Formation of Simple Organic Molecules in the Interstellar Medium

ABRAHAM F. JALBOUT, FLAVIO F. CONTRERAS-TORRES, ANED de LEON

Instituto de Química, Universidad Nacional Autónoma de Mexico, México D. F.

ABSTRACT: In this work we present a methodology for the synthesis of simple molecules from basic formaldehyde (H_2CO) precursors. We have approached this challenging problem by considering a basic dimerization scheme that eventually leads to diose and methyl formate, using an HCO^+ proton source. This species was chosen due to its ample abundance in the atmosphere. © 2007 Wiley Periodicals, Inc. Int J Quantum Chem 108: 598–606, 2008

Key words: sugar synthesis; methyl formate; formaldehyde; ab initio calculations

1. Introduction

It was previously proposed [1, 2] that the formation of formose and glycoladehyde could be done in a variety of chemical reactions. In these studies very modest attention was dedicated towards the development of such issues. The initial arguments were defended on speculative terms and limited empirical evidence. It is believed that a keen understanding of these reaction pathways can shed some light on the formation of biological molecules in the interstellar medium (ISM). [3] There exist only scant investigations, which address the development of a mechanism for the formation of extended sugar systems from basic ISM precursors.

Correspondence to: A. F. Jalbout; e-mail: ajalbout@u.arizona.edu

In this work we advance on the concept that the reaction of formaldehyde (H_2CO) with a proton source (HCO^+) may lead to sugars (such as diose). Because of the fact that formaldehyde is a common interstellar molecule, we believe that it can react with a proton source to yield larger molecular species. Additionally, we propose that methyl formate, an important potential atmospheric product, should also form from our mechanism [4].

More than 75% of known interstellar chemical species are organic molecules [5]. There are many important gas phase interstellar reactions, which are dominated by two body, exothermic, ion–molecule reactions, which permit theoretically feasible mechanistic pathways leading to interstellar organics, including the more complex species (up to 12 atoms; [6]). It is also well known that molecular hydrogen (H_2), H_3^+, HCO^+, and H_3O^+ are all present in the ISM (H_2 is the most abundant inter-

stellar chemical species) which suggests protonation as an important ion–molecule reaction [7].

Because of the fact that formaldehyde ($CH_2{=}O$) is significantly abundant among the ~140 known interstellar molecules, and protonated formaldehyde ($CH_2{=}OH^+$) and glycoaldehyde ($HOCH_2CH{=}O$) have been detected by radio telescope astronomy [8–10] we can use these as starting points for further elucidation of their molecular interactions. Also, the HCO^+ molecule has been shown to be present in the ISM and has also been demonstrated to be relatively reactive [11, 12]. Therefore, we believe that a reaction between the two species should lead to simple sugars and serve as a precursor to the building blocks of life.

It was suggested by Butlerow that formaldehyde reacts under basic [$Ca(OH)_2$ solution] conditions to form sugars. This reaction was identified and labeled as the formose reaction and consisted of a series of aldol condensation mechanisms [2]. In his report he mentioned that the first step in this process [from pure formaldehyde (CH_2O) to glycoaldehyde ($CH_2O)_2$] is the most difficult part of the mechanism. We believe that a Nazarov mechanism can be used to explain this principle [13] and has been shown to be successful in recent studies.

In our previous study [13] we demonstrated that H_3O^+ could react with H_2CO to yield the simplest sugar (diose or glycoaldehyde). We have tried several other proton sources but the lowest energy pathways involved the hydronium cation as the proton source. As the calculations showed, this system was quite sensitive to the methods employed, and only through careful calculations we were able to adequately model the mechanism.

We developed a mechanism by which the two formaldehyde species undergo dimerization in a π-stacking arrangement by which two H_2CO molecules form a head to tail van der Waals intermediate. However, in this study we show that when HCO^+ is used (which is more abundant than H_3O^+ in the ISM) the barriers for the formation of these products are reduced.

We propose that HCO^+ can also be formed under the same reaction conditions as previously examined form the H_3O^+ case [13]. In this work we proposed that protonated formaldehyde (H_2COH^+) [14], which was an experimentally viable product in [13, 15] can decompose into hydrogen gas and HCO^+. This process has an experimental energy of reaction of about 35 kcal/mol with a forward barrier of around 82 kcal/mol. Further CCSD (T) ab initio calculations reveal that the computed barriers and energies of reaction are within 2% of error with respect to the exper-

imental data. Therefore, we believe that HCO^+ should be present in trace amounts in an experimental environment and in the ISM.

