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Interconversion of ROC^+ and RCO^+ ($R = H$ and CH_3): Gas-Phase Catalysis by Argon and Dinitrogen

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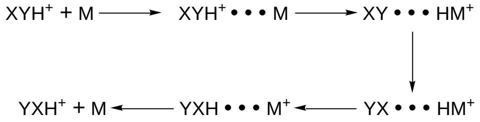
Molecular orbital calculations using density functional theory at the B3LYP/6-311++G(d,p) level have been used to optimize structures for ions $COR^+\cdots M$ and $M\cdots RCO^+$ and also for the transition structures $COR^+\cdots M$-(ts) for their interconversion ($R = H$, CH_3 and $M = Ar$ and N_2). For the unsolvated ions and for ions $COH^+\cdots M$, $M\cdots HCO^+$, and $COH^+\cdots M$(ts) the optimized structures were used for single-point calculations at QCISD(T)(full)/6-311++G(2df,p). Critical points on the COH^+ and $ArCOH^+$ potential energy surfaces were also optimized at MP2(full)/6-311++G(3df,3pd). For the uncomplexed ions COR^+, the barriers to 1,2-migration of R^+ at B3LYP/6-311++G(d,p) are 35.4 kcal mol^{-1} for $R = H$ and 14.2 kcal mol^{-1} for $R = CH_3$. Inclusion of a dinitrogen molecule removes this barrier by permitting COR^+ to deposit R^+ on N_2 followed by CO retrieving the R^+ to produce the lower energy isomer, RCO^+. Argon has a lower R^+ affinity than the oxygen atom of CO and does not remove R^+ from COR^+. Preferential stabilization by argon of the transition structure for the 1,2-migration of R^+ over stabilization of COR^+ at the minimum results in a reduction in the barrier to rearrangement. The gas-phase rearrangements of ions COR^+ via "solvated" transition structures $COR^+\cdots Ar$(ts) are calculated to have barriers of 8.3 kcal mol^{-1} for $R = H$ and 5.7 kcal mol^{-1} for $R = CH_3$, while for $COH^+\cdots Ar$ at MP2(full)/6-311++G(3df,3pd) the barrier is only 2.0 kcal mol^{-1}. These findings indicate noble gas atoms may catalyze the rearrangement of cations rather than simply cool them by collisions.

Introduction

There are several examples of the efficient conversion of high-energy ions into lower energy isomers by interaction with a neutral molecule.[1] For example, HOC^+ reacts with H_2 to give, as one channel, the lower energy isomer HCO^+.[2] Similarly, both CO and CO_2 catalyze the interconversion of HCN^+ and CNH^+,[3] NO assists in the conversion of $HNNO^+$ into $NNOH^+$ (prior to dissociation into N_2 and OH^+),[4,5] and there are several examples of neutral molecules catalyzing the conversion of radical cations into isomeric distonic ions.[6] In each of these examples there is a substantial barrier to the proton shift and the occurrences of these reactions have been explained in terms of the "back and forth" mechanism outlined in Scheme 1.[4] Base M first "solvates" the higher energy isomer XYH^+ and then plucks off the proton to form ion HM^+, which is "solvated" by XY through Y. Rotation of the neutral XY fragment in this complex to form HM^+ "solvated" by XY through X followed by transfer of the proton to X and subsequent dissociation results in formation of the lower energy isomer YXH^+. Since there is little or no barrier to proton-transfer reactions, the requirement for the above reaction sequence to occur is that the catalyst M have a proton affinity between those of atoms X and Y in molecule XY. Similarly, interconversion of cations involving the migration of a methyl group may also be catalyzed by neutral molecules having methyl cation affinities between those of the two sites for methylation in a molecule, and recently, it was shown that Xe and N_2 catalyze the rearrangement of $CH_3NO_2^+$ into CH_3ONO^+.[7]

