Kinetics of the reactions of ONOO⁻ with small molecules

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Abstract

Rate constants and product distributions have been measured for a number of simple molecules reacting with ONOO⁻ at 200 and 300 K. NO, CO, H_2, CH_4, N_2O, and H_2O did not react with ONOO⁻. HCl and HCN underwent proton transfer in addition to other competing channels. Charge transfer from ONOO⁻ was observed exclusively with O_3 and NO_2. SO_2 and HCl underwent exchange for NO in ONOO⁻. HCN was the only substance to show substantial chemistry, producing CNO⁻ and NO_2⁻ in addition to the proton transfer channel. Rate constants for the reactive substances were generally rapid, occurring at >10% of the collision rate constant.
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1. Introduction

Fehsenfeld et al. [1] first made the peroxide isomer of NO_3⁻ (peroxynitrite) in the gas phase in 1969 when they studied the reactions of O_4⁻ and CO_4⁻ with NO,

$$O_4{}^- + NO \rightarrow ONOO^- + O_2 \qquad (1)$$

and

$$CO_4{}^- + NO \rightarrow ONOO^- + CO_2. \qquad (2)$$
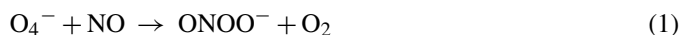
However, it was five years later when it was realized that this was a peroxide isomer and not the more stable D_{3h} isomer with a central N [2]. The identification came from the observation that the NO_3⁻ produced in reactions (1) and (2) also reacted with CO_2,

$$ONOO^- + CO_2 \rightarrow CO_3{}^- + O_2 \qquad (3)$$
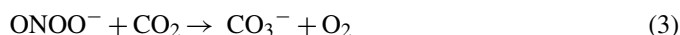
while NO_3⁻ produced via other reactions did not react with CO_2. In that study, it was also determined that NO reacted with the peroxide isomer, although the present study shows that to be incorrect. They also found that ONOO⁻ is formed by the

reactions of O_2⁻$(H_2O)_{0,1}$ with NO. Fahey et al. later extended the water cluster study to sizes up to $n = 4$ [3].

While the work described above found that this ion was important in atmospheric ion chemistry, only one other kinetics study of ONOO⁻ in the gas phase has been made. Fehsenfeld found that ONOO⁻ reacted rapidly with atomic hydrogen to form both NO_2⁻ and OH⁻ [4]. Interest in this ion has grown considerably in recent years due to its importance in biological systems, where the reaction of NO with superoxide, O_2⁻, forms peroxynitrite [5–7]. In addition, the protonated form HOONO has been found to be important in atmospheric chemistry [8]. These applications have resulted in a number of theoretical papers on the structure and energetics of ONOO⁻ [9–12]. The calculations have found that the *cis* isomer is slightly more stable than the *trans* isomer with a relatively large barrier between them.

For these reasons, we have undertaken a study of the chemistry of ONOO⁻ with small molecules in a selected ion flow tube (SIFT). We report branching percentages and rate constants at 200 and 300 K. These reactivity studies are supplemented by ab initio calculations.

2. Experimental

The experiments were performed using the Air Force Research Laboratory selected ion flow tube (SIFT) which is

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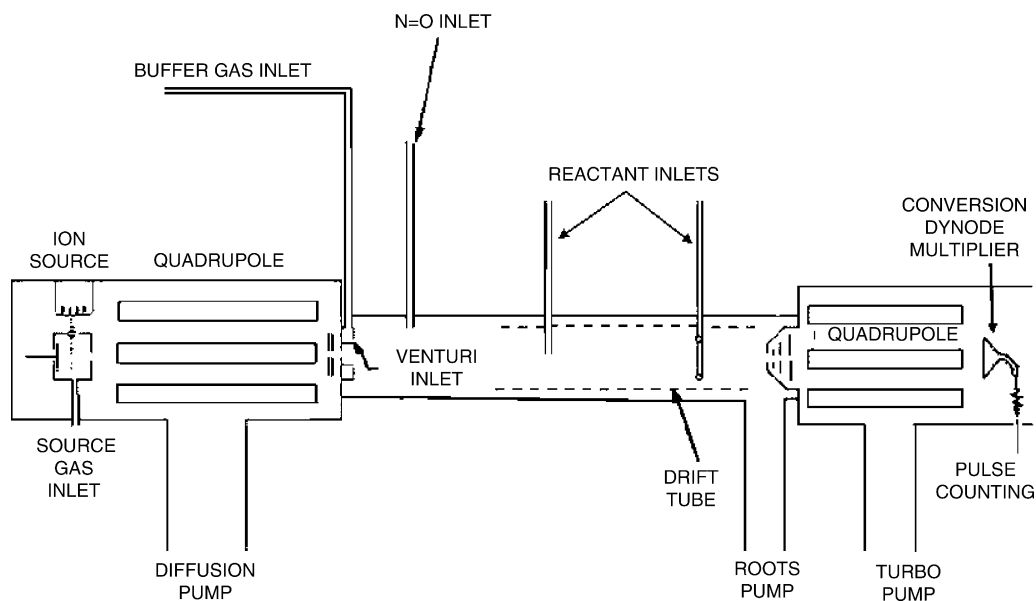
Fig. 1. Schematic representation of the SIFT.