In another recent study [15] we proposed that larger extended sugars could also be produced from a similar formose reaction as in the synthesis of glycoladehyde. We were able to experimentally confirm the presence of the triose and tetrose sugars. Theoretical calculations were also performed, which suggested the potential existence of these species. In this work, we have refined and reperformed these experiments with greater accuracy to reveal that methyl formate (another important ISM molecule) is also present in the experimental conditions. In these experiments we increased the concentration of formaldehyde to promote such a reaction. The results were favorable and suggest that HCO^+ does mediate the formose reaction for synthesis of simple sugars and methyl formate.

The molecules used in this study are quite important since they have been observed under various interstellar conditions. These species have been located in the Sgr B2 (N-LMH) source. Recently, it has been shown [10] that a series of formaldehyde reactions could mediate the formation of methyl formate and other intermediates. In the work herein, we propose that HCO^+ (a common interstellar component) can mediate the formation of protonated glycoaldehyde and methyl formate by directly interacting with H_2CO complexes.

2. Theoretical Calculations

The quantum chemical computations carried out in this study were performed with the Gaussian 03 package of computer codes [16]. We selected the MP2/6-311+G** method for geometry optimizations and frequency calculations, which was followed by single point calculations performed at the CCSD (T)/6-311+G** level of theory. There is plenty of information about these methods in other sources [17, 18]. The theory level combination used in this study has been shown to produce reasonably good agreement with the experiment and is generally quite accurate.

Vibrational frequency calculations were performed on all structures, if there were no imaginary frequencies than the structure was identified as a minimum structure, if one imaginary frequency was computed than it was labeled as a transition state. Also, intrinsic reaction coordinate (IRC) analysis calculations were used to verify that the pro-
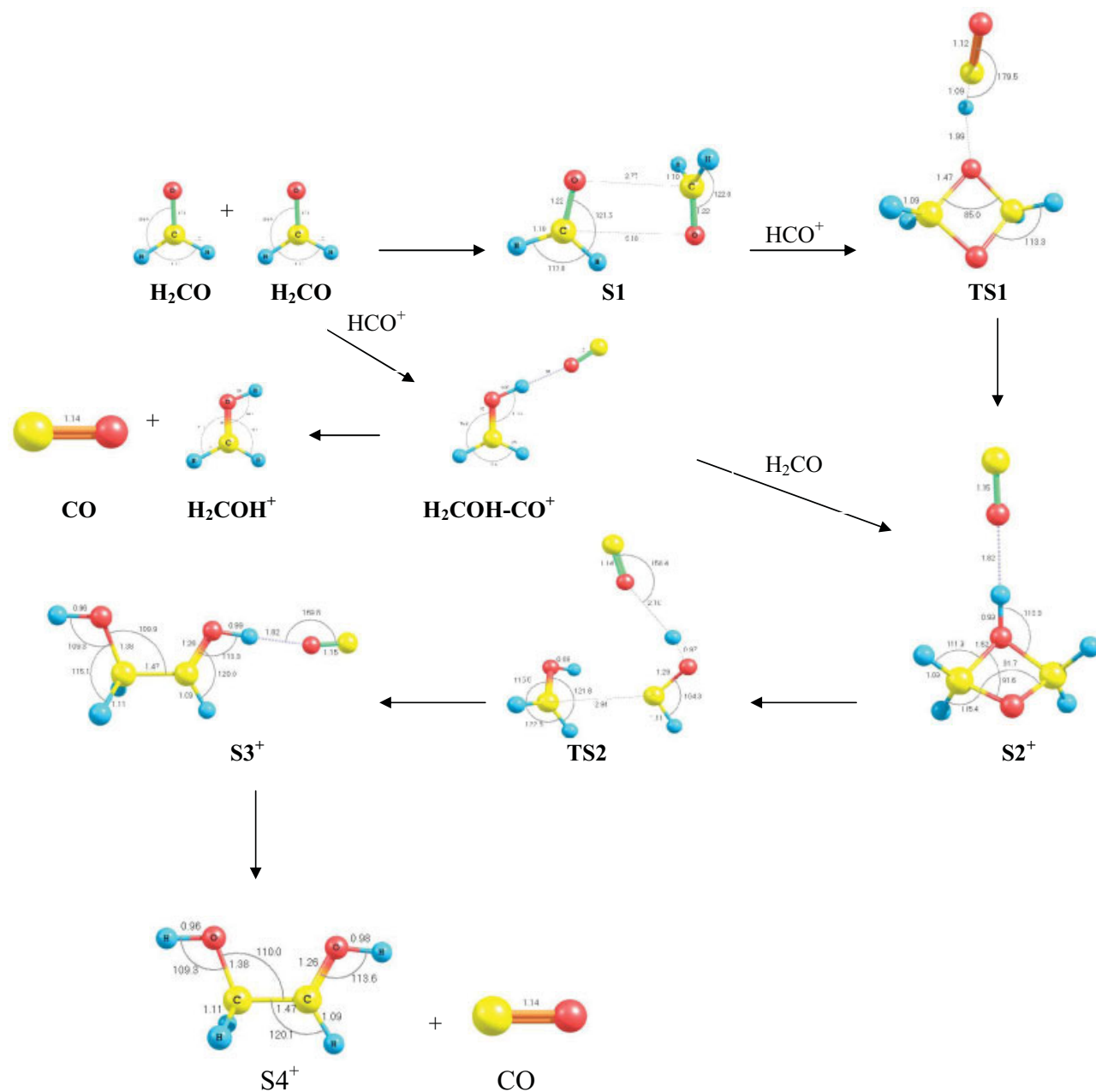
FIGURE 1. Structures and geometrical parameters for all species studied in this work for the formation of protonated diose computed at the MP2/6-311+G** level of theory, where bond lengths are shown in angstroms (Å) and bond angles are in degrees (°). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