SCHEME 1



Here, we examine the effect of catalysts on the rearrangement of COR^+ into RCO^+ ($R = H$ and CH_3). Both the proton[8] and methyl cation[9] affinities of N_2 are between those of the C and O of CO,[10−13] and N_2 should therefore be capable of functioning as a catalyst for the interconversion of COR^+ and RCO^+. A more interesting possibility is that molecules that have *lower* proton affinities than the oxygen atom of CO may function as catalysts by preferentially stabilizing the transition structure. Noble gas atoms are possible candidates for such a catalytic role and complexes $M\cdots HCO^+$, where $X = He$[14] and $X = Ar$[15] have recently been studied by infrared spectroscopy and both $He\cdots HCO^+$ and $Ar\cdots HCO^+$ have also been the subject of a recent high-level molecular orbital theoretical treatment.[16] Both ions were found to be linear, and $Ar\cdots HCO^+$ was calculated to have a dissociation energy of 3.5 kcal mol^{-1} after inclusion of a correction of 0.7 kcal mol^{-1} for basis set superposition errors. Argon has a considerably higher proton affinity than helium and is therefore a better potential catalyst for the rearrangement of COR^+. The proton affinity of argon (calculated to be 90.6 kcal mol^{-1} [17]) is lower than that of the oxygen of CO (estimated to be 104.2 kcal mol^{-1} by combining the experimental proton affinity for CO of 141.9 kcal mol^{-1},[10] where protonation occurs on carbon, and the calculated difference in proton affinities of the two atoms[11]), and consequently, the $COH^+\cdots Ar$ complex is expected to have a higher binding energy than $Ar\cdots HCO^+$. Furthermore, the transition structure for interconversion of COH^+ and HCO^+ has the proton less tightly bound than those in the structures at the minima, and it is therefore probable that the transition structure has the largest solvation energy. The

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TABLE 1: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1})

molecule	B3LYP[a]	zero-point	QCI[b]	MP2[c]
CO	−113.349 05	3.2	−113.192 78	−113.180 20
CH_3^+	−39.491 47	19.6	−39.415 75	
Ar	−527.553 87		−527.098 22	−527.110 26
N_2	−109.559 69	3.5	−109.411 52	
ArH^+	−527.698 01	3.8	−527.246 67	−527.261 00
N_2H^+	−109.753 50	10.0	−109.607 16	
$ArCH_3^+$	−567.072 33	22.7	−566.542 32	
$N_2CH_3^+$	−149.124 97	28.3	−148.901 80	
HCO^+	−113.581 82	10.3	−113.427 86	−113.420 00
COH^+	−113.519 34	8.4	−113.362 95	−113.346 58
COH^+ [d]	−113.458 39	5.9	−113.303 14	−113.280 26
$Ar\cdots HCO^+$	−641.141 49	10.6	−640.532 57	−640.538 32
$COH^+\cdots Ar$	−641.090 79	8.4	−640.479 32	−640.478 59
$COH^+\cdots Ar$[d]	−641.056 21	7.1	−640.446 42	−640.450 20
$N_2\cdots HCO^+$	−223.157 67	14.7	−222.855 01	
$CO\cdots HN_2^+$	−223.125 97	13.7	−222.821 68	
$COH^+\cdots N_2$[d]	−223.105 78	13.6	−222.803 94	
CH_3CO^+	−152.969 68	27.9	−152.737 53	
$COCH_3^+$	−152.879 02	27.0	−152.646 68	
$COCH_3^+$ [d]	−152.853 21	24.9	−152.619 96	
$Ar\cdots CH_3CO^+$	−680.524 54	28.0		
$COCH_3^+\cdots Ar$	−680.434 33	27.1		
$COCH_3^+\cdots Ar$[d]	−680.422 27	26.0		
$N_2\cdots CH_3CO^+$	−262.534 72	32.0		
$CO\cdots CH_3N_2^+$	−262.477 92	31.8		
$N_2\cdots CH_3^+\cdots CO$[d]	−262.465 13	31.5		

[a] B3LYP/6-311++G(d,p). [b] QCISD(T)(full)/6-311++G(2df,p). [c] MP2(full)/6-311++G(3df,3pd). [d] ts = transition structure.

consequence of a larger stabilization for the transition structure will be a reduction in the barrier to interconversion.

In this study we report the effect of N_2 and Ar on the profiles to rearrangement of COR^+ where R = H and CH_3.

Computational Methods

All molecular orbital calculations were performed using Gaussian 94.[18] Structure optimizations were carried out using the CALCALL routine along with molecular orbital calculations employing density functional theory (DFT) at the B3LYP level.[19,20] The 6-311++G(d,p) basis set[21−25] was used for all structure optimizations, and then for the COH^+ and $COH^+\cdots M$ systems these geometries were used for single-point calculations at QCISD(T)(full)/6-311++G(2df,p).[26,27] For each transition state, intrinsic reaction coordinate (IRC) calculations[28] were performed to establish that the structure was indeed for the migration of R^+ from one N atom to the other and not for transferring R^+ from N_2 to the catalyst. To check further the validity of the DFT calculations, the critical points on the COH^+ and $COH^+\cdots Ar$ potential energy surfaces were subjected to structure optimizations at MP2(full)/6-311++G(3df,3pd).[29]

The overall conclusions on the relative energies of reactants and transition states from the two different levels of theory for $COH^+\cdots M$ were very similar, and consequently, we decided that it was unnecessary to perform QCI calculations on the larger $COCH_3^+\cdots M$ ions. All the computed energies are given in Table 1, and the optimized structures are given in Figures 1 and 2.

