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Review

Proton transport in the catalyzed gas-phase isomerization of protonated molecules

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ABSTRACT

Recent theoretical and experimental results for selected ions and ion/molecule reactions are examined which provide insight into fundamental aspects of the isomerization of protonated heteronuclear molecules. The isomerization is viewed in terms of a "proton transport" mechanism in which a "foreign" molecule transports the proton from a high-energy site to a low-energy site of the protonated molecule and thereby catalyzes the isomerization.

Keywords: ion/molecule reactions; proton transfer; isomerization; catalysis.

INTRODUCTION

The motion of protons is of fundamental importance in chemistry: both chemistry in solution and chemistry in the gas phase. Insight into such motion in the gas phase is accessible from measurements with modern mass spectrometric techniques which can monitor protonated species. For example, our experience in the Ion Chemistry Laboratory at York University with bimolecular reactions of protonated ions which we investigated using a flowing afterglow (FA) selected-ion flow tube (SIFT) mass spectrometer has taught us that the direct transfer of a proton from one molecule to another in the gas phase is often extremely facile when thermodynamically allowed [1]. Reversible and sequential proton transfers become effective as the proton transfer reaction approaches thermoneutrality. For example, in a stimulating article very recently published in this journal [2], Henchman et al. demonstrated the importance of sequential proton transfer for H/D isotope exchange reactions in systems of the type $XH_nH^+/XD_n(X = O, N, C)$. These authors presented a kinetic model for proton motion which involves a sequence of proton/deuteron transfers within the reaction intermediate, as exemplified by

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reaction 1:

$$H_3O^+ + D_2O \rightarrow [H_3O^+ \cdots D_2O \rightleftharpoons H_2O \cdots HD_2O^+$$
$$\rightleftharpoons H_2DO^+ \cdots HDO] \rightarrow H_2DO^+ + HDO \qquad (1)$$

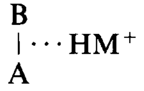
One key feature of the proton motion in reaction 1 is that the heavy-atom site of protonation of both molecules remains unchanged (since both contain only one heavy atom) so that isotope exchange is the only possible outcome of the bimolecular reaction. There are new consequences possible when one of the molecules has more than one heavy atom. Now proton motion can involve a change in the heavy-atom site of protonation and so can lead to structural isomerization. This is illustrated by the generalized reaction 2 for a protonated diatomic molecule AB:

$$ABH^+ + M \rightarrow [ABH^+ \cdots M \rightleftharpoons AB \cdots HM^+ \rightleftharpoons BA \cdots HM^+$$
$$\rightleftharpoons BAH^+ \cdots M] \rightarrow BAH^+ + M \qquad (2)$$

In the intermediate of such a reaction the molecule M "transports" the proton from one atom of the diatomic molecule to the other. If the molecule M has a proton affinity intermediate between those of the sites B and A of molecule AB, it can pick up the proton from site B and the molecule AB simply needs to rotate within the weakly-bound adduct for the proton to be deposited at site A, and so for isomerization from ABH^+ to BAH^+ to take place. The complete potential energy profile of the isomerization reaction 2 therefore involves four intermediates and three barriers with the transition structures **I**, **II** and **III**:

$$AB \cdot\cdot H^+ \cdot\cdot M$$

I



$$\begin{matrix} B \\ | \\ A \end{matrix} \cdots HM^+$$

II

$$BA \cdot\cdot H^+ \cdot\cdot M$$

III

In the absence of the molecule M the isomerization of the protonated molecule would have to occur unimolecularly. Theory has shown that the activation energy required for such unimolecular isomerization is often too large for the isomerization to occur at room temperature. However, the presence of a "transporter" molecule M provides an alternate lower energy path for the isomerization of a protonated molecule, viz. it catalyzes the isomerization. Figure 1 compares schematic potential energy/reaction coordinate profiles for the isomerization of HAB^+ in the absence and presence of a transporter molecule M to illustrate this point.

"Forth and back" proton motion leading to the isomerization of a protonated heteronuclear molecule in the gas phase was first invoked in 1989 by Ferguson [3] in his explanation of the mechanism of the charge transfer

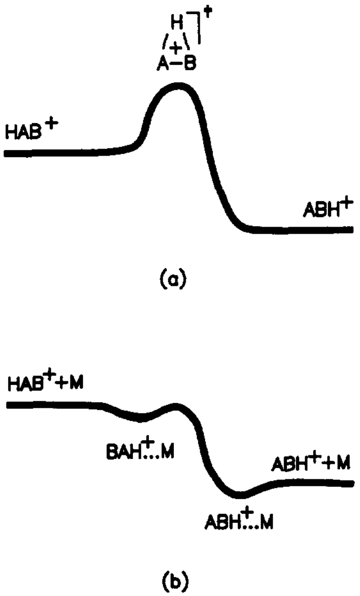


Fig. 1. Schematic potential energy/reaction coordinate profiles for the isomerization of HAB^+ in the absence (a) and presence (b) of the "transporter" molecule M. Part (b) shows only the barrier for the rate-determining step. Several intermediates and barriers are present in the actual potential energy profile (see eqn. 2).