posed transition states connected their respective products.

In recent investigations [19] we have considered an H_3O^+ proton source, however, in this work we consider HCO^+ as the proton source. In this work the proton source can be regarded as a catalyst since permits the reaction of H_2CO subunits in the formation of larger sugars. All of the geometrical structures for the protonated diose potential energy surface and transition states are shown in Figure 1, and energies (total and relative) are presented in Table I. The figure displays all bond lengths in

TABLE I
Relative energies in kcal mol^{-1} for structures in Figures 1–2.

Species	MP2/ 6-311+G**	MP2/ 6-311+G** (0 K)	[a]CCSD (T)/ 6-311+G**	[b]CCSD (T)/ 6-311+G** (0 K)
ΔE_1	−3.95	−2.492	−4.05	−2.59
ΔE_2	−31.0 (−31.67)	−24.55 (−25.51)	−45.26 (−31.2)	−38.81 (−25.06)
ΔH_{F2}	−12.5 (−13.90)	−7.18 (−7.44)	−22.05 (−13.42)	−16.71 (−6.938)
ΔH_{R2}	18.5 (17.70)	17.38 (18.10)	23.20 (17.78)	22.10 (18.12)
ΔE_{3a}	−32.1	−29.51	−47.51	−44.91
ΔE_{3b}	6.77	5.91	7.86	7.011
ΔE_{3c}	−2.83	2.46	−1.80	3.501
ΔE_4	−28.6 (−27.60)	−28.31 (−28.88)	−28.19 (−27.20)	−27.89 (−28.53)
ΔH_{F4}	43.63 (50.91)	39.85 (48.33)	39.52 (45.79)	35.73 (43.21)
ΔH_{R4}	72.25 (78.47)	68.16 (77.22)	67.70 (72.99)	63.62 (71.74)
ΔE_5	6.06	3.57	7.05	4.56

Relative energies in kcal mol^{-1}, where 0 K means that the sum of electronic and zero-point energies were used to calculate the energy of reaction. ΔE are the energies of reaction which are ΔE_1: $H_2CO + H_2CO \rightarrow$ **S1**, ΔE_2: **S1** + HCO$^+ \rightarrow$ **S2$^+$**, ΔE_{3a}: $H_2CO +$ HCO$^+ \rightarrow H_2COH$—CO$^+$, ΔE_{3b}: H_2COH—CO$^+ \rightarrow H_2COH^+ + CO$; ΔE_{3c}: H_2COH—CO$^+ + H_2CO \rightarrow$ **S2$^+$**, ΔE_4: **S2$^+$** $\rightarrow$ **S3$^+$**, ΔE_5: **S3$^+$** $\rightarrow$ **S4$^+$** + CO; and the forward barrier heights are (the reverse barrier heights are denoted ΔH_R) ΔH_{F2}: **S1** + HCO$^+ \rightarrow$ **TS1**; ΔH_{F4}: **S2$^+$** $\rightarrow$ **TS2**. The values in parenthesis are extracted from [13], which are computed using H_3O^+ as the proton source.
[a] MP2/6-311+G** geometries are used.
[b] MP2/6-311+G** geometries and ZPE used.

