHO^+ + C_2H$	charge	0.40	−133	3.3	3.4
			$CH_3CO^+ + C_2H_2$	H^-	0.30	−541		
			$CH_3CHOH^+ + C_2$	H^+	0.15	−7		
			also, *m/z* 28 (CO^+ or $C_2H_4^+$), *m/z* 29 (HCO^+ or $C_2H_5^+$), and *m/z* 42 ($C_2H_2O^+$) products, all <5%					
30	$C_2H_2^+$	CH_3CHO	$CH_3CHO^+ + C_2H_2$	charge	0.55	−118	2.8	3.4
			$CH_3CO^+ + C_2H_3$	H^-	0.45	−194		

[a] kJ mol^{-1}. [b] In units of 10^{-9} cm^3 s^{-1}. Error estimates for rate constants are ±20% except reaction 14 (±25%) and reaction 18 (±35%). [c] In units of 10^{-9} cm^3 s^{-1} . Collision rates have been calculated using the parametrized trajectory calculation method of Su and Chesnavich,[9] with dipole moments and polarizabilities from various sources.[10,11] [d] The reactive isomer constituted about 65% of the ions.

TABLE 3: Calculated Energies in the $H_2CO^+ + H_2$ and $H_2CO^+ + C_2H_2$ Systems

	ΔH (G2 MP2) kJ mol^{-1}
$H_2CO^+ + H_2$	
$H_2COH_2^+$ TS (II)	+28.3
$HCOH^+ + H_2$	+23.3
$H_2CO^+ + H_2$	0.0
$H_2CO^+{\cdot}H_2$ (I)	−8.0
$H_2COH^+ + H$	−17.3
$H_2COH^+{\cdot}H$ (III)	−24.7
$H_2CO^+ + C_2H_2$	
$H_2CO + C_2H_2^+$	0.0
$HCOH^+ + C_2H_2$	−20.8
$H_2CO^+ + C_2H_2$	−44.1[a]
$HCO + C_2H_3^+$	−48.0
$C_2H_4CO^+$ TS (V)	−49.2
$C_2H_4^+ + CO$	−263.5[b]
$CHCHCHOH^+$	−270.9
$C_2H_4^+{\cdot}CO$ (VI)	−277.7
cyclic CH_2CHCHO^+ (IV)	−299.6

[a] Experimental value (NIST database) = −50.2 kJ mol^{-1}. [b] Experimental value (NIST database) = −262.1 kJ mol^{-1}.

acetylene C-atom that is now bonded to O, forming a cyclic $[CH_2CH_2CO]^+$ transition state. Once through this transition state, the original CO and CC bonds can dissociate, leading to the weakly bonded intermediate $C_2H_4^+{\cdot}CO$ (VI) in the exit channel with a calculated bonding energy of −14.2 kJ mol^{-1} (compared to the separated products), which then dissociates to the $C_2H_4^+ + CO$ products. Both of the reactions starting from $C_2H_2^+ + H_2CO$ or from $H_2CO^+ + C_2H_2$ may proceed through cyclic adduct IV. The $C_2H_2^+ + H_2CO$ reaction is the more energetic of these, and in this case, the extra energy of the complex may allow the weakly bonded migrating H-atom in TST V (Figure 2) to be lost, yielding the $C_3H_3O^+$ minor product of reaction 16 shown in Table 2. The reactions of other alkynes may also proceed through similar cyclic intermediates. Alkyl substitution can have significant effects on the energies of the complexes and the transition states of these intermediates, which may facilitate or hinder various competitive channels. Note that the energies of all the intermediates are lower than those of the reactants, allowing reactions without an overall energy barrier, and these reactions would therefore be possible at low interstellar temperatures.

The first mechanism, requiring sequential hydrogen shifts, does not require carbon exchange between H_2CO^+ and C_2H_2, so the leaving CO contains the carbon from the H_2CO reactant. The second mechanism requires carbon exchange, because the $C_2H_4^+$ product contains one carbon atom from C_2H_2 and one from H_2CO. An indication of which mechanism operates could be provided by labeling the carbon in H_2CO.

It should be noted that the second mechanism (the cyclic intermediate undergoing carbon exchange) is applicable if the carbon that leaves in CO is highly unsaturated with only one bound H-atom in the transition state. This applies to most, but not all, of the observed H_2 and H_2^+ transfer processes in Tables 1 and 2. H_2 transfer and loss of CO also occurred in the reactions of H_2CO with $C_3H_4^+$ generated from allene and with $C_3H_5^+$ generated from ethene. If the same mechanism (of the cyclic intermediate undergoing carbon exchange) occurred in these cases, then two hydrogen shifts from the carbon of the hydrocarbon reactant ion that becomes incorporated in the CO molecule would be necessary.

