

REACTIONS OF  $\text{NNOH}^+$  AND  $\text{HNNO}^+$  IONS WITH  $\text{CH}_4$  AND  $\text{NO}$ 

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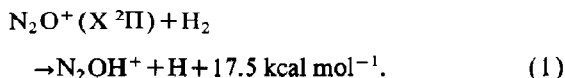
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Received 3 January 1989; in final form 27 January 1989

Published measurements for the reactions of  $\text{N}_2\text{OH}^+$  with  $\text{CH}_4$  and  $\text{NO}$  are interpreted. Two species of different reactivity are established to be the isomers  $\text{NNOH}^+$  and  $\text{HNNO}^+$ , the latter lying energetically above the more stable  $\text{NNOH}^+$  by  $6 \pm 1.5$  kcal  $\text{mol}^{-1}$ . This is in excellent agreement with recent theoretical calculations. Both ions react with  $\text{NO}$  to produce  $\text{NO}^+ + \text{OH} + \text{N}_2$ .  $\text{N}_2\text{OH}^+$  reacts by a simple dissociative charge transfer, the unstable neutral product breaks at its weakest bond, the only exoergic reaction path. The less stable, more energetic  $\text{HNNO}^+$  ion reacts with  $\text{NO}$  in a more complicated manner.

## 1. Introduction

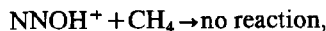
It has been reported [1] that two species of  $\text{N}_2\text{OH}^+$ , having differing reactivities with  $\text{NO}$  and  $\text{CH}_4$ , are produced by the reaction



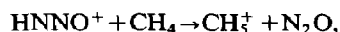
With the benefit of recent experience with the protonated isomeric ions  $\text{HCO}^+$  and  $\text{HOC}^+$  [2] it is possible to analyze these data and deduce detailed thermochemical and mechanistic reaction information.

## 2. Results and discussion

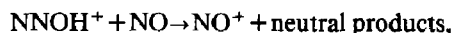
The results previously reported [1] showed that two ions of different reactivity were produced in reaction (1), with an abundance of  $\approx 80\%$  for the most stable and  $\approx 20\%$  for the less stable, i.e. most energetic ion. In order to facilitate the present discussion we anticipate our conclusion below and identify these ions straight away as the most stable form of protonated  $\text{N}_2\text{O}$ ,  $\text{NNOH}^+$  and the less stable isomer  $\text{HNNO}^+$ . The reactivities reported [1] were



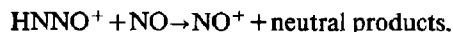
$$k_2 < 10^{-12} \text{ cm}^3 \text{ s}^{-1}, \quad (2)$$



$$k_3 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}. \quad (3)$$



$$k_4 = 8.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \pm 30\%, \quad (4)$$



$$k_5 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \pm 30\%. \quad (5)$$

The neutral products of (4) and (5) were assumed to be  $\text{HN}_2\text{O}$  in both cases but this is unlikely as  $\text{HN}_2\text{O}$  is not a very stable molecule. Production of  $\text{HN}_2\text{O}$  is very endoergic in both cases. The only exoergic reaction channel requires the neutrals to be  $\text{N}_2 + \text{OH}$ . The  $\text{H}-\text{NNO}$  bond energy has been calculated to be  $15.8$  kcal  $\text{mol}^{-1}$  while  $\text{NNOH}$  is unstable with respect to  $\text{N}_2\text{O} + \text{H}$  dissociation [3]. Both  $\text{N}_2\text{OH}$  isomers are thermodynamically unstable towards  $\text{N}_2 + \text{OH}$  dissociation.

2.1. Nature of the two  $\text{N}_2\text{OH}^+$  ions

The proton affinities (PAs) of many molecules including  $\text{N}_2\text{O}$  and  $\text{CH}_4$  are reliably known to within a few kcal  $\text{mol}^{-1}$  [4]. Recently we have refined

slightly the proton affinity scale in the  $\approx 130$ – $140$  kcal mol $^{-1}$  range, which includes  $N_2O$  and  $CH_4$  and have improved the precision to better than  $\pm 1$  kcal mol $^{-1}$  [5]. Relative PAs are straightforward to measure using van't Hoff plots, the persistent problem has been to obtain reliable fixed absolute points for the scale. The most recent values [5] are  $PA(CH_4) = 130.0 \pm 1$  and  $PA(N_2O) = 137.1 \pm 1$  kcal mol $^{-1}$ . These values do not differ significantly from the NBS values [4] of 132 and 136.5 kcal mol $^{-1}$  respectively, for the purposes of this paper. The proton affinity of  $N_2O$  refers to the most stable isomer  $NNOH^+$ , which we identify below from its more efficient reaction with  $NO$ , which has also been determined recently theoretically [6].