shown in Fig. 1 [13]. Ions were created in one of two upstream ion sources, mass selected, and injected into a buffer gas that carried the ions down the flow tube. Previous experience showed that adding NO directly to our ion source led to the more stable isomer of NO_3^-. Therefore, the $ONOO^-$ was created in the flow tube by either reaction (1) or (2). The NO was added through an upstream inlet in sufficient quantity so that the reaction forming $ONOO^-$ was complete prior to the introduction of the reactant neutral further downstream. After reaction, the ions were sampled through a truncated nose cone aperture, mass analyzed, and detected by a discrete dynode electron multiplier detector. A flow tube is ideal for doing this type of experiment because varying the position in the flow tube where the various gases are introduced allows for time separation.

Several techniques were used to generate the O_4^- and CO_4^- precursor ions. Our laboratory currently has two types of ion sources available for producing ions: a moderate pressure electron impact ion source (normal) [13] and a supersonic expansion electron impact ion source [14]. Using O_4^- instead of CO_4^- was preferred since reaction (1) is faster than reaction (2) and, consequently, less NO was present in the flow tube. Having NO present in the flow tube can cause complications as outlined below. Unfortunately, O_4^- is unstable in a helium buffer with respect to thermal dissociation [15]. CO_4^- is stable with respect to thermal dissociation, but it was both difficult to make in our ion sources and required injection at low energy to avoid collision induced dissociation to O_2^-. The low injection energy contributed to low signal levels. Previous experience in making CO_4^- in the normal source showed that only weak signals could be generated [16]. Therefore, we started with the supersonic source expecting that large amounts of O_4^- could be made in a pure O_2 expansion and that entraining CO_2 would lead to large quantities of CO_4^- [17]. This did produce CO_4^- but with low signal (typically <100 counts s^{-1}). After struggling to get a limited amount of data with this source, O_2^- was injected into an

oxygen buffer to form O_4^- by three-body association. At 300 K, this resulted in approximately a 50:50 mixture of O_2^- and O_4^-. In that situation, O_4^- was formed continuously along the flow tube, complicating the kinetics observed, and this method was abandoned at room temperature.

At 200 K, injection of O_2^- into an oxygen buffer yielded mainly O_4^- at high signal level and most of the 200 K data were taken with this method. Since we have not previously measured flight times and end corrections in an oxygen buffer, we calibrated this method by studying the HCl reaction both in an O_2 buffer and in a He buffer, where the $ONOO^-$ was made from CO_4^-. Within our uncertainty, the rate constants were the same. Thus, no additional corrections were made.

Finally, to obtain room temperature rates more easily, we used the normal source with a mixture of O_2 and CO_2 added. At start up, surprisingly large signals (several hundred counts s^{-1}) were found, but the signal quickly decayed away. This observation indicated a problem caused by electrons heating the source which, in turn, slowed the clustering reactions that form CO_4^-. Cooling the source to $-15\,^\circ$C mitigated this issue, giving signals on the order of a few hundred counts s^{-1}. Most of the room temperature data were thus taken with this method. The signals obtained this way were not as stable as usual, resulting in more scatter than typical.