angstrom (Å) and bond angles in degrees (°). Also, the relative energies are plotted in Figure 2 for the formation of diose. Figure 3 shows the general pathway for the formation of methyl formate; Figure 4 presents the energy profile for which the relative energies are presented in Table II.
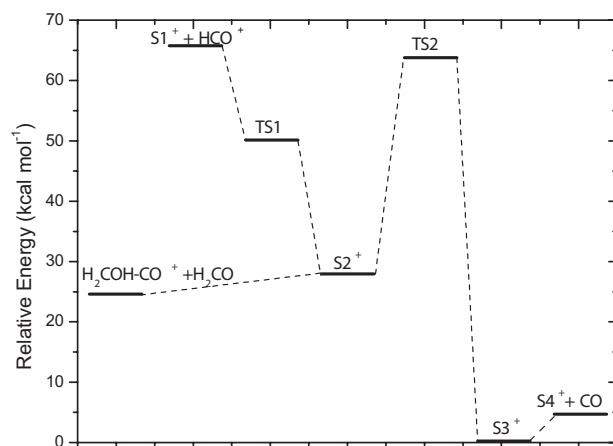

FIGURE 2. Relative energy diagram (relative to the lowest point on the singlet cation potential energy surface which is **S3$^+$**) in kcal/mol which was computed using the CCSD (T)/6-311+G**//MP2/6-311+G** level of theory.

3. Reaction Mechanisms

3.1. H$_2$CO DIMERIZATION AND HCO$^+$ ADDITION

The reaction mechanism for this pathway is depicted in Figure 1 and the values of the energies for this reaction are shown in Table I (where the values in parenthesis correspond to the parameters computed using H_3O^+ as the proton source [13]). In this work we are proposing a method and mechanism by which sugars and other simple organic species can be formed from formaldehyde (H$_2$CO) starting components. The started complex is shown as structure **S1** from Figure 1, and the energies suggest that this is a favorable pathway.

The reaction then proceeds through a cyclic structure labeled as **S2$^+$** after the addition of H$^+$ from the HCO$^+$ source. This process occurs through **TS1** with a negative barrier height and an exothermic energy of reaction as the table demonstrates. The values obtained for the reaction energy are slightly lower than the values obtained for the H_3O^+ mediated mechanism [9] that has energies of reaction of −25.5 kcal/mol (MP2) and −25.1 kcal/mol [CCSD (T)]. However, the barrier heights are more negative for this species than for the H_3O^+
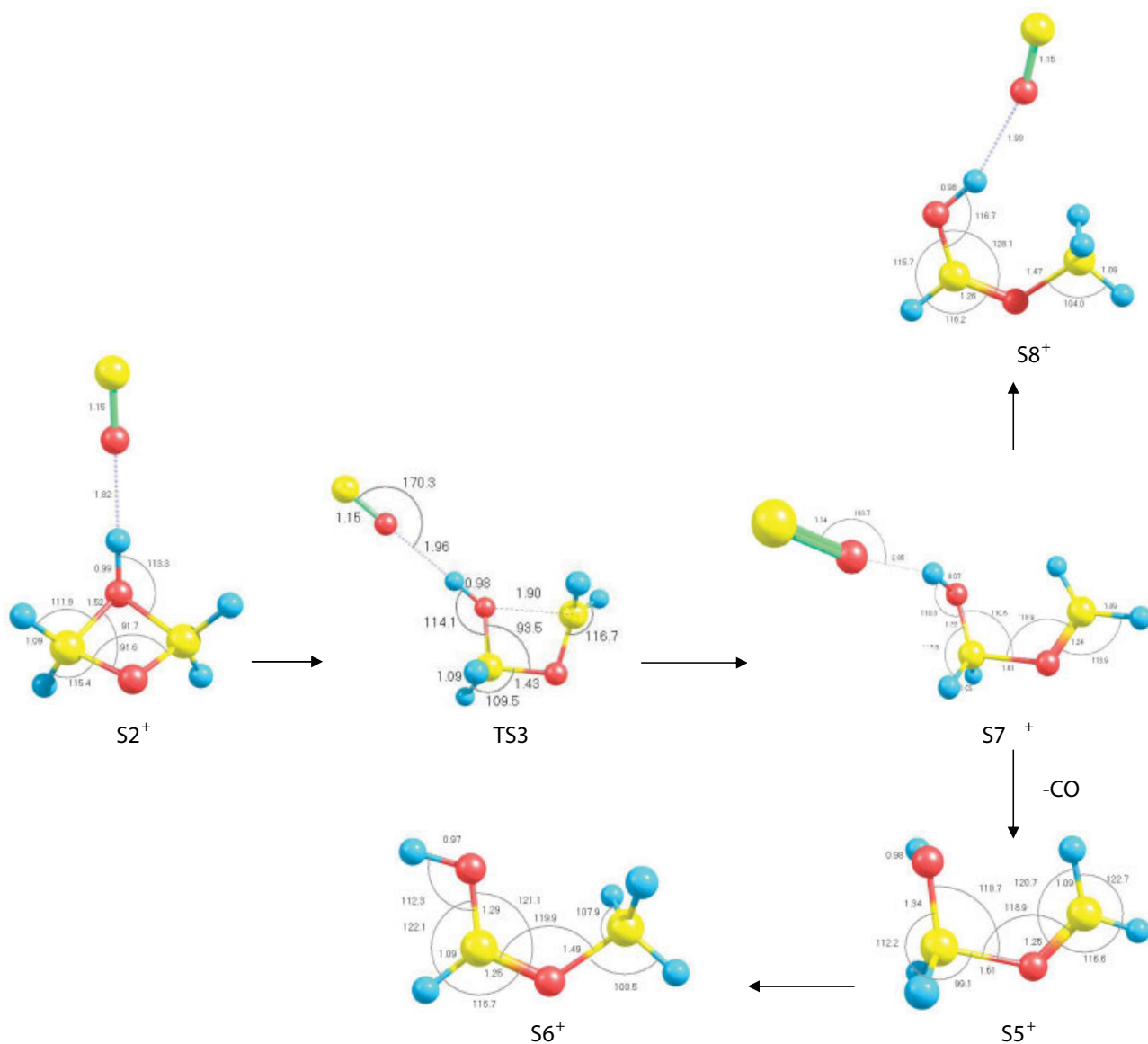
FIGURE 3. Structures and geometrical parameters for all species studied in this work for the formation of protonated methyl formate computed at the MP2/6-311+G** level of theory, where bond lengths are shown in angstroms (Å) and bond angles are in degrees (°). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