Table 1 also lists the reactions of protonated formaldehyde H_2COH^+ with some hydrocarbons. The reactions of H_2COH^+ with C_2H_2 and C_2H_4 cannot yield proton transfer, because it is endothermic, and instead yield adducts directly or with the elimination of H_2 or H_2O, respectively. It is interesting that the reactions of H_2COH^+ with acetylene, allene, propyne, and diacetylene yield hydrogenated hydrocarbon ions, similar to the radical ion systems. In the case of allene and propyne, hydrogenation occurs by the transfer of $H^+ + H_2$ (or of $H_2^+ +$ H). Note that the product of the reaction of H_2COH^+ with C_2H_2 may require the insertion of C_2 into the ion. We have also observed C_2 insertion channels in the reactions of C_2^+ and C_2H^+ with hydrocarbons, and these will be presented elsewhere. The reactions of H_2COH^+ with allene and propyne yield $C_3H_n^+$ ions similar to those from the reactions of H_2CO^+, plus one H-atom. In these cases, we could quantify the product distributions, and we note that the reactions of H_2COH^+ with allene and propyne proceed at equal rates and yield identical product distributions. This suggests that these reactions may proceed through an identical reaction complex.

Comparing the reactions of the radical and protonated systems, we also note that the ion $C_3H_3O^+$ is the major product of the $H_2COH^+ + C_2H_2$ system and is also present as a product of the $C_2H_2^+ + H_2CO$ system. In the latter reaction, it may result from H loss from the cyclic $C_3H_4O^+$ intermediate (IV or V in Figure 2), and in the protonated system, it may result similarly by H_2 loss from an analogous cyclic $C_3H_5O^+$ intermediate. There is a need to study reactions such as the charge-transfer reaction of $C_2H_2^+ + H_2CO$ at higher energies, because the $H_2CO/C_2H_2^+$ system represents a quasiresonant process in which complex formation is not favored. The reaction exothermicity can appear as product recoil velocity. The very exothermic channels such as $C_2H_4^+ + CO$ may be expected to form highly excited products.

Finally, we may compare the reactions of the $C_2H_n^+$ ions with H_2CO and CH_3CHO. All of these reactions give significant charge-transfer channels. The distinguishing feature is the occurrence of hydride transfer (H^-) in the reactions of all of the three ions with CH_3CHO, presumably as a result of the stability of the CH_3CO^+ product ion.

The $H_2CO^+ + H_2$ System. The chemistry of ions reacting with neutrals in hydrogen-dominated interstellar clouds and planetary atmospheres is important only if the ions do not react with H_2. According to literature data,[14,18,19] H_2CO^+ does not react with H_2, although three possible exothermic or near-exothermic channels may be considered: H transfer from H_2 to yield $CH_3O^+ + H$ is slightly endothermic (+7 kJ mol^{-1}); $H_2COH^+ + H$ is exothermic by 53 kJ mol^{-1}; association to yield CH_3OH^+ is exothermic by 146 kJ mol^{-1}. In the present study, we carefully examined the $H_2CO^+ + H_2$ system which could yield both $m/z = 31$ or 32 product ions on the basis of these exothermic channels. As noted in the Experimental Section, to avoid breakup of the H_2CO^+ ion during injection, it was necessary to inject O_2^+ as the reagent ion. O_2^+ then generates H_2CO^+ within the SIFT flow tube by reaction with H_2CO that is introduced through the upstream inlet. Under these conditions, some H_2COH^+ ($m/z = 31$) is formed also by the reaction of H_2CO^+ with H_2CO and with trace H_2O impurity. In addition, some O_2^+ ($m/z = 32$) was observed from unreacted O_2^+ ions. These are the same ions, or have the same m/z, as the expected products and are included during product analysis from the $H_2CO^+ + H_2$ reaction.