The only tenable explanation for the existence of two species of  $N_2OH^+$  with different reactivities is the occurrence of the two isomers obtained by protonating either O or the terminal N atom. Neither  $N_2O$  nor  $N_2O^+$  have excited electronic states within 3 eV of their ground states [7] and protonation cannot change this enough to yield a state within 17.5 kcal mol $^{-1}$  (0.76 eV) of the ground state, the energy available in (1).

Vibrational excitation can also be excluded as the source of energy in the more energetic isomeric ion. The additional energy of this ion inferred below,  $\approx 6$  kcal mol $^{-1}$  or  $\approx 2100$  cm $^{-1}$ , might be consistent with the N–N stretching mode, 2224 cm $^{-1}$  in  $N_2O$ , 1737 cm $^{-1}$  in  $N_2O^+$  [7]. The original experiments [1] were carried out in Ar buffer gas as well as He, in order to test this point. The results were negative, there was no difference in ion behavior in the two buffers. Vibrationally excited ions are quenched with rate constants generally greater than  $10^{-12}$  cm $^3$  s $^{-1}$  by Ar and the systematics of ion vibrational quenching have now been sufficiently well outlined [8] that there can be little doubt that any vibrational excitation of  $N_2OH^+$  ions would have been substantially quenched in far less than the experimental flow time,  $\approx 10^{-2}$  s. Efficient vibrational excitation of  $N_2O^+$ ,  $NO_2^+$ ,  $CO_2^+$  and other ions have been observed experimentally in Ar buffered drift tubes at low energies [9] and it follows from detailed balance that quenching must be efficient as well.

In addition vibrational excitation as the source of the higher energy species would be inconsistent with

its slower reaction with  $NO$ . No case is known in which a slow, exoergic charge-transfer rate constant is diminished by vibrational excitation; indeed the converse is often generally true [9].

It would be difficult to find an explanation for added isomeric energy to substantially diminish a rate constant as observed. It will be shown below that the identification of the two isomers leads to a straightforward explanation of this result.

## 2.2. Reactions with $CH_4$

The proton transfer reaction of the most stable form of  $N_2OH^+$  with  $CH_4$  is endoergic by 7.3 kcal mol $^{-1}$  [5] accounting for the major ion's failure to react. The more energetic ion, corresponding to a lower  $N_2O$  proton affinity, fortuitously reacts with a low rate constant,  $k_3 \approx 1.3\%$   $k_L$ , where  $k_L$  is the Langevin collision rate constant  $\approx 10^{-9}$  cm $^3$  s $^{-1}$ . Exoergic proton transfers for such simple molecular systems almost invariably have near Langevin rate constants. There are almost no known exceptions to this. It is clear that (3) is slightly endoergic, allowing us to determine its energy. The maximum endoergicity is determined by assuming that the fraction of reactants in the high energy tail of the Boltzmann distribution having sufficient energy, i.e. those with relative kinetic energy  $\geq \Delta H$ , react at the collision rate. This gives  $\Delta H = kT \ln(k_L/k_3) = 2.6$  kcal mol $^{-1}$ . We assume the true endoergicity then to be between this value and zero, i.e.  $1.3 \pm 1.3$  kcal mol $^{-1}$  and thereby find the proton affinity relevant to the higher energy state to be  $131.3 \pm 1.3$  kcal mol $^{-1}$ . The energy difference between the two isomers is then  $6.0 \pm 1.3$  kcal mol $^{-1}$ .

Recently, Yamashita and Morokuma [6] have treated the problem of  $N_2OH^+$  isomers theoretically. They find the most stable form to be a trans configuration of  $NNOH^+$  and the next most stable to be trans  $HNNO^+$ , 7.1 kcal mol $^{-1}$  higher in energy. This is remarkably good agreement between experiment and theory. Their absolute proton affinity, for protonating on the O atom is 142.2 kcal mol $^{-1}$ , in fairly good agreement with the experimental value of  $137.3 \pm 1$  kcal mol $^{-1}$  [5] and their relative energies for the two isomers are better than their absolute values. They also found a large,  $> 80$  kcal mol $^{-1}$ , barrier separating the two isomers and predicted (being

unaware of the observations, which were not previously analyzed in detail) that both isomeric forms would be observable. The energy ordering of the O- and N-protonated isomers is also consistent with the present inference based on their reactivity with NO, discussed next. It is so exceptional to find a more energetic species of ion reacting more slowly with a neutral that we consider that the mechanistic explanation of the NO reactions given below offers solid support for the theoretical result.