Results and Discussion

(a) Structures. *(i) CO, HCO^+ (**1**), COH^+ Transition Structure (**2**), and COH^+ (**3**).* The optimized structures for CO, HCO^+, and COH^+ given in Figure 1 are in excellent agreement with those from previous theoretical studies[11,30] and also with experimental r_e values (for HCO^+, C−H is 1.0972 Å and C−O is 1.1047 Å;[31] for COH^+, O−H is 0.975 Å and C−O is 1.1570 Å[32]). The structural changes accompanying protonation of CO, namely, shortening of the C−O distance by protonation on C and lengthening of this distance by protonation on O, have been noted previously and will not be discussed in detail here. Similarly, previous Hartree−Fock level calculations[14] gave COH^+ to be bent, but inclusion of electron correlation leads to

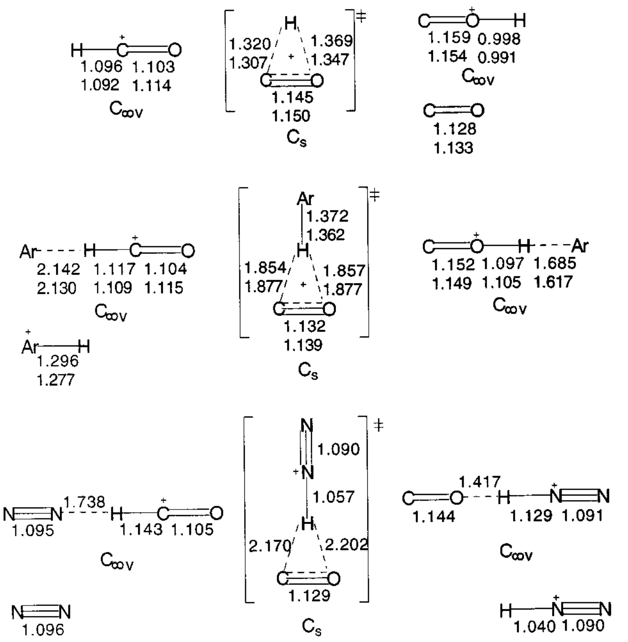


Figure 1. Geometric parameters for $HCO^+\cdots M$ ions. Bond lengths are in angstroms and angles are in degrees. Higher numbers are at B3LYP/6-311++G(d,p) and lower ones at MP2(full)/6-311++G(3df,3pd).

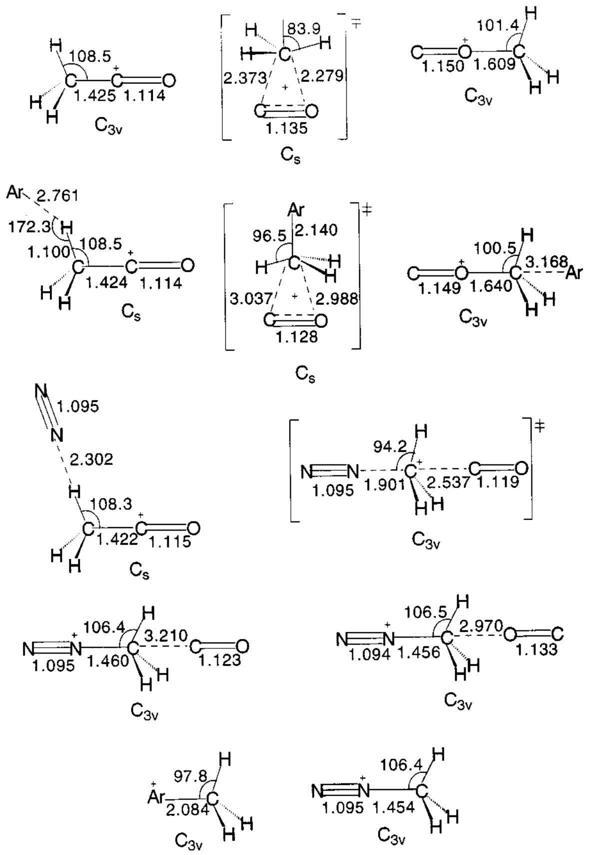
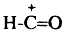
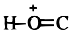


Figure 2. Geometric parameters for $CH_3CO^+\cdots M$ ions. Bond lengths are in angstroms and angles are in degrees.

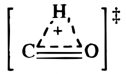
a linear structure for this ion. Optimization at B3LYP/6-311++G(d,p) also gave COH^+ to be linear, but bending requires little energy as shown by the low frequencies for the degenerate bending vibrations. The transition structure for interconversion between COH^+ and HCO^+ has a C−O distance between those in the two ions, but, consistent with Hammond's postulate,[33] it is closer to that in the higher energy isomer COH^+. The O−H distance, however, is larger than C−H, indicating that, on rearrangement of COH^+, H migration is well under way in the transition structure. This is consistent with the low bending frequencies calculated for COH^+.