reaction of $HNNO^+$ with NO and the idea was applied later by Petrie et al. [4] and McEwan [5] to account for the isomerization reactions of HOC^+ with H_2 and of the radical cation $HCN^{\cdot +}$ with CO and CO_2. Quite independently, in our own laboratory, we have needed to invoke a proton transport mechanism in the interpretation of the results of our studies for insertion reactions of SiH^+ with oxygenated molecules to produce $SiOH^+$ [6]. It is the purpose of this article to draw together the results of these particular studies and, in doing so, to illustrate several intrinsic features of the proton transport mechanism for the isomerization of protonated heteronuclear molecules in the gas phase. The mechanism has precedence in the gas phase where it has been applied to the isomerization of anions [7], and is fundamental to reactions in solution such as the acid- or base-catalyzed pyrolysis of amides and the keto–enol isomerization of carbonyl compounds containing α hydrogen atoms [8]. It is also the mechanism of choice for enzyme-catalyzed racemization which produces D-alanine required in the construction of cell walls [9].

INTRAMOLECULAR ISOMERIZATION

State-of-the-art ab initio MO calculations are now sufficiently accurate to provide useful values for energy differences and barrier heights for the

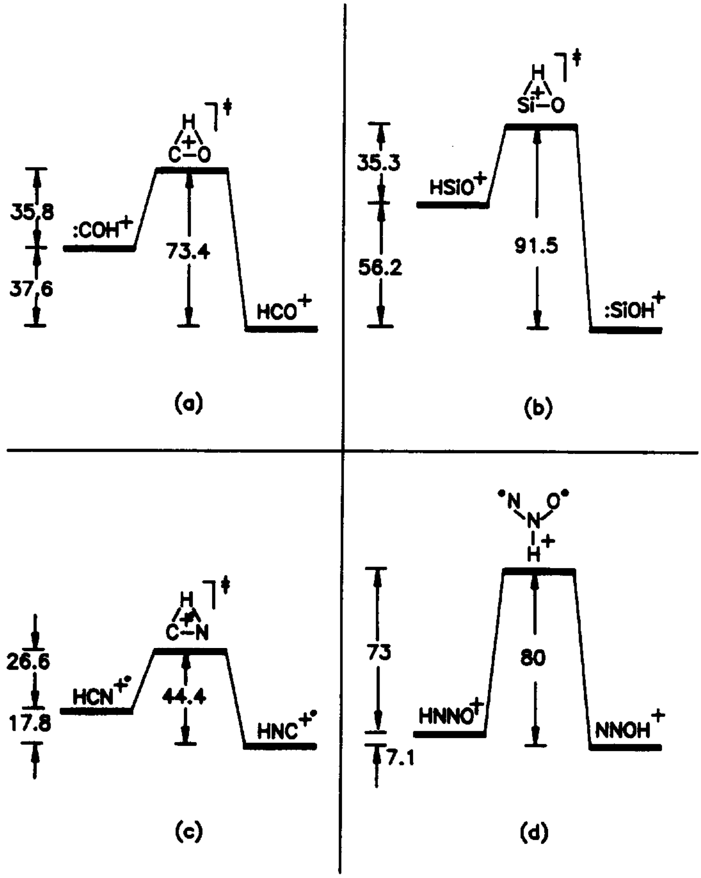


Fig. 2. Computed energies (in kcal mol^{-1}) for the ground state isomers and for the transition structures of the 1, 2 or 1, 3 proton mirgrations in (a) $[CO, H]^+$, (b) $[SiO, H]^+$, (c) $[CN, H]^{\cdot +}$ and (d) $[N_2O, H]^+$.

isomerization of small protonated molecules at least. This is certainly the case for several of the systems of interest in this article. Numerous ab initio MO calculations have now been reported for the structures and energies of the ground state isomers of $[CO, H]^+$, $[SiO, H]^+$ and $[CN, H]^{\cdot +}$ and of the transition states for their 1, 2 proton migrations. Selected results are shown in Fig. 2. The energies provided in Fig. 2a for $[CO, H]^+$ are taken from the work of Nobes and Radom [10] who used large basis sets with incorporation of electron correlation. The results of calculations for $[SiO, H]^+$ at the MP4(fc)6-311(3df, 3pd)//MP2(full)/6-311G(3df, 3pd) level of theory reported by Srinivas et al. [11] are given in Fig. 2b. The energies provided for $[CN, H]^{\cdot +}$ by Koch et al. [12] at the MP2/6-31G**//6-31G level of theory are given in Fig. 2c. The energies of the ground state isomers of protonated N_2O have been calculated by Yamashita and Morokuma [13] at the MP4SDQ/6-311G**//MP2/6-31G* level of theory and are given in Fig. 2d. In this latter case, a preliminary search failed to locate a four-center transition state for a direct 1,3 proton shift, but the singlet and triplet biradical intermediates which connect the N- and O-protonated isomers were found to lie $\approx 80\,\mathrm{kcal\,mol^{-1}}$ higher in energy than the N-protonated isomer [13].