When H_2CO^+ was produced from O_2^+, no reaction was observed upon the addition of large amounts of H_2 ($k < 1.5 \times 10^{-13}$ cm^3 s^{-1}), although some H_2COH^+ at $m/z = 31$ was formed. The formation of the $m/z = 31$ ion is accounted for by small traces of water impurity in the very large flows of hydrogen used. This observation is explained if it is assumed that the H_2COH^+ signal arose from the H_2O^+ that was generated from trace amounts of O_2^{+*} reacting with H_2O in the hydrogen. This H_2O^+ then formed H_3O^+, which in turn proton-transferred to H_2CO forming the $m/z = 31$ ion. This finding was confirmed by carrying out the reaction of H_2CO^+ and deuterium, where a similar increase in the H_2COH^+ signal occurred at $m/z = 31$. If D_2 was involved in this reaction, the peak would have been at $m/z = 32$ from H_2COD^+. We conclude, therefore, that the minimal reactivity observed in the $H_2CO^+ + H_2$ system was due to trace amounts of impurities in the helium carrier and hydrogen reactant gases. The rate coefficient for the reaction of $H_2CO^+ + H_2$ has a value of less than 1.5×10^{-13} cm^3 s^{-1}.

Concluding Remarks and Some Astrochemical Implications. Our observation that the $H_2CO^+ + H_2$ system is slow or unreactive at 290 K is consistent with the literature, although H-atom transfer to form H_2COH^+ is an exothermic process. However, many ion−molecule reactions exhibit negative temperature coefficients if the transition states of the products are below the energies of the reactants. Such reactions may be slow at 290 K but fast at interstellar temperatures of 10−50 K. Therefore, we further examined this system by probing the H_2CO^+/H_2 potential surface using ab initio calculations. A very recent study by Liu and Anderson[18] has also examined the potential surface of the H_2CO^+/H_2 system. They have undertaken G3 level calculations of structures I, II, and III with good agreement in structure energies compared to the present results.

The results in Table 3 and Figure 2 show a noncovalent adduct $H_2CO^+\cdot H_2$ (ion I, energy −8.0 kJ mol^{-1}), which could be stabilized as a weakly bound complex in high-pressure environments such as planetary atmospheres. The calculations also show an H-transfer product $H_2COH^+ + H$ (−17.3 kJ mol^{-1}) and the complex $H_2COH^+\cdot H$ (ion III, −24.7 kJ mol^{-1}), all at lower energies than the reactants. However, forming the H_2COH^+ ion by H-transfer requires a transition state (ion II) with an energy 28.3 kJ mol^{-1} above the reactants. Another possible reaction pathway proceeding through the $HCOH^+$ isomer of H_2CO^+ requires a high-energy intermediate with a calculated energy 23.3 kJ mol^{-1} above the reactants. Reactions with positive activation energies of this magnitude will be insignificant at our experimental temperature of 300 K and even more so at much lower interstellar temperatures. Therefore, the calculations are consistent with the room-temperature observation that the $H_2CO^+ + H_2$ system is nonreactive. H_2CO^+ is therefore able to live long enough to react with other molecules in the interstellar medium. However, the protonation of H_2CO^+ by H_2 may be possible in high-energy plasmas and shock waves where high-energy collisions might activate the system.

In reference to the reactions of the hydrocarbon ions in Table 2, most of these ions, except C_2H^+ and $C_2H_2^+$, also do not react with H_2.[20] As a result, once formed in the interstellar medium, they can remain stable and able to react with other major components including H_2CO, resulting in the observed hydrogenation reactions. In fact, H_2 transfer appears to be a unique pathway for the hydrogenation of these unsaturated ions. The product hydrocarbon ions may then react with hydrocarbons or product molecules leading to more complex and more highly saturated products. Some of the product ions of the initial reactions with H_2CO may react with a further H_2CO molecule by association leading to $ROCH_2^+$ oxocarbonium ions.

We note that adduct formation was observed in a small number of the reactions studied in this paper. While exothermic bimolecular reactions occurring at the relatively high (~0.5 Torr) pressures in the SIFT might be expected at lower pressures (i.e., in an ICR experiment), the reverse is not necessarily true. Some bimolecular association reactions observed in low-pressure ICR experiments appear as termolecular processes in the SIFT, because collisional stabilization is faster than radiative stabilization at flow tube pressures. A comparison of measurements made by the two techniques has been presented in an earlier paper.[21]

Eventually, the complex and saturated molecules generated by these reactions are subject to dissociative processes in interstellar clouds. An important dissociative process in these hydrogen-dominated ionized environments is the highly exothermic dissociative proton transfer from H_3^+ ions, which can result in dehydrogenation by the loss of H_2 and the loss of other small, stable molecules such as CO, H_2CO, and HCN.[22] Cycles of associative and hydrogenation reactions, such as those presented in this paper, and dissociative reactions can lead toward steady-state populations of molecules in interstellar clouds.

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