$\mathrm{H{-}\overset{+}{C}{=}O}$

1

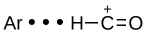

$\mathrm{H{-}\overset{+}{O}{=}C}$

2

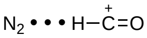


3

(ii) Ions M···HCO⁺. Interaction with argon and with dinitrogen results in changes to structures **1**−**3**, and the magnitude of the changes is dependent upon the proton affinity of the interacting molecule. For example, argon has a much lower proton affinity than the C of CO and interacts only very weakly with the proton, as shown by the large Ar···H distance in **4** of 2.142 Å (the experimental value of 2.13 Å[15] is reproduced at MP2(full)/6-311++G(3df,3pd)). This interaction results in slight elongations of the H−C and C−O distances of 0.021 and 0.001 Å, respectively. The stabilization of **4** relative to the separated species Ar and HCO^+ is 3.5 kcal mol^{-1} at B3LYP/6-311++G(d,p), 4.0 kcal mol^{-1} at QCISD(T)(full)/6-311++G(2df,p), and 4.8 kcal mol^{-1} at MP2(full)/6-311++G-(3df,3pd). These dissociation energies do not compensate for basis set superposition errors and will therefore be slightly too high. Previous calculations on this complexed ion showed the counterpoise correction to be 0.6−0.8 kcal mol^{-1} and the dissociation energy to be 3.2−4.2 kcal mol^{-1}.[16]


$\mathrm{Ar\cdots H{-}\overset{+}{C}{=}O}$

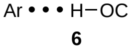
4


$\mathrm{N_2\cdots H{-}\overset{+}{C}{=}O}$

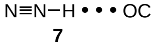
5

Dinitrogen molecule has a higher proton affinity than argon, and solvation of HCO^+ by N_2 results in a stabilization of 9.5 kcal mol^{-1} at B3LYP/6-311++G(d,p) and 9.2 kcal mol^{-1} at QCISD(T)/6-311++G(2df,p). The C−H distance in **5** is longer than that in **4** and is 0.047 Å longer than in the isolated ion **1**. The N···H distance of 1.738 Å in **5**, compared with a distance of 1.09 Å in the isolated N_2H^+, indicates a relatively weak interaction, and a Mulliken population analysis[34] showed there to be essentially no net transfer of positive charge onto the N_2 molecule.

(iii) Ions COH⁺···M. The oxygen atom of CO has a proton affinity closer to that of argon, and consequently, interaction with argon is more stabilizing for COH^+ than for HCO^+. The dissociation energy of **6** is calculated to be 11.8 kcal mol^{-1} at B3LYP/6-311++G(d,p), 12.2 kcal mol^{-1} at QCISD(T)(full)/6-311++G(2df,p), and 14.6 kcal mol^{-1} at MP2(full)/6-311++G-(3df,3pd). At B3LYP/6-311++G(d,p), the O−H distance in **6** is 0.099 Å longer than that in the isolated ion **3** and the C−O distance is 0.007 Å shorter. Finally, the Ar−H distance (1.685 Å) in **6** is much shorter than that in **4** but is considerably longer than that in ArH^+ (1.296 Å). The argon atom in **6** is calculated to have a charge of +0.26.


$\mathrm{Ar\cdots H{-}\overset{+}{O}C}$

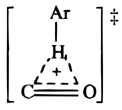
6


$\mathrm{N{\equiv}\overset{+}{N}{-}H\cdots OC}$

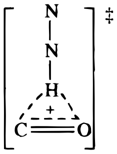
7

We were unable to locate a structure for ion $N_2\cdots HOC^+$. All attempts at optimizing this ion resulted in migration of the proton to N_2. Ion **7**, N_2H^+ "solvated" by the oxygen of CO, is at a minimum and is calculated to require 14.3 kcal mol^{-1} at B3LYP/6-311++G(d,p) for dissociation into N_2H^+ and CO. Comparison of **7** with the structure of isolated N_2H^+ shows the N−H distance to be increased by 0.089 Å by interaction with OC, but the N−N distance is increased by only 0.001 Å. The C−O distance of 1.144 Å in **7** is 0.016 Å longer than that in CO, and a small amount of positive charge (+0.11) is located on the CO fragment.