The results of the calculations for the four protonated molecules given in Fig. 2 indicate barriers for the unimolecular isomerization of the isolated high-energy forms in the range 27–73 $\mathrm{kcal\,mol^{-1}}$. Clearly these barriers are sufficiently large to prevent the unimolecular isomerization of the isolated ions at 298 K. Consequently, the calculations predict that the isomeric pairs given in Fig. 2a–d can exist as distinct species under normal conditions of temperature. Indeed, all eight isomers indicated in Fig. 2 have now been isolated and characterized in the gas phase: COH^+ and HCO^+ [5,14,15]; $HSiO^+$ and $SiOH^+$ [5,11]; $HCN^{\cdot +}$ and $CNH^{\cdot +}$ [4,5]; and $HNNO^+$ and $NNOH^+$ [16].

ISOMERIZATION BY PROTON TRANSPORT

Isomerization prior to reaction

It was the observation of a charge transfer reaction of the high-energy $HNNO^+$ isomer with $NO^{\cdot}$ that prompted Ferguson [3] to first propose an isomerization mechanism involving proton transport. $HNNO^+$ is one of two isomers of protonated nitrous oxide accessible to the reaction of $N_2O^{\cdot +}$ with H_2. Reactivity measurements with CH_4 and $NO^{\cdot}$, together with a comparison with predictions made by theory (see Fig. 2d), have shown that the two isomers produced in this reaction correspond to the protonation of the O atom and the terminal $N^{\cdot}$ atom in NNO [3,16]. Of particular interest to Ferguson were the reactions of the two isomers with $NO^{\cdot}$. Both are observed to yield the ionic product NO^+ according to reactions 3 and 4

$$NNOH^+ + NO^{\cdot} \rightarrow NO^+ + (OH^{\cdot} + N_2) \tag{3}$$

$$HNNO^+ + NO^{\cdot} \rightarrow NO^+ + (OH^{\cdot} + N_2) \tag{4}$$

with rate coefficients of 8.6×10^{-11} and $1.4 \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, respectively [16]. Ferguson noted that both isomers should yield the neutral products $OH^{\cdot}$ and N_2 in order to be exothermic, but that this was sterically improbable in the case of the reaction of the $HNNO^+$ isomer in which the $H^{\cdot}$ and O atoms, whose bonding is required to supply the exothermicity, are not in proximity. He suggested that the neutral $OH^{\cdot}$ product could be explained if the isomerization of $HNNO^+$ to $NNOH^+$ occurs first in the reaction intermediate, prior to reaction with $NO^{\cdot}$, as illustrated in reaction 5. Thus

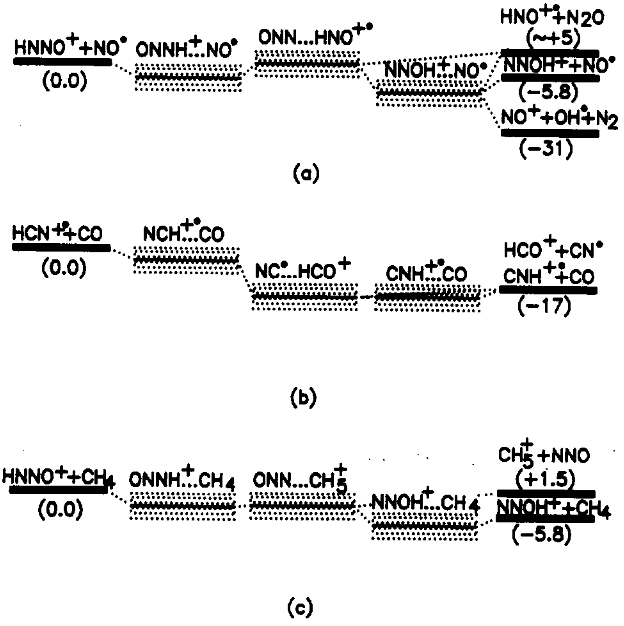


Fig. 3. Energy diagrams for the proton transport mechanism applied to the reactions of (a) HN_2O^+ with $NO^{\cdot}$, (b) $HCN^{\cdot +}$ with CO, and (c) HN_2O^+ with CH_4. The energy for the third intermediate (see reaction 2) is not shown. All energies are given in kcal mol^{-1}. An interaction energy of -5 ± 5 kcal mol^{-1} has been assumed for all electrostatic interactions of ions with molecules. The possible contribution to this energy from electron exchange in the case of the interactions involving radical species has been ignored.