mediated case, which has a forward barrier height of -7.4 kcal/mol (MP2) and -6.9 kcal/mol [CCSD (T)]. The reason for this probably has to do the increased charge stabilization effect of the oxygen in H_3O^+ versus hydrogen in HCO^+. Interestingly after the proton is transferred the lowest energy structure is rotated to yield a hydrogen bonded complex to the oxygen atom instead of carbon. This is accounted for by the increased stabilization of such an effect.

3.2. FORMATION OF PROTONATED FORMALDEHYDE

Experimentally our measurement [13] have shown that H_2COH^+ cation (protonated formaldehyde) is also a potential product. We believe that the formation of this important product can occur by H_2CO reactions with HCO^+ leading to an H_2COH—CO^+ intermediate. From the table we can see that the energy of reaction for this process (ΔE_{3a}) highly exothermic which are similar to those
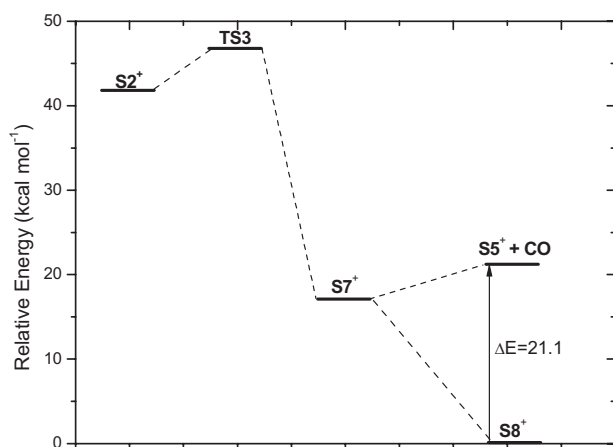
FIGURE 4. Relative energy diagram (relative to the lowest point on the singlet cation potential energy surface which is **S8$^+$**) for the formation of methyl formate in kcal/mol which was computed using the CCSD (T)/6-311+G**//MP2/6-311+G** level of theory.

for the H$_3$O$^+$ mechanism. The dissociation energy (ΔE_{3b}) of H$_2$COH—CO$^+$ into H$_2$COH and CO is rather low, which is slightly higher than the dissociation of H$_2$COH—H$_3$O$^+$ into H$_2$COH$^+$ and H$_2$O by around 20 kcal/mol. This increased value for the dissociation is due to the weaker interactions in CO relative to the hydrogen bonds in H$_3$O$^+$, which makes it a stronger hydrogen donor.

We therefore believe that there will be an experimental abundance of H$_2$COH$^+$ due to the low threshold for its dissociation. Our experimental spectrum for the H$_3$O$^+$ reaction with formaldehyde shows that there is a significant amount of protonated formaldehyde [13, 15] also present. Therefore,

if one was able to locate H$_2$COH—CO$^+$, then it should be natural for H$_2$COH$^+$ to coexist in nearly equal concentrations. The main advantage of the HCO$^+$ species is that the initial step in the reaction process (of H$_2$CO reaction with HCO$^+$), suggests that it is a better catalyst than H$_3$O$^+$.