(iv) Transition Strucures COH⁺···M. Comparison of transition structures **8** and **9** with that for the uncatalyzed reaction show both the C−H and O−H distances to be greatly elongated by the presence of an inert gas molecule. Structures **8** and **9** both have one imaginary frequency in which the predominant motion is displacement of the proton in a direction parallel to the C−O bond. They are best described as having the proton attached to the catalyst with this ion being solvated by the π-system of CO. At B3LYP/6-311++G(d,p) the dissociation energies for removal of CO from **8** and **9** are 6.8 and 2.0 kcal mol^{-1}, respectively.

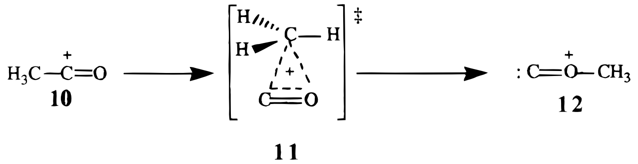


8



9

*(v) CH₃CO⁺ (**10**), COCH₃⁺ Transition Structure (**11**), and COCH₃⁺ (**12**).* Addition of a methyl cation to CO results in similar but smaller changes to the C−O distance as occurs on protonation. Methylation at C then produces a decrease of 0.014 Å, while methylation at oxygen elongates the C−O distance by 0.022 Å (Figure 2). The C−C distance in **10** of 1.425 Å is shorter than a normal C−C bond by about 0.1 Å, while the O−C distance in **12** of 1.609 Å is almost 0.2 Å longer than a characteristic C−O single bond. Transition structure **11** has large OC and CC distances, and the CH_3 fragment is almost planar. These structural parameters indicate that CH_3^+ is largely detached from the CO, and at B3LYP/6-311++G(d,p) the transition structure is only 6.8 kcal mol^{-1} lower in energy than the dissociation products, CH_3^+ plus CO. A Mulliken population analysis[33] gave a charge of +0.72 on the CH_3 group in **11**.



(vi) Ions M···CH₃CO⁺. Argon and dinitrogen both interact very weakly with CH_3CO^+ (Ar by 0.4 kcal mol^{-1} and N_2 by 2.3 kcal mol^{-1}). In both instances the preferred position for the "solvating" molecule is adjacent to one of the H atoms of the methyl group and not along the C_3 axis of CH_3CO^+, and in both ion−molecule complexes the structure of the CH_3CO^+ portion is almost identical with that of the isolated CH_3CO^+ ion.

(vii) Ions COCH₃⁺···M. Ion $COCH_3^+\cdots Ar$ has C_{3v} symmetry. The argon is weakly attached to the methyl group as shown by the long Ar−C distance (3.168 Å) and small dissociation energy (0.6 kcal mol^{-1}). We were unable to locate a minimum for $COCH_3^+\cdots N_2$ and found that N_2 plucks off

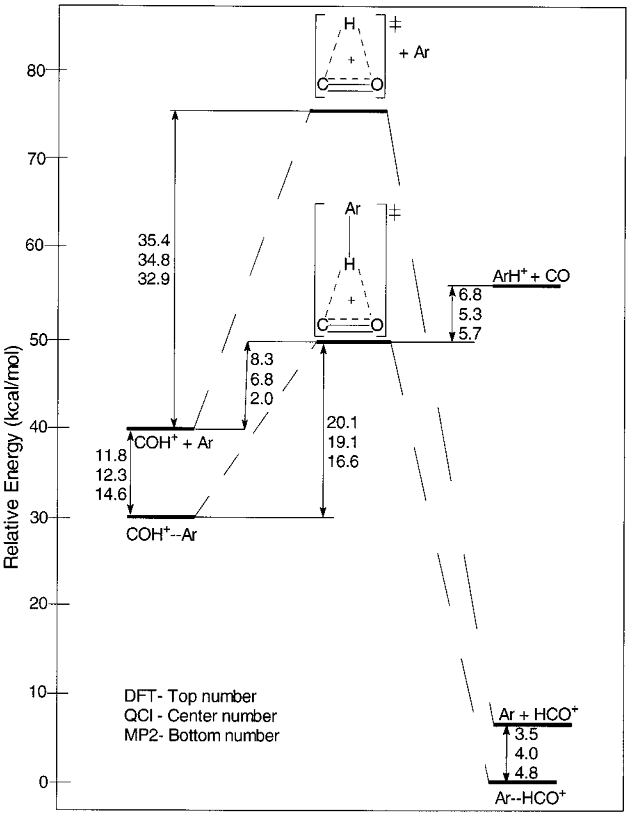


Figure 3. Reaction profile for Ar + COH$^+$ at 298 K.

CH_3^+ to give $N_2CH_3^+\cdots OC$, a combination that is 1.6 kcal mol^{-1} lower in energy than $N_2CH_3^+$ plus OC.