$NO^{\cdot}$ was invoked in the reaction mechanism

$$ONNH^+ + NO^{\cdot} \rightarrow [ONNH^+ \cdot\cdot NO^{\cdot} \rightleftharpoons ONN \cdot\cdot HNO^{\cdot +}$$

$$\rightleftharpoons NNO \cdot\cdot HNO^{\cdot +} \rightleftharpoons NNOH^+ \cdot\cdot NO^{\cdot}] \rightarrow NO^+ + OH^{\cdot} + N_2 \qquad (5)$$

first as a transporter molecule to transfer the proton from the N to the O site of N_2O, and then as the donor of an electron in the charge transfer step. The proton affinity of $NO^{\cdot}$ actually lies below that of the N site of N_2O so that overall proton transfer is endothermic by ≈ 5 kcal mol^{-1}, but proton transfer within the intermediate is facilitated by the relative kinetic energy of the initial collision which results from the attractive electrostatic interaction between the reactants and which is sufficient to overcome the barrier for proton transfer. This is illustrated in the potential energy profile which is sketched in Fig. 3a and which assumes an energy of -5 ± 5 kcal mol^{-1} (probably an underestimate) for the interaction of NNO with $HNO^{\cdot +}$.

It is interesting to note also that the isomerization to form $NNOH^+$ apparently does not compete with NO^+ formation in the reaction of $HNNO^+$

with $NO^{\cdot}$ at room temperature, even though it is exothermic overall by 5.8 kcal mol^{-1} (see Fig. 3a).

Isomerization reactions with H_2

$COH^+ + H_2$

The production, characterization and reactions of the two isomers of protonated CO have been extensively investigated. As yet, this is the only system, of the four described in Fig. 2, for which both isomers have been characterized spectroscopically [14,15]. The bimolecular reaction of HOC^+ with H_2 provides the first established example of a bimolecular isomerization reaction of a protonated molecule. The isomerization reaction has been observed directly in a SIFT apparatus by Freeman et al. [17] and indirectly in a tandem ICR mass spectrometer by Wagner-Redecker et al. [18] to proceed in competition with proton transfer. The SIFT experiments revealed the occurrence of reactions 6 and 7

$$HOC^+ + H_2 \longrightarrow HCO^+ + H_2 \qquad (6a)$$

$$\longrightarrow H_3^+ + CO \qquad (6b)$$

$$DOC^+ + H_2 \xrightarrow{0.43} HCO^+ + HD \qquad (7a)$$

$$\xrightarrow{0.57} H_2D^+ + CO \qquad (7b)$$

with rate coefficients of 4.7×10^{-10} and 6.2×10^{-10} cm^3 molecule^{-1} s^{-1} respectively. We propose here that a potential energy profile as shown in Fig. 4a applies to these reactions. The profile is based on the computations of Dixon et al. [19] and Nobes and Radom [10] and describes the energetics of the isomerization reaction 8:

$$HOC^+ + H_2 \rightarrow [COH^+ \cdot\cdot H_2 \rightleftharpoons CO \cdot\cdot H_3^+ \rightleftharpoons OC \cdot\cdot H_3^+ \rightleftharpoons OCH^+ \cdot\cdot H_2]$$
$$\rightarrow HCO^+ + H_2 \qquad (8)$$

The branching ratio measured for the competition between isomerization and proton transfer cannot be rationalized without knowing the efficiency of formation of the transition structure $CO \cdot\cdot H_3^+$ and the height of a possible barrier to the rotation of CO in the critical isomerization step, but the observation of HCO^+ as a product ion is consistent with a proton transport mechanism.

$HSiO^+ + H_2$

The silicon analogue of protonated CO shows a reverse order of stability. According to theory, SiO protonated at silicon is less stable than its isomer