Now in the next step of this mechanism we can consider the possibility of H$_2$COH—CO$^+$ forming **S2$^+$**. Unfortunately, we were not able to locate transition states which connect connects H$_2$COH—CO$^+$ to **S2$^+$**, however the energy of reaction for its formation (ΔE_{3c}) is quite low as the table shows, which is an interesting result. This calculation says that H$_2$COH—CO$^+$ may be a very important initiation step in the formation of diose, since **S2$^+$** formation is an integral component in the last steps of this mechanism.

3.3. DIOSE FORMATION

In this step we will now progress from diose intermediate (**S3$^+$**) that is initiated from **S2$^+$**. For this process, a ringed transition state is formed by which hydrogen migration and C—C bond formation both occur, that is very similar to the transition state observed in the H$_3$O$^+$ case [13]. The barrier height for this process (ΔH_{F4}) is large with an energy of reaction of around −28 kcal/mol. While the energy of reaction is similar to the value of the H$_3$O$^+$ mediated case, the barrier is lowered by around 10 kcal/mol. Therefore, by the use of HCO$^+$ in this mechanism the barrier is reduced, which can lead to an increased production of the proposed molecular species.

Finally, **S3$^+$** dissociates into **S4$^+$** (protonated diose) and CO gas. This process is essentially barrier-

TABLE II _____

Relative energies in kcal mol^{-1} for structures in Figure 3.

Species	MP2/6-311+G**	MP2/6-311+G** (0 K)	[a]CCSD (T)/6-311+G**	[b]CCSD (T)/6-311+G** (0 K)
ΔE_6	−23.39	−24.63	−23.70	−24.93
ΔH_{F6}	8.44	7.29	7.33	6.17
ΔH_{R6}	31.82	31.91	31.02	31.11
ΔE_7	3.77	3.22	4.61	4.06
ΔE_8	−18.55	−18.12	−17.48	−17.04
ΔE_9	22.32	21.33	22.09	21.10
ΔE_{10}	−22.26	−21.83	−20.88	−20.46

Relative energies in kcal mol^{-1}, where 0 K means that the sum of electronic and zero-point energies were used to calculate the energy of reaction. The energies of reaction (ΔE) are denoted as ΔE_{6-10} are for: **S2$^+$** → **S7$^+$**, **S7$^+$** → **S5$^+$** + CO, **S7$^+$** → **S8$^+$**, **S8$^+$** → **S5$^+$** + CO, **S5$^+$** → **S6$^+$**, and ΔH_{F6} is the forward barriers (ΔH_{R6} is the reverse barrier) for **S2$^+$** → **TS3**.
[a] Represents the CCSD (T) energies at the MP2 geometries.
[b] Zero-point energies computed using MP2 frequencies.

less that requires around 4.6 kcal/mol, which is significantly lower than the 25 kcal/mol required for the dissociation of diose-H_2O^+ into protonated diose ($S4^+$) and H_2O. We believe that the HCO^+ species should yield higher concentrations of the diose species. The results of this pathway are graphically depicted in Figure 2. As we can see the lowest energy structure is $S3^+$, and the reverse barrier towards $S2^+$ is quite high, so that once it is formed the sugar will probably remain intact without further isomerization.

3.4. METHYL FORMATE SYNTHESIS

For this mechanism we will use the previously reported ringed structures (see Fig. 1) for the intermediate product in our proposed sugar synthesis from the formose reaction. The geometrical structures for the HCO^+ potential energy surface leading to methyl formate is shown in Figure 3 and the relative energies (based on Table II) are shown in Figure 4. It is apparent that the ringed intermediate ($S2^+$, formed in the previous steps) goes through a ring opening transition state (TS3) to form the reaction product ($S7^+$) complexed with CO. From basic organic chemistry we know that this product can tautomerize into a protonated methyl formate-CO complex ($S8^+$), which of course can dissociate into methyl formate ($S6^+$ + H_2O). On the other hand, $S7^+$ can dissociate into $S5^+$ and CO that can again tautomerize into methyl formate (protonated). This can be adequately represented by the following scheme:

Reaction Product   **Methyl formate**
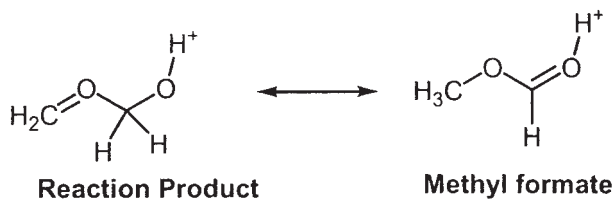
The HCO^+ energy profile for this process is shown in Figure 4, were Table II shows the relative energies where ΔE_{6-10} correspond: $S2^+ \rightarrow S7^+$, $S7^+ \rightarrow S5^+$ + CO, $S7^+ \rightarrow S8^+$, $S8^+ \rightarrow S5^+$ + CO, $S2^+ \rightarrow S6^+$, and ΔH_{F6} is the forward barriers (ΔH_{R6} is the reverse barrier) for $S2^+ \rightarrow$ TS3. The data in the table tells us that the barrier is relatively low suggesting that this is a possibility. It is important to note that the tautomerization process of $S7^+$ is around -17 kcal/mol, which makes this a probable mechanism.