Several other difficulties warrant mentioning. The introduction of NO into the flow tube made product identification problematic in some experiments because of secondary reactions of the product ions with NO. Also, an NO_2 impurity was usually present in the NO. This was determined by the presence of a peak at NO_2^- with an abundance that varied, but was always less than one third of the $ONOO^-$ signal. The amount of NO_2 was reduced by trapping the NO at around $-90\,^\circ$C [18]. Early in the day, the NO_2^- signal was typically small and increased during the course of a day as the silica gel in the trap became saturated, allowing more NO_2 to pass through the trap. This

Table 1
Rate constants and product distributions for reactions of $ONOO^-$

Reaction	k (300 K) cm^3 s^{-1}	k (200 K) cm^3 s^{-1}	ΔH_{rxn}^{298K} (kJ mol^{-1})
$CO_4^- + NO \rightarrow ONOO^- + CO_2$	3.6 (−11)[a] {7.0 (−10)}[b]		−75
$ONOO^- + NO \rightarrow$ products	nr	nr	−134
$ONOO^- + CO_2 \rightarrow CO_3^- + NO_2$	3.5 (−10) {7.5 (−10)}	8e (−10) {7.5 (−10)}	55
$ONOO^- + CO \rightarrow$ products		nr	
$ONOO^- + H_2 \rightarrow$ products		nr	
$ONOO^- + CH_4 \rightarrow$ products		nr	
$ONOO^- + N_2O \rightarrow$ products		nr	
$ONOO^- + H_2O \rightarrow$ products	nr		
$ONOO^- + SO_2 \rightarrow O_2SO_2^- + NO$[c]	1.8 (−9) {1.6 (−9)}	2.2 (−9) {1.9 (−9)}	
$ONOO^- + SO_2 \rightarrow SO_3^- + NO_2$			−140
$ONOO^- + SO_2 \rightarrow NO_2^- + SO_3$			−176
$ONOO^- + SO_2 \rightarrow (ONOO \cdot SO_2)^-$			
$ONOO^- + HCl \rightarrow Cl^- + ONOOH$ (90%,75%)[d]	1.2 (−9) {1.4 (−9)}	1.3 (e − 9) {1.6 (−9)}	−49
$ONOO^- + HCl \rightarrow O_2HCl^- + NO$ (10%,25%)			
$ONOO^- + O_3 \rightarrow O_3^- + (O_2 + NO)$ >87%	7.5 (−10) {9.7 (−10)}	1.2 (−9) {1.03 (−9)}	−5
$ONOO^- + O_3 \rightarrow NO_2^- + 2O_2$ <13%			−2
$ONOO^- + HCN \rightarrow CN^- + ONOOH$ (14%)	4.2 (−10) {3.5 (−9)}		21
$ONOO^- + HCN \rightarrow CNO^- + HNO_2$ (74%)			−324
$ONOO^- + HCN \rightarrow NO_2^- + HOCN$ (12%)			−313
$ONOO^- + NO_2 \rightarrow NO_2^- + ON + OO$	9.5 (−10) {8.7 (−10)}		−20
$O_2SO_2^- + NO \rightarrow SO_3^- + NO$		∼5 (−11)[e] {6.9 (−10)}	

Thermochemistry is taken from the NIST Webbook [19], except for $ONOO^-$ and $ONOOH$ for which values from Mak and Wong [12] were used.

[a] 3.6 (−11) is a shorthand for 3.6×10^{-11}.

[b] Numbers in {} are the collision rate constant calculated by the Su-Chesnavich parameterization [20,21].

[c] SO_3^- was observed (as SO_5^- in an O_2 buffer) but appears to be mainly from the reaction of $O_2SO_2^- + NO$. Determination of branching percentages was difficult due to reactions with NO and O_2. See text for details.

[d] (90%, 75%) are the branching percentages at 300 K and 200 K, respectively.

[e] Factor of 2 uncertainty.

impurity caused minor problems with product ion identification. However, when ambiguities occurred, it was possible to purge the trap overnight and measure the products early the next day when less NO_2 was present. The last problem encountered stems from persistent traces of the reagent gases from previous experiments, presumably from outgassing of the inlet lines. It was impractical to change all our inlet lines after every reagent and our previous experience indicates that it can take weeks for some of the gases to completely vanish [13]. Consequently, this contamination added a small uncertainty to the rate constant (∼10%).