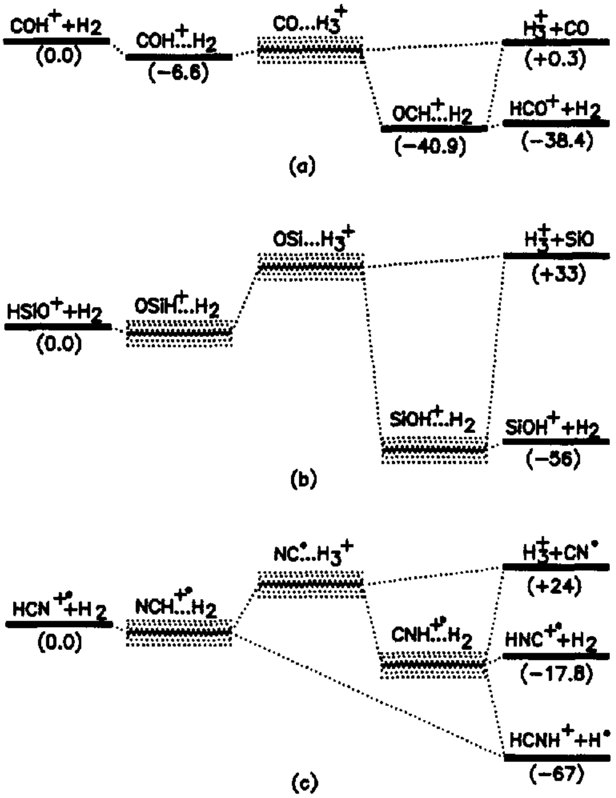


Fig. 4. Energy diagrams for the proton transport mechanism applied to the reactions of hydrogen with the high-energy isomers of (a) COH^+, (b) $HSiO^+$, and (c) $HCN^{\cdot +}$. The energy for the third intermediate (see reaction 2) is not shown. All energies are given in kcal mol^{-1}. Unless indicated otherwise, an interaction energy of -5 ± 5 kcal mol^{-1} has been assumed for all electrostatic interactions of ions with molecules. The possible contribution to this energy from electron exchange in the case of the interactions involving radical species has been ignored.

which is protonated at oxygen, as was shown in Fig. 2b [11,20]. Recent SIFT studies have revealed that, unlike COH^+, $HSiO^+$ does not react with H_2 to isomerize to $SiOH^+$ [6]. The failure of this isomerization can be understood in terms of the proton transport mechanism elucidated by the potential energy profile given in Fig. 4(b). The high energy of the $SiO \cdots H_3^+$ presents a barrier which is too large for the transfer of a proton from $HSiO^+$ to H_2 to occur. This barrier can be estimated to be ≈ 25 kcal mol^{-1} if an energy of ≈ 5 kcal mol^{-1} is assumed for the interaction of H_3^+ and SiO.

$HCN^+ + H_2$

As in the reaction of $HSiO^+$ with H_2, a barrier prevents the intramolecular isomerization in the reaction of $HCN^{\cdot +}$ with H_2. This is evident from the potential energy profile in Fig. 4c. The barrier can be estimated to be $\approx 15\,\text{kcal mol}^{-1}$ if $10\,\text{kcal mol}^{-1}$ is taken to be the interaction energy between H_3^+ and $CN^{\cdot}$ ($CN^{\cdot}$ has a substantial dipole moment of 1.45 D). Experimental results reported by Petrie et al. [4] indicate that the high-energy isomer of $[CN,H]^{\cdot +}$ reacts with H_2 by $H^{\cdot}$ atom abstraction instead of isomerization according to reaction 9

$$HCN^{\cdot +} + H_2 \rightarrow HCNH^+ + H^{\cdot} \tag{9}$$

with rate coefficients of $8.6 \times 10^{-10}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$. Figure 4c shows that the abstraction of a hydrogen atom from the high-energy isomer can proceed more directly without formation of the high-energy intermediate $NC^{\cdot}..H_3^+$.

$HNNO^+ + H_2$

The exothermic isomerization reaction of $HNNO^+$ with H_2 has not been reported, nor is it expected to occur on the basis of the proton transport mechanism. The transfer of the proton from $HNNO^+$ to H_2 is at least $25\,\text{kcal mol}^{-1}$ more endothermic than the corresponding reaction with $NO^{\cdot}$.

Other bimolecular isomerization reactions

$HCN^{\cdot +} + CO, CO_2$

$HCN^{\cdot +}$ has been reported by Petrie et al. [4] to isomerize to $CNH^{\cdot +}$ in reactions with both CO and CO_2, with rate coefficients of 4.6×10^{-10} and $5.0 \times 10^{-10}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ respectively. Since the proton affinities of both CO ($141.4\,\text{kcal mol}^{-1}$) [21] and CO_2 ($128.5\,\text{kcal mol}^{-1}$) [21] lie between the proton affinities of the C site ($125\,\text{kcal mol}^{-1}$) [4] and the N site ($\approx 142\,\text{kcal mol}^{-1}$) [4] of $CN^{\cdot}$, the proton transport mechanisms indicated by equations 10 and 11 are both energetically allowed:

$$\begin{aligned}&HCN^{\cdot +} + CO \rightarrow [NCH^{\cdot +} \cdot\cdot CO \rightleftharpoons NC^{\cdot} \cdot\cdot HCO^+ \rightleftharpoons CN^{\cdot} \cdot\cdot HCO^+\\&\rightleftharpoons CNH^{\cdot +} \cdot\cdot CO] \rightarrow HNC^{\cdot +} + CO\end{aligned} \tag{10}$$

$$\begin{aligned}&HCN^{\cdot +} \cdot\cdot CO_2 \rightarrow [NCH^{\cdot +} \cdot\cdot CO_2 \rightleftharpoons NC^{\cdot} \cdot\cdot HCO_2^+ \rightleftharpoons CN^{\cdot} \cdot\cdot HCO_2^+\\&\rightleftharpoons CNH^{\cdot +} \cdot\cdot CO_2] \rightarrow HNC^{\cdot +} + CO_2\end{aligned} \tag{11}$$