(viii) Transition Structures $COCH_3^+\cdots M$. Attachment of an argon to the methyl group of transition structure **11** resulted in increases of ~0.7 Å in the already large C−C and C−O distances, and the complexed transition structure is only 0.5 kcal mol^{-1} lower in energy than separated $ArCH_3^+$ plus CO. In the argon-complexed transition structure the methyl group is essentially attached to the argon, although interaction with the π-bond of CO results in the Ar−C distance being 0.056 Å longer than in isolated $ArCH_3^+$ and the methyl group is slightly flattened (angle Ar−C−H is 96.5° compared with 97.8° in the isolated ion).

On the $C_2H_3ON_2^+$ surface we were unable to locate a minimum for $N_2\cdots H_3COC^+$, and since interconversion between $N_2CH_3^+\cdots OC$ and $N_2CH_3^+\cdots CO$ proceeds through dissociation/recombination, then the only transition structure on the reaction profile is for transfer of the methyl group on N_2 in $N_2CH_3^+\cdots CO$ to the carbon atom, i.e., to form the structure at the global minimum $N_2\cdots CH_3CO^+$. This transition structure has long N−C (1.901 Å) and C−C (2.537 Å) distances, and the NCH angle of 94.2° indicates that the methyl group is closer to being planar but is still angled toward N_2 rather than toward CO; i.e., the transition structure is closer to the higher energy structure $N_2CH_3^+\cdots CO$.

(b) Energetics and Profiles to Rearrangement. The profiles for rearrangement of COR$^+$ to RCO$^+$ in the presence of catalysts Ar and N_2, constructed from enthalpies corrected to 298 K, are given in Figures 3−6. Each profile has different features and will therefore be discussed separately.

(i) $COH^+\cdots Ar$. For the rearrangement of COH$^+$ to HCO$^+$ in the absence of any catalyst, the profile is given by the upper set of energy levels in Figure 3. The barrier for the uncatalyzed reaction is 35.4 kcal mol^{-1} at B3LYP/6-311++G(d,p) and 34.8 kcal mol^{-1} at QCISD(T)(full)/6-311++G(2df,p). Addition of an argon atom stabilizes each of the structures, with the largest effect being on the structure in which the proton is least firmly attached, the transition structure, and the smallest on the product ion HCO$^+$, where the proton is most strongly bound. The net effect of attaching one argon atom is to produce the profile involving only the lowest energy levels. Here, the calculated barriers are 20.1 kcal mol^{-1} (at B3LYP/6-311++G(d,p)) and 19.1 kcal mol^{-1} (at QCISD(T)(full)/6-311++G(2df,p)); i.e., the calculated barriers are reduced by about ~15 kcal mol^{-1} from those in the uncatalyzed reaction. In solution, a large number of solvent molecules are involved in solvating an ion, and modeling such a process by only one interacting molecule is clearly insufficient to give an accurate solvation energy. However, the first solvent molecule added generally has the largest effect, and the numbers given here then provide a crude estimate of the effect of solvation by argon on this 1,2-proton migration.

The most interesting aspect of Figure 3 is for the rearrangement of COH$^+$ in the gas phase. When COH$^+$ and argon collide, the sum of the energies of these molecules is lower than that of the solvated transition structure by only 8.3 kcal mol^{-1} at B3LYP/6-311++G(d,p) and by 6.8 kcal mol^{-1} at QCISD(T)(full)/6-311++G(2df,p); i.e., the effective barrier to rearrangement of COH$^+$ is drastically reduced by using argon as a catalyst in the gas phase. Furthermore, if the colliding atom and ion are hot, then a significant fraction of COH$^+$ may be induced to rearrange to HCO$^+$ during the course of the collision. Such a rearrangement has important implications for gas-phase ion−molecule chemistry where collisions with noble gas atoms are frequently used to thermally stabilize ions. Our findings now suggest that, depending upon the proximity of R$^+$ affinities, noble gas atoms may in fact catalyze the rearrangement of an ion rather than simply cool it by collisions.

(ii) $CO\cdots HN_2^+$. N_2 has a higher proton affinity than the oxygen atom of CO, and we found that there is no barrier to proton transfer from COH$^+$ to N_2. Ion−molecule complex $COH^+\cdots N_2$ therefore does not exist, and in this system the lowest energy levels on the profile in Figure 4 are for $CO\cdots HN_2^+$ rearranging, through a transition structure that resembles N_2H^+ interacting with the π-system of CO, to the structure at the global minimum, $N_2\cdots HCO^+$. The barrier to this process is 12.3 kcal mol^{-1} at B3LYP/6-311++G(d,p) and 10.7 kcal mol^{-1} at QCISD(T)(full)/6-311++G(2df,p).