The dissociation of $S8^+ \rightarrow S5^+$ + CO is around 21.1 kcal/mol but should also be present under experimental conditions. The barrier for this tautomerization processes low enough to actually facilitate (which is energetically favorably) the formation of protonated methyl formate. Preliminary computations using the H_3O^+ source shows that the current potential energy surface has a much lower barrier than that one. This result is interesting since under atmospheric conditions (where HCO^+ is abundant) we predict that methyl formate should be actively present. Figure 4 graphically depicts the relative energies for the processes being described herein.

As mentioned, experiments were also conducted, which are available in previous works [13, 15]. From the experiments, we depicted that various isomers should be formed. The peak at 31 corresponds to protonated formaldehyde, 49 is the formaldehyde-water cluster, 61 is probably the protonated diose, all of which were previously determined [13]. In a different study we observed peaks at 91 that correspond to the triose species, and 121 is the tetrose sugar which were also reported [15]. However, new peaks at 30, 32, 44, 46 were identified which probably correspond to the following structures (Abrell L, Private Communication):
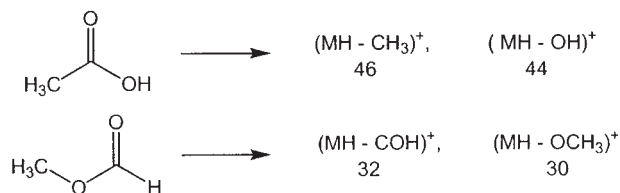
From our calculations we were only able to locate the methyl formate species located at a m/z of 30. From our previous work this species appeared to have a rather high concentration suggesting that it is present in rather high concentrations. The MH—COH^+ species can probably be formed by direct interaction of HCO^+ with the MH fragment leading to this molecule, however, the current computed barriers are too high to confirm this prediction. As a result of the current calculations, we believe that methyl formate should be formed in addition to diose and extended sugars.

4. Discussion and Concluding Remarks

We have presented in this work a mechanism by which HCO^+ can influence the formation of simple

sugars in the ISM. In this mechanism we have presented the structures and reaction scheme in Figure 1, and the relative energies plotted in Figure 2. From this table it is clear that the main hurdle in this reaction mechanism is the first step of initiation due to the high energy required for the formation of the starting products (H_2COH—CO^+ and $S2^+$). Alternatively, we have demonstrated that the reaction of H_2COH—CO^+ with H_2CO is a low energy process leading to $S2^+$, the formation of H_2COH—CO^+ from the reaction of HCO^+ and H_2CO requires a significant input of energy. One can readily see from the figure that the progression of $S2^+$ to $S3^+$ through $TS2$ is relatively low in energy. We have used two decimal points for the energies since it was shown that that is as accurate as can generally be accounted for in calculations of this nature [20].

After this we discussed the dissociation of $S3^+$ into $S4^+$ and CO to be a very low energy process. We strongly believe as mentioned earlier that the experimental spectrum of the HCO^+ mediated mechanism should contain a mixture of H_2COH^+ (m/z = 31.02) $\longleftrightarrow$ H_2COH—CO^+ (m/z = 59.0) and $S4^+$ (m/z = 61.03)+ CO(m/z = 28.01). The reason for this is the relatively low energy associated with the latter processes. While the products at masses 44 and 46 were observed, we believe that they may contribute to some other by-product of the experimental procedure. What does concur with theory is the presence of peaks at 30, 32 that correct to MH—COH^+ (at 32) and methyl formate at 30. We were unable to determine a computational mechanism leading to the creation of species at the m/z value of 32, but the methyl formate appears to be present in high experimental concentrations and is also a viable theoretical pathway, with a small barrier for its formation. Another possibility is that the reactive hydroxymethylene (HCOH) radical species can form which can then react with other products present from the reaction to yield the species observed at a peak of 32.

The HCO^+ molecule is an ideal choice due to the fact that it donates protons more readily possibly leading to the lower energy of dissociation in the last steps of our reaction. As is the case in the majority of these mechanisms the first initial step of the reaction is the most energetically expensive. We believe that these calculations can help to further shed light on the formation of simple molecules in the ISM. In this work we have demonstrated that HCO^+ can also theoretically lead to simple sugars with a relatively low energy of reaction. Additionally, this is the first report by which the formation of methyl formate is proposed and experimentally proposed from a gas phase formose reaction. This is a very exciting finding, since these are both atmospherically abundant complexes that can provide an explanation for the origins of life. If we can form diose this way, higher-level sugars (i.e., ribose) are just a few steps away. Also, in this work we have probed the possibility of methyl formate forming using HCO^+. This molecule is of recent interest [16] and through our mechanism we believe that it should exist under atmospheric/interstellar conditions.