The potential energy profile which is being proposed here for the reaction of $HCN^{\cdot +}$ with CO is shown in Fig. 3b. In this particular case, proton transfer and isomerization have been shown by experiment to be about equally exothermic (by $17\,\text{kcal mol}^{-1}$) [4]. However, it is interesting to note that, while isomerization to $HNC^{\cdot+}$ predominates in the reaction of $HCN^{\cdot+}$ with CO, some proton transfer is observed experimentally ($k \approx 3 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$) [4]. In terms of the proton transport mechanism, this observation implies that the lifetime of the intermediate $NC^{\cdot}\cdots HCO^+$ is sufficiently long for $NC^{\cdot}$ to rotate and abstract a proton from HCO^+ before $NC^{\cdot}\cdots HCO^+$ separates into the proton transfer products. This lifetime should be dependent on internal energy so that an experimental study of the branching ratio of proton transfer to isomerization as a function of relative KE should provide an interesting test of the proton transport mechanism, as has been suggested by Petrie et al. [4].

For the reaction between HCN^+ and CO_2, Petrie et al. [4] report charge transfer to be a minor product channel which accounts for about 0.3% of the total reaction which leads predominantly to isomerization. Also, it is interesting to note from the studies of Petrie et al. [4] that isomerization is not always observed for reactions of $HCN^{\cdot+}$ with other molecules having proton affinities appropriate for isomerization if other exothermic processes are possible. For example, only $H^{\cdot}$ atom abstraction is observed with CH_4 (PA = 130.0 kcal mol^{-1}) [21] and charge transfer is the predominant product observed with N_2O (PA = 137.3 kcal mol^{-1}) [21].

$HNNO^+ + CH_4$

This reaction has been reported to proceed exclusively by proton transfer with a rate constant at 300 K of $1.4 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ [16]. The relative kinetic energy dependence of this rate constant indicates that the proton transfer reaction is endothermic by 1.5 kcal mol^{-1} overall [22]. Apparently the isomerization to $NNOH^+$ does not take place in spite of the fact that it is predicted by theory [13] to be exothermic by 7.1 kcal mol^{-1} (see Fig. 2d) and by experiment [22] to be exothermic by 6.2 ± 0.5 kcal mol^{-1}. How can we account for this result in terms of the proton transport mechanism for isomerization given in reaction 12?

$$HNNO^+ + CH_4 \rightarrow [ONNH^+\cdot\cdot CH_4 \rightleftharpoons ONN\cdot\cdot CH_5^+ \rightleftharpoons NNO\cdot\cdot CH_5^+ \rightleftharpoons NNOH^+\cdot\cdot CH_4] \rightarrow NNOH^+ + CH_4 \qquad (12)$$

The transfer of a proton to the transporter molecule should proceed without a barrier. Since the proton transfer from $HNNO^+$ to CH_4 is endothermic overall by only 1.5 kcal mol^{-1} [22], the energy of the intermediate $ONN\cdot\cdot CH_5^+$ should lie below the initial energy of $HNNO^+ + CH_4$, as shown in Fig. 3c, when account is taken of attractive electrostatic interaction between the reactants. Consequently the failure for the isomerization to compete with proton transfer must be attributed to some other barrier. One likely candidate is a barrier for the rotation of the ONN molecule which is required to make the O site available for protonation.

$COH^+ + CO$

Isomerization has also been observed to occur in the unique bimolecular reaction 13

$$HOC^+ + CO \rightarrow HCO^+ + CO \tag{13}$$

in which the molecule initially protonated and the transporter molecule are identical. Freeman et al. [17] have reported a rate coefficient of 6.0×10^{-10} cm^3 molecule^{-1} s^{-1} for this reaction. Two mechanisms can lead to isomerization in this special case: a direct proton transfer to the reactant molecule or intramolecular isomerization involving the reactant CO molecule as a transporter. The results available so far do not distinguish between these two mechanisms. Isotopic labelling experiments would identify which CO molecule is retained in the product isomer and so provide insight into the competition between these two mechanisms, but such experiments have not been performed yet.