In the gas phase a collision between COH$^+$ and N_2 will simply result in transfer of the proton to N_2, and this will be followed by a transfer back to the carbon of CO. Both these transfers are exothermic, and conversion of COH$^+$ to HCO$^+$ then should be efficiently catalyzed by N_2.

(iii) $COCH_3^+\cdots Ar$. For the uncatalyzed reaction, the barrier to 1,2-methyl migration in $COCH_3^+$ is 14.2 kcal mol^{-1} at B3LYP/6-311++G(d,p) (upper profile in Figure 5). This is compared with a value of 35.4 kcal mol^{-1} for the 1,2-proton shift, and the much smaller barrier is attributed to the greater ability of CH_3 (relative to H) to carry the positive charge in the transition structure.

The methyl cation affinities of both atoms in CO are higher than that of argon, and interaction with an argon atom has little stabilizing effect on both CH_3CO^+ and $COCH_3^+$ (both are less than 1 kcal mol^{-1}). However, argon interacts more strongly with the methyl group in the transition structure and the overall effect is to reduce the barrier for the gas-phase reaction to 5.7 from 14.2 kcal mol^{-1}.

(iv) $CO\cdots CH_3N_2^+$. The methyl cation affinity of N_2 is between those of O and C in CO, and consequently, as in the

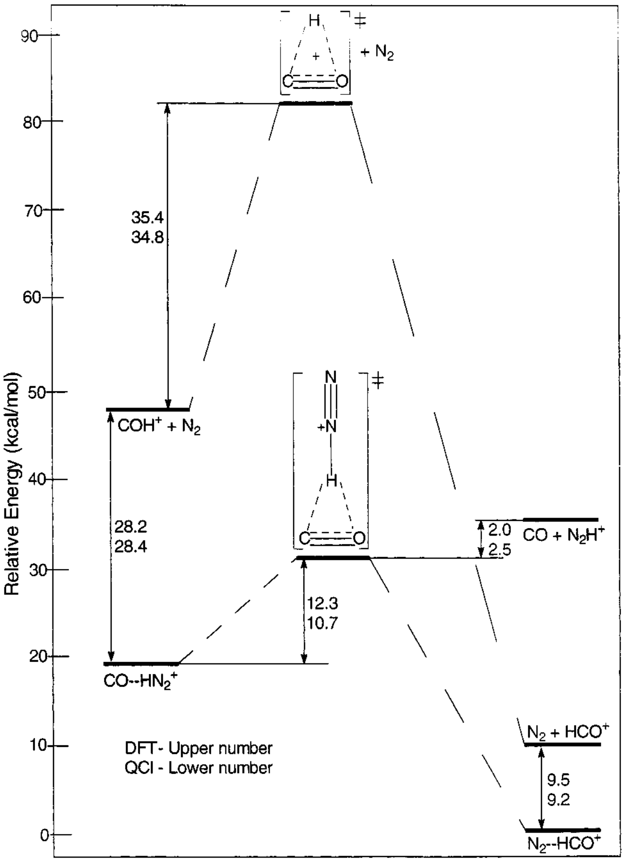


Figure 4. Reaction profile for $N_2 + COH^+$ at 298 K.

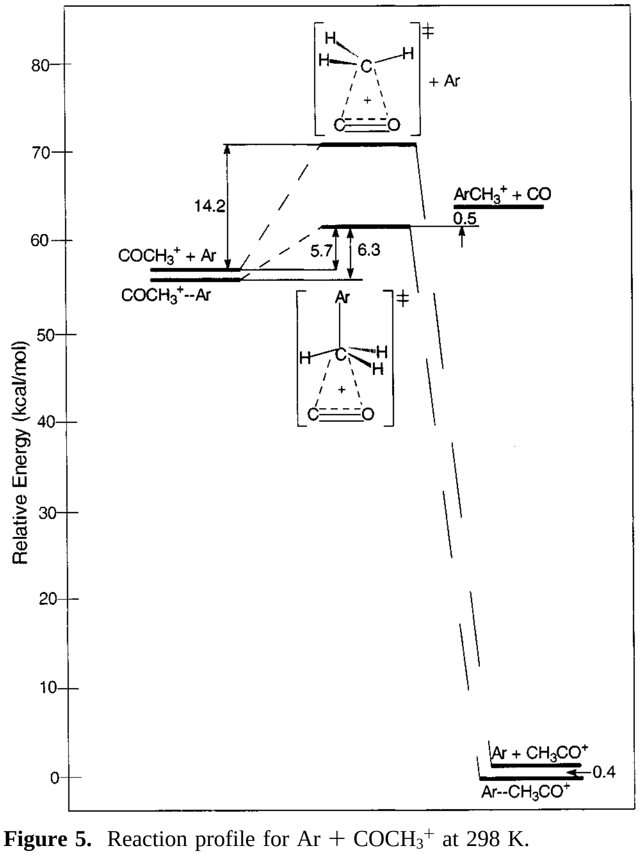


Figure 5. Reaction profile for $Ar + COCH_3^+$ at 298 K.