These difficulties were all minor and did not prevent any measurements from being made, but they did add uncertainty to the data. Normally, we report relative and absolute uncertainties in the rate constant of ±15% and ±25%, respectively. However, for these measurements, we add 10% uncertainty to each of these numbers so that the relative and absolute uncertainties are ±25% and ±35%, respectively. Product uncertainties are discussed below for the individual reactions.

3. Results and discussion

Table 1 lists rate constants and product branching percentages for the reactions studied. Whenever possible, measurements were done at both 200 and 300 K, unless no reaction was found, in which case the measurement was not repeated at the other temperature. As a check, we studied reaction (2) and found a rate constant in excellent agreement with our previous study [16]

and slightly lower than the NOAA value of 4.8×10^{-11} cm^3 s^{-1} [1].

3.1. NO, NO_2 and CO_2 reactions

The only previous measurements of $ONOO^-$ reactivity were done at NOAA [1,2,4]. They reported a rate constant for the reaction of $ONOO^-$ with H atoms [4] and also saw reactions with NO and CO_2, but rate constants were not reported for the latter two reactions [2]. The H atom reaction has not been repeated here, but the other two reactions have been studied again. In contrast to the previous study, we observed no reaction between $ONOO^-$ and NO if the NO trap was clean and purged. The thermochemistry [12,19] shows that this reaction is considerably exothermic, so a barrier to reaction must exist. If the trap was at least partially saturated, we did observe the NO_2^- product observed in the NOAA laboratory. Therefore, we attribute the NO_2^- observed to the charge transfer reaction of $ONOO^-$ with an NO_2 impurity in the NO, especially since the rate constant for the reaction with NO_2 was found to be large in the present study (see Table 1). Since normal D_{3h} NO_3^- does not react with NO_2, the observation of reaction with NO/NO_2 was still a useful identifier of the NO_3^- peroxide isomer in the NOAA experiments.

The reaction of $ONOO^-$ with CO_2 was found to be about 50% efficient at room temperature, i.e., the observed rate constant was 50% of the collision rate constant [20,21]. The rate constant increased to essentially collisional at 200 K. A power

law fit shows a negative temperature dependence of T^{-2} over the limited range studied. The product was found to be CO_3^-, in agreement with the NOAA observation. However, the published thermochemistry indicates that the reaction is endothermic by 55 kJ mol^{-1}. This value reflects a recent G3 calculation of the heat of formation of $ONOO^-$ (-108 kJ mol^{-1}) [12] and values taken from the NIST Webbook for the other species [19]. It is surprising that the literature values for CO_3^- were quite uncertain (-480 ± 40 kJ mol^{-1}), given the importance of this ion in the atmosphere. However, using the NOAA equilibrium measurement [22] for reaction (4):

$$O_3^- + CO_2 \Leftrightarrow CO_3^- + O_2 \tag{4}$$

and a modern value of the heat of formation of O_3^- [19], one finds that the heat of formation of CO_3^- is ≤ -505 kJ mol^{-1}, implying that the reaction endothermicity is <30 kJ mol^{-1}. As modern calculations on systems of this size are quite accurate, we performed structure calculations at several levels using *Gaussian*'03 W as shown in Table 2 [23]. The issue of whether the C_{2v} or D_{3h} isomer of CO_3^- is the most stable has not been settled in the literature [24–28]. A careful investigation of the effects of various theoretical methods on the energies of these isomers determined using several basis sets of different sizes by Cappa and Elrod showed that the results were highly dependent on the method used. The authors cautioned that a definitive result concerning the minimum energy structure could not be found [24]. Therefore, we have determined the heat of formation for both isomers at the G3, G2, and CBS-Q levels of theory as seen in Table 2. This cross section of the typical methods for calculating thermochemical properties demonstrates the range of energetics obtainable. The geometries obtained from the current calculations agree well with previous structure calculations [24]; thus, these molecular parameters have not been repeated here. For the C_{2v} isomer, the heat of formation for CO_3^- ranges from -541 to -553 kJ mol^{-1}, which makes the reaction enthalpy of $ONOO^-$ with CO_2 at least 7 kJ mol^{-1} exothermic. Similarly, for the D_{3h}

isomer, the heat of formation for CO_3^- ranges from -542 to -562 kJ mol^{-1}, which makes the reaction of $ONOO^-$ with CO_2 also more than 7 kJ mol^{-1} exothermic. The three calculations in Table 2 indicate that the D_{3h} form is slightly lower in energy by anywhere from 0.4 to 8 kJ mol^{-1}. However, as discussed above, a definitive recommendation for the calculated value of the heat of formation is impossible. This issue clearly requires further investigation beyond the scope of this article.