Isomerization following reaction

$HSiO^+/SiOH^+$

Our own introduction to the proton transport mechanism for the isomerization of protonated molecules came about in connection with our study of reactions of ground state SiH^+ with a variety of O atom donor molecules including O_2, CO_2, N_2O and SO_2 [6]. We were searching for a chemical route to the formation at thermal energies of $HSiO^+$, the high-energy isomer of $[SiO, H]^+$ [11,20]. HSi^+ has an O atom affinity, $OA = 122 \pm 7$ kcal mol^{-1} [23], and so was expected to accept an O atom from molecules with lower O atom affinities, viz. N_2O ($OA = 40.0$ kcal mol^{-1}) [23] and possibly O_2 ($OA = 119.2$ kcal mol^{-1}) [23], to form $HSiO^+$.

Of the four reactions of SiH^+ which were investigated, three were observed to produce the low-energy isomer $SiOH^+$ in what corresponds formally to an insertion as shown in reaction 14:

$$SiH^+ + XO \rightarrow SiOH^+ + X \tag{14}$$

Only the reaction with N_2O produced the high-energy isomer $HSiO^+$ in what is an O atom transfer as shown in reaction 15:

$$SiH^+ + N_2O \rightarrow HSiO^+ + N_2 \tag{15}$$

$$SiH^+ + O_2 \rightarrow HSiO_2^+ \tag{16}$$

The reaction with O_2, reaction 16, was observed to be very slow, $k < 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in He at 0.35 Torr, and the adduct ion $HSiO_2^+$ seemed to be the only product ion. Table 1 provides a summary of

TABLE 1

Product distributions and bimolecular rate coefficients (in units of $10^{-9}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$) for reactions of SiH^+ with various molecules measured at 295 ± 2 K using the SIFT technique [6]

Molecule (PA)[a]	Products	P.D.[b]	K_{expt}[c]	k_{c}[d]	ΔH°_{298}[e]
O_2 (101.9)	$HSiO_2^+$	1.0	$\leqslant 0.005$		
	$SiOH^+ + O$	0.0			−64
	$HSiO^+ + O$	0.0			−3
CO_2 (130.9)	$SiOH^+ + CO$	0.78	0.19	0.91	−52
	$HCO^+ + SiO$	0.22			−5
N_2O (138.8)	$SiOH^+ + N_2$	0.77	0.56	1.0	−139
	$HSiO^+ + N_2$	0.23			−78
SO_2 (152.1)	$SiOH^+ + SO$	1.0	1.2	1.9	−48

[a] The proton affinity is given in parentheses at 298 K in kcal mol^{-1} from S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data, 13 (1984) 695.

[b] Primary product ions which contribute more than 5%. The product distributions are estimated to be accurate to ±30%.

[c] The accuracy of the rate coefficients is estimated to be within ± 30%. The measurements were made in helium buffer gas at 0.35 Torr and, in the case of N_2O, in hydrogen buffer gas at 0.35 Torr as well.

[d] The collision rate coefficients are derived using the combined variational transition state theory–classical trajectory model of T. Su and W.J. Chesnavich, J. Chem. Phys., 76 (1982) 5183.

[e] The standard enthalpy changes for reaction are uncertain by about ±5 kcal mol^{-1}.

product distributions and bimolecular rate coefficients obtained for the four reactions of SiH^+ [6].

Table 1 shows that the insertion channel is very exothermic for all four reactions of SiH^+. The observation of the three insertion reactions, as well as the failure to observe insertion with O_2, may be understood in terms of a proton transport mechanism initiated by O atom transfer within the intermediate complex as shown in reaction 17:

$$\begin{aligned} &SiH^+ + OX \rightarrow [HSi^+ \cdot\cdot OX \rightleftharpoons HSiO^+ \cdot\cdot X \rightleftharpoons OSiH^+ \cdot\cdot X \rightleftharpoons OSi \cdot\cdot XH^+ \\ &\quad \rightleftharpoons SiO \cdot\cdot XH^+ \rightleftharpoons SiOH^+ \cdot\cdot X] \rightarrow SiOH^+ + X \qquad (17) \end{aligned}$$

Figure 5 provides plausible potential energy diagrams for three of the four reactions (the energetics for the reaction with SO_2 are not known completely) which indicate that O atom transfer should be feasible in all cases, at least within the intermediate complex. (O atom transfer is endothermic overall by 6 and 10 kcal mol^{-1} in the cases of CO_2 and SO_2 respectively, but an ion/neutral interaction energy ≈ 10 kcal mol^{-1} should allow the transfer within the complex.) However, for the reaction with O_2, the barrier for isomerization lies substantially above the initial energy of the reactants: the O atom, which