### 2.3. Reactions with NO

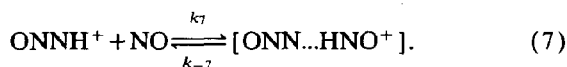
The only exoergic products for NO reaction are



which is exoergic by 25 and 31 kcal mol<sup>-1</sup> for the two isomers and these must therefore be the products. This leads to some very interesting, and informative considerations regarding the reaction mechanism.

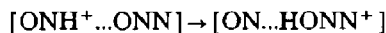
For the most stable, O-atom-protonated N<sub>2</sub>OH<sup>+</sup> isomer, no obvious problem is presented. The process is viewed as a simple dissociative charge transfer yielding NO<sup>+</sup> and the unstable NNOH breaks in the only exoergic way possible to produce N<sub>2</sub> + OH. Many such dissociative charge transfers are known, including reactions of Ar<sub>2</sub><sup>+</sup>, Ne<sub>2</sub><sup>+</sup> and He<sub>2</sub><sup>+</sup> with NO and other neutrals and reactions of N<sub>4</sub><sup>+</sup> [10]. Usually of course dissociative charge transfer involves dissociation of the reactant ion.

The dissociative charge transfer of the more energetic HNNO<sup>+</sup> isomer cannot be so simple, since the H and O whose bonding is required to supply the exoergicity of the reaction, are not in proximity. The lower rate constant for (5) relative to (4) reflects this complexity. We propose the following sequential reaction scheme. Initial endoergic proton transfer from HNNO<sup>+</sup> to NO, producing HNO<sup>+</sup> and NNO which are then trapped in the potential well of the complex, since separation to HNO<sup>+</sup> + N<sub>2</sub>O is endoergic by ≈ 4 kcal mol<sup>-1</sup>,



The endoergicity is overcome by the relative kinetic energy of the collision resulting from the at-

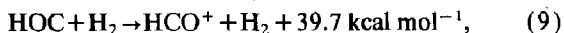
tractive electrostatic potential,  $U(r) \approx e^2\alpha/2r^4$ , where  $\alpha$  is the polarizability of NO (1.70 Å<sup>3</sup>). The dipole moment of NO is negligibly small. One can estimate the potential well depth to be ≈ 6 kcal mol<sup>-1</sup> by comparison with dissociation energies of small ion clusters with N<sub>2</sub> which has a similar polarizability (1.74 Å<sup>3</sup>), e.g. O<sub>2</sub><sup>+</sup>·N<sub>2</sub> (5.7), NO<sup>+</sup>·N<sub>2</sub> (5.2), CH<sub>3</sub><sup>+</sup>·N<sub>2</sub> (6.8) and C<sub>2</sub>H<sub>3</sub><sup>+</sup>·N<sub>2</sub> (6.9), where experimental bond energies in kcal mol<sup>-1</sup> are given in parentheses. [11]. The resulting potential well is even deeper since the polarizability of N<sub>2</sub>O (3.03 Å<sup>3</sup>) is even larger. The two entities, HNO<sup>+</sup> and NNO can more or less freely rotate within the weakly bound complex and when the proton of HNO<sup>+</sup> comes into proximity with the O atom of ONN, the exoergic proton transfer to form NNOH<sup>+</sup> occurs. At this point the system is in the same configuration as arises in the collisions of reaction (4) and dissociative charge transfer will occur, as in (4), leading to the same products, NO<sup>+</sup> + OH + N<sub>2</sub>,



From the small rate constant  $k_5 = 1.4 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, ≈ 2%  $k_t$ , it is clear that unimolecular decomposition,  $k_{-7}$  is fast compared to the rotation-proton transfer-dissociative charge transfer sequence of eq. (8).

From the ratio of rate constants for reactions (5) and (4), 0.16, one can crudely estimate that the sequence of reactions prior to dissociative charge transfer, i.e. endoergic proton transfer from HNNO<sup>+</sup> to NO, followed by exoergic proton transfer from HNNO<sup>+</sup> to the O atom of NNO, all occurring in the collision complex, takes place on ≈ 16% of the reactant HNNO<sup>+</sup> + NO collisions.