Curvature in the $ONOO^-$ decay was seen for some of the reactions and we could not always determine the cause. Most of the decay ($\sim 85\%$) is in the initial fast reacting part and we assume that this decline represents the rate constant of interest. Since the chemistry occurring in the flow tube is quite complex, several explanations are possible. Calculations show that both *cis* and *trans* isomers of $ONOO^-$ exist and that they differ in energy by only a few kJ mol^{-1} with a large barrier separating them [12]. The double decay may indicate that both isomers are present. If so, we cannot differentiate which decay is from the *cis* isomer and which is from the *trans* isomer. In addition, CO_4^- could not be injected cleanly and about 10% of the ions dissociated into O_2^-. A small HCO_4^- signal was also present due to incomplete mass separation in the upstream quadrupole. The O_2^- present could then associate with NO in the reaction region to form $ONOO^-$. The presence of small amounts of normal NO_3^- could also not be ruled out, coming from either the source chemistry or from isomerization during reaction with the various reagents. Since the nature of the curvature is unknown, we only report the rate constant representing the bulk of the ion signal decay.

3.2. CO, H₂, CH₄, N₂O and H₂O reactions

CO, H_2, CH_4, N_2O, and H_2O were not found to undergo reaction. We calculated the heat of reaction for reaction (5) to form the O_2CO^- peroxide ion at the G3 level and found the reaction of $ONOO^- + CO$ to be 126 kJ mol^{-1} endothermic for the *cis* isomer.

$$ONOO^- + CO \rightarrow O_2CO^- + NO \tag{5}$$

A *trans* isomer exists and is ca. 5 kJ mol^{-1} higher in energy at the G3 level of theory. Both peroxide isomers of CO_3^- are over 373 kJ mol^{-1} (3.86 eV) higher in energy than the C_{2v} and D_{3h} isomers at the G3 level.

Similarly, the NOAA result that $O_2^-(H_2O)$ reacts with NO to form $ONOO^-$ indicates that this reaction is exothermic and, therefore, the reaction of H_2O with $ONOO^-$ should be endothermic [3]. While there is a form of $N_2O_2^-$ that is similar to CO_3^-, the published data indicate that the reaction is 153 kJ mol^{-1} endothermic [12,19]. H_2 and CH_4 were not expected to react, but were measured in any case.

3.3. SO₂ reaction

The reaction of SO_2 occurs at the collision rate within the uncertainty at both temperatures. Product identification was problematic in this reaction. The observed ions were SO_3^-, SO_4^-, SO_5^-, NO_2^-, and a $[ONOO \cdot SO_2]^-$ cluster. The product

Table 2
Energetics of CO_3^- isomers at various levels of theory

	Energy (0 K) hartrees	Enthalpy (298 K) hartrees	ΔH_f^{298K} (kJ mol^{-1})
CO_3^- D_{3h}			
G2	-263.491410	-263.487311	-549.8
G3	-263.678666	-263.674567	-541.8
CBS-Q	-263.512010	-263.507942	-562.1
CO_3^- C_{2v}			
G2	-263.491138	-263.486936	-548.8
G3	-263.678623	-263.674421	-541.4
CBS-Q	-263.508699	-263.504531	-553.1
CO_3 D_{3h}			
G2	-263.347695	-263.343782	-172.9
G3	-263.533978	-263.530065	-162.4
CBS-Q	-263.359911	-263.356017	-163.2
CO_3 C_{2v}			
G2	-263.350515	-263.346266	-179.4
G3	-263.536637	-263.532388	-168.5
CBS-Q	-263.364752	-263.360537	-175.1