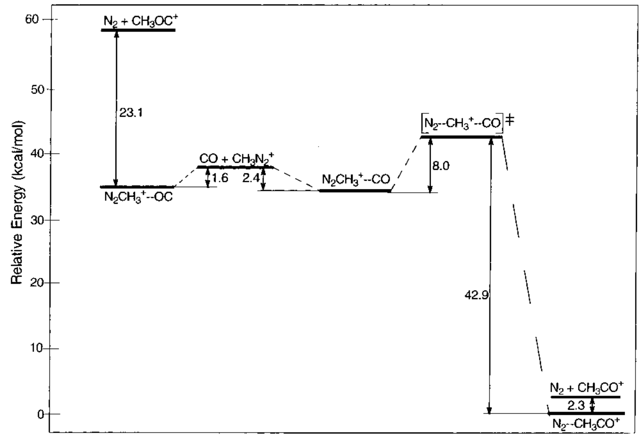


Figure 6. Reaction profile for $N_2 + COCH_3^+$ at 298 K.

TABLE 2: Barriers[a] to the 1,2-Migration of R^+ in COR^+

molecular combination	B3LYP[b]	QCI[c]	MP2[d]
(a) Proton ($R = H^+$)			
(i) from $COH^+ + M$			
no catalyst	35.4	34.8	32.9
$COH^+ + Ar$	8.3	6.8	2.0
$COH^+ + N_2$	−15.9	−17.7	
(ii) from $COH^+\cdots M$			
$COH^+\cdots Ar$	20.1	19.1	16.6
$COH^+\cdots N_2$	12.3	10.7	
(b) Methyl Cation ($R = CH_3^+$)			
(i) from $COCH_3^+ + M$			
no catalyst	14.2	14.8	
$COCH_3^+ + Ar$	5.7		
$COCH_3^+ + N_2$	−16.0		
(ii) from $COCH_3^+\cdots M$			
$COCH_3^+\cdots Ar$	6.3		
$CO\cdots CH_3N_2^+$	7.2		

[a] In kcal mol^{-1}. [b] B3LYP/6-311++G(d,p). [c] QCISD(T)(full)/6-311++G(2df,p). [d] MP2(full)/6-311++G(3df,3pd).

case of rearrangement in COH^+ catalyzed by N_2, the 1,2-migration of CH_3^+ can occur simply by transfer of CH_3^+ from $COCH_3^+$ to N_2 and then switching the CH_3^+ back to the C of CO. In the latter step there is a barrier of 5.6 kcal mol^{-1}, but the transition structure to this process is much lower in energy than the initial reactants N_2 and CH_3OC^+.

$N_2CH_3^+$ forms weakly bound complexes with CO, with a slight preference for binding to carbon. Rearrangement of N_2-$CH_3^+\cdots CO$ to N_2 plus CH_3CO^+ involves a transition structure in which CH_3^+ is loosely bound to both N_2 and CO and lies 8 kcal mol^{-1} above $N_2CH_3^+\cdots CO$.

Conclusions

The proton and methyl cation affinities of N_2 are higher than those of the oxygen of CO but lower than those of the carbon. N_2 then plucks off R from COR^+ ($R = H, CH_3$) and returns it to the carbon atom, thereby converting COR^+ into RCO^+. Assuming that the intermediate ion−molecule complexes are not stabilized by collisions, then these N_2-assisted processes both occur without barriers. These reactions are examples of the "back and forth" mechanism proposed by Ferguson.

Argon has lower proton and methyl cation affinities than both oxygen and carbon of CO and therefore cannot fully remove R^+ from the oxygen atom. However, argon forms ion−atom complexes with COR^+ and RCO^+ ($R = H, CH_3$) and also with the transition structures for their interconversion, and the stabilizations arising from these interactions are largest in the transition structures. The net effect on the reaction profile of including one argon atom attached to each structure is to reduce the barriers to rearrangement from around 35 to about 20 kcal mol^{-1} when R = H and from 14.2 to 6.3 kcal mol^{-1} when R =

CH_3. Furthermore, gas-phase reactants COR^+ and argon are only slightly lower in energy than the solvated transition structure $COR^+\cdots Ar$, and this raises the possibility that in some collisions between Ar and COR^+ rearrangement to RCO^+ will occur. Argon is frequently used in gas-phase ion−molecule chemistry to thermally stabilize ions by collisions. The results of our theoretical studies indicate that experimentalists should be aware that argon can in some systems function as a catalyst to convert ions into lower energy isomers.

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