It is quite clear that the lower rate constant,  $k_5$ , for the more energetic reactant with NO, implicates it as being the species requiring additional rearrangement, i.e. as being HNNO<sup>+</sup> and not NNOH<sup>+</sup>. The first two steps of this mechanism, leading from the least stable HNNO<sup>+</sup> to the more stable NNOH<sup>+</sup>, by the intervention of a transient HNO<sup>+</sup> is quite similar to the reaction reported by Freeman et al. [2], in which HOC<sup>+</sup> converts to the more stable HCO<sup>+</sup> via the intervention of H<sub>3</sub><sup>+</sup>,



The slightly endoergic reaction (10) undoubtedly precedes (9), which is the two-step reaction (10) followed by the very exothermic proton transfer back to CO. The endoergicity of (10) is so slight,  $\approx kT$  (300 K), that comparable  $\text{H}_3^+$  and  $\text{HCO}^+$  yields are produced in the  $\text{HOC}^+$  reaction with  $\text{H}_2$  at thermal energy. The analogous scheme, the reaction of  $\text{HNNO}^+$  with  $\text{H}_2$  to produce  $\text{NNOH}^+$  cannot occur because reaction to produce  $\text{H}_3^+$ , the first step, would be far too endoergic,  $\approx 30 \text{ kcal mol}^{-1}$ .

One prediction is that at higher relative energy, i.e.  $\text{KE}_{\text{c.m.}} > 3 \text{ kcal mol}^{-1}$ , the product of  $\text{ONNH}^+ + \text{NO}$  reaction will increasingly become  $\text{HNO}^+ + \text{N}_2\text{O}$ , rather than  $\text{NO}^+ + \text{OH} + \text{N}_2$ . This is analogous to the endothermic trapping reactions  $\text{C}_3\text{H}^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}_2^+ + \text{H} - 1.0 \text{ kcal mol}^{-1}$  and  $\text{Si}^+ + \text{O}_2 \rightarrow \text{SiO}^+ + \text{O} - 6.6 \text{ kcal mol}^{-1}$ , which facilitate rapid three-body association at thermal energy but rapidly dominate as binary reactions at elevated kinetic energies [12]. This type of reaction, in which relative translational energy is converted to internal energy of the system, leading to long-lived complexes, has been called the "endothermic trapping model" [12] and has been used with considerable success to rationalize several exceptionally efficient three-body associations of hydrocarbon ions with  $\text{H}_2$ , and the anomalously fast three-body association of  $\text{Si}^+$  ions with  $\text{O}_2$ . This is closely analogous to the formation of Feshbach resonances in atomic and molecular physics, which lead to enhancements in such processes as electron-ion recombination (dielectronic recombination).

One might predict that the two processes (4) and (5) will have different energy dependences. Presumably the direct dissociative charge transfer (4) will have only a slight energy dependence while (5) involving complex formation will decrease much more rapidly with relative energy.

### 3. Conclusions

Experiments in the literature reporting measurements on two species of protonated nitrous oxide re-

acting with different rates with  $\text{CH}_4$  and  $\text{NO}$  have been interpreted as being due to the existence of two isomers, O-protonated  $\text{N}_2\text{O}$  and the N-protonated  $\text{N}_2\text{O}$  at  $6 \pm 1.3 \text{ kcal mol}^{-1}$  higher energy. Their energy difference is deduced from the reactivity with  $\text{CH}_4$  and their structures by the reactivity with  $\text{NO}$ . The  $\text{NO}$  reaction products are shown to be  $\text{NO}^+ + \text{OH} + \text{N}_2$  and the mechanisms to be simple dissociative charge transfer for the more stable  $\text{NNOH}^+$  and a complex three-step process for  $\text{HNNO}^+$ , involving endoergic proton transfer to  $\text{NO}$ , exoergic proton transfer back to the O atom of  $\text{N}_2\text{O}$  and then the same dissociative charge transfer that occurs between  $\text{NNOH}^+$  and  $\text{NO}$ .

### Acknowledgement

The author gratefully acknowledges the contribution of Professor Norman Twiddy in bringing this problem and relevant references to his attention, and thanks Professor Arthur Fontijn for providing the  $\text{HNNO}$  information.

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