Recent experimental work [10] explores the possibility of methyl formate synthesis from various reactions was proposed our model is unique in that HCO^+ directly interacts with the H_2CO intermediates (through lower barriers) to yield these molecules. Their model assumes that protonated formaldehyde will react with H_2CO, but what they failed to note is the energy required for this process. The process to carry out such a mechanism is significantly more favorable in energy to allow for the two H_2CO to interact together and then undergo ring-closing mediation with an external proton source than to do it independently.

In other work it has been demonstrated [13, 16] that without H_3O^+ or in this case HCO^+ the barriers for the interaction between two H_2CO are too large as to prevent favorable interactions from occurring. The current model presented is an elegant, and useful tool in understanding how we can control the synthesis of molecules, and use it as a template for understanding organic chemistry in the ISM. The calculations carried out with H_3O^+ [13] show significantly higher energy barriers than with HCO^+ probably due to the proton affinity of the former compound. In addition, HCO^+ is also more abundant in the atmosphere it is of more practicality when trying to understand interstellar behavior.

To summarize we have demonstrated how HCO^+ can be used to facilitate the formose reaction. While the experimental reactions [13, 15] were carried out with H_3O^+, the concentrations of H_2CO were increased to further facilitate the formation of HCO^+. While there are experimental works demonstrating that HCO^+ can be manufactured in a laboratory setting [12] the experiments show small peaks at m/z at 29 (relatively weak) which probably correspond to HCO^+. This is the first report of its kind that describes the synthesis of methyl formate from a gas phase formose reaction. In addition to this, it is the first study to propose a mechanism

by which HCO^+ can interact with formaldehyde to form simple organic compounds. The discovery of these molecules in the ISM is of current theoretical and experimental interest in our research group.

References

1. Breslow, R. Tetrahedron Lett 1959, 21, 22.
2. Breslow, R. J Am Chem Soc 1958, 80, 3719.
3. Benner, S. A.; Ricardo, A.; Carrigan, M. Curr Opin Chem Biol 2004, 8, 672.
4. Gilbert, W. Nature 1986, 319, 618.
5. Muller, H.; Schloder, F.; Stutzki, J.; Winnewisser, G. J Mol Spectrosc 2005, 742, 215.
6. Herbst, E.; Klemperer, W. Phys Today 1976, 29, 32.
7. Hansel, A.; Singary, W.; Wisthaler, A.; Schwarzmann, M.; Lindinger, W. Int J Mass Spectrom Ion Proc 1997, 167/168.
8. Halfen, D.; Apponi, A.; Woolf, N.; Polt, R.; Ziurys, L. Astrophys J 2006, 639, 237.
9. Zubay, G. Chemtracts 1999, 12, 432.
10. Horn, A.; Mollendal, H.; Sekiguchi, O.; Uggerud, E.; Roberts, H.; Herbst, E.; Viggiano, A. A.; Fridgen, T. D. Astrophys J 2004, 611, 605.
11. Ekern, S.; Gomez, L.; Szczepanski, J.; Vala, M. Chem Phys 2007, 331, 219.
12. Smith, M. A.; Schlemmer, S.; von Richthofen, J.; Gerlich, D. Astrophys J 2002, 578, L87.
13. Jalbout, A. F.; Abrell, L. M.; Adamowicz, L.; Polt, R.; Ziurys, L. M. Astrobiol J 2007, 7, 433.
14. Jalbout, A. F. J Mol Struct (THEOCHEM) 2002, 594, 129.
15. Jalbout, A. F. Mol Phys 2007, 105, 941.
16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B. 05; Gaussian: Pittsburgh, PA, 2003.
17. Foresman, J. B.; Frisch, A. E. Exploring Chemistry with Electronic Structure Methods, 2nd ed.; Gaussian: Pittsburgh, PA, 1996.
18. Jalbout, A. F.; Nazari, F.; Turker, L. J Mol Struct (THEOCHEM) 2004, 1, 627.
19. (a) Drougas, E.; Kosmas, A. M.; Jalbout, A. F. J Phys Chem A 2004, 108, 5972; (b) Drougas, E.; Jalbout, A. F.; Kosmas, A. M. J Phys Chem A 2003, 107, 11386.
20. Jalbout, A. F. J Theor Comput Chem 2007, 6, 269.