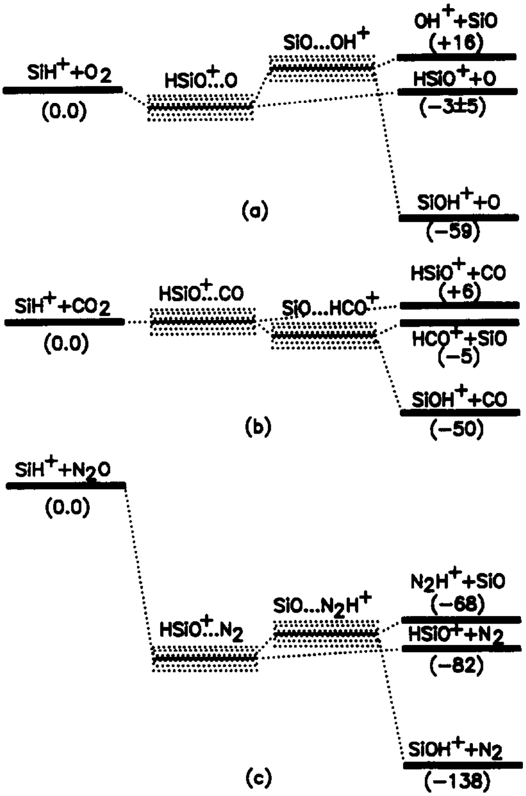


Fig. 5. Energy diagrams for the proton transport mechanism initiated by the O atom transfer reactions of SiH^+ with (a) O_2, (b) CO_2, and (c) N_2O. All energies are given in kcal mol^{-1}. An interaction energy of -5 ± 5 kcal mol^{-1} has been assumed for all electrostatic interactions of ions with molecules.

potentially is the proton transporter in this case, has a proton affinity which lies too far outside the proton affinity bracket defined by the two sites of protonation of SiO. Figure 5 also shows that the barrier for isomerization lies below the initial energy of the reactants for the reactions with CO_2 and N_2O. In the proton transport mechanism for the reaction with N_2O, the transfer of a proton from $HSiO^+$ to N_2 is endothermic by 15 ± 3 kcal mol^{-1} so that the transport mechanism will not serve to isomerize $HSiO^+$ unless more than this amount of internal energy is deposited in the $HSiO^+$ ion by the O atom transfer. Indeed, as is evident from Fig. 5c, in this case the initial O atom transfer is sufficiently exothermic (78 kcal mol^{-1}) to deposit enough internal energy into HSiO for the transport mechanism to occur. It is interesting to note that unimolecular isomerization without the participation of the N_2 molecule also becomes energetically allowed.

Formation of the high-energy isomer $HSiO^+$ is endothermic overall for the reactions of SiH^+ with CO_2 and SO_2, and probably also for the reaction with O_2. The O atom transfer reaction with N_2O is of course exothermic overall so that $HSiO^+$ and N_2 may depart as products immediately after the initial O atom transfer step as shown in Fig. 5c.

CONCLUSIONS

Theoretical calculations and laboratory measurements for the structural isomerization reactions investigated in this article have established the following fundamental behaviour in the gas phase.

(i) The high-energy isomers of the protonated heteronuclear molecules CO, SiO, $CN^{\cdot}$ and N_2O exist as stable species at room temperature. The experimental observation that they do not isomerize spontaneously at room temperature is explained by theory which predicts an energy barrier of at least 27 kcal mol^{-1} for their unimolecular isomerizations.

(ii) The isomerization of a protonated molecule can be catalyzed in bimolecular reactions by molecules which transport the proton in the reaction intermediate from one site of the protonated molecule to another. The transporter molecule should have a proton affinity not more than about 10 kcal mol^{-1} (depending on the interaction energy of the reactants) lower than the proton affinity of the high-energy site of the protonated molecule, and lower than the proton affinity of the low-energy site of the protonated molecule.

(iii) The isomerization of protonated molecules in exothermic bimolecular reactions may be inhibited in the reaction intermediate by the energy required to transfer the proton from the high-energy site of the protonated molecule to the transporter molecule, or by the energy required to rotate the molecule into a position to receive the proton at the low-energy site. Rotational barriers may be particularly effective in isomerization reactions involving larger, longer protonated molecules. Also, the isomerization may be pre-empted by other exothermic reactions which may occur prior to proton transfer to the transporter molecule, or prior to the subsequent rotation required for receiving the proton from the protonated transporter molecule. The reactions of the radical cation $HCN^{\cdot +}$ with CH_4 and N_2O serve to emphasize this point.

(iv) The isomerization of protonated molecules may precede, or be driven by, another reaction occurring in the reaction intermediate.

The gas-phase ion/molecule reactions which have been examined in this article are somewhat limited in number and type, but the insight which has been derived from them should have further-reaching consequences. The intrinsic features which have been elucidated here for the structural isomerization of the protonated heteronuclear molecules COH^+, $HSiO^+$, $HCN^{\cdot +}$ and

$HNNO^+$ should apply to the isomerization of analogous protonated molecules. They should relate to the isomerization of larger protonated molecules, including molecules with many sites of protonation. Also, they may provide the basis for models of isomerization occurring in solution in which solvent molecules can take on the role of proton transporters.

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