of the reaction of ONOO$^-$ with SO$_2$ was found to be SO$_4^-$ in the peroxide form [2]. However, we have found that SO$_4^-$ peroxide reacts with NO to produce SO$_3^-$ as shown in Table 1. When CO$_4^-$ was used as the starting ion to produce ONOO$^-$, SO$_3^-$ was found to be the main product ion. However, the experiments performed in the O$_2$ buffer using considerably less NO to make ONOO$^-$ showed that this result was mainly an artifact. In the O$_2$ buffer, any SO$_3^-$ formed showed up as SO$_5^-$. The SO$_5^-$ ion was only observed in an O$_2$ buffer and was the result of the clustering of O$_2$ to SO$_3^-$ [29]. The cluster ion, [ONOO·SO$_2$]$^-$, was <1% of the products at room temperature in a helium buffer and about 5% and 12% in He and O$_2$ buffers, respectively, at 200 K. In addition, we have found that SO$_4^-$ formed from the reaction of CO$_4^-$ with SO$_2$ reacted with NO to form SO$_3^-$. Thus, the ratio of (SO$_3^-$ + SO$_5^-$) to SO$_4^-$ observed depended on the amount of NO added. Particularly, little SO$_4^-$ was observed in a helium buffer where large quantities of NO were added to quench the CO$_4^-$. In the O$_2$ buffer at 200 K, more SO$_4^-$ than SO$_5^-$ is observed. Therefore, it was difficult to know whether SO$_3^-$ was directly formed in the reaction of ONOO$^-$ with SO$_2$. At most, SO$_3^-$ accounted for 40% of the products, but the branching percentage for SO$_3^-$ is likely to be considerably lower.

Similarly, we have mixed results for the presence of the NO$_2^-$ product, which is related to the SO$_3^-$ product since only the location of the charge differs in the two channels. At room temperature, little NO$_2^-$ was found, while at 200 K, the amount of NO$_2$ is <10%. This limit stems from the fact that the amount of NO$_2^-$ observed also depended on the NO flow and, therefore, might be exclusively from a side reaction involving the NO$_2$ impurity. Thus, NO for SO$_2$ "ligand exchange" in ONOO$^-$ is the only definitive bimolecular reaction observed; although, the direct production of SO$_3^-$ and NO$_2^-$ is possible and is exothermic. The amount of clustering in an O$_2$ buffer indicates that production of the cluster ion will be important at the higher pressures of the atmosphere.

3.4. O$_3$ reaction

Charge transfer from ONOO$^-$ to O$_3$ was found to be rapid, i.e. occurred at the collision rate within the uncertainties. Over 87% of the reaction proceeded by charge transfer. The NO$_2^-$ ion signal increased with increasing O$_3$ concentration; however, this increase was attributed to the reaction of O$_3^-$ with NO to produce NO$_2^-$ (also formed from an NO$_2$ impurity), which further reacts with O$_3$ present in the flow tube to form normal (non-peroxide) NO$_3^-$ [30]. The presence of two forms of NO$_3^-$ (one reactive and one unreactive) leads to curvature in the rate constant plots because the two isomers of NO$_3^-$ have the same mass. Taking the initial decline to represent the ONOO$^-$ reactivity mostly solved this problem, as evidenced by the rate constant being near the collisional value.

The temperature dependence observed may in part be a result of large uncertainty in this reaction because of the secondary chemistry. Charge transfer is just slightly exothermic if the neutrals formed are O$_2$ and NO. We performed calculations at the G3 level to find the energetics of the neutral peroxide structure

of NO$_3$, but only a weakly bound van der Waals structure was found. Isomerization to normal NO$_3$ would increase the exothermicity by about 20 kJ mol^{-1}.

3.5. HCl and HCN reactions

HCl mainly underwent proton transfer at approximately the collision rate. NO for HCl exchange in ONOO$^-$ to form O$_2$HCl$^-$ accounted for about 10 and 25% of the reactivity at 300 K and 200 K, respectively. The O$_2$HCl$^-$ product underwent a secondary reaction with HCl to form Cl$^-$(HCl). G3 calculations [12] for HOONO indicate that the proton transfer reaction is exothermic by 49 kJ mol^{-1}.

Reaction with HCN was also rapid and produced three products. The main products formed were CNO$^-$ and HNO$_2$, accounting for about 75% of the reactivity. This channel is very exothermic and separation of the HNO$_2$ into H plus NO$_2$ neutrals is essentially thermoneutral. Proton transfer to form CN$^-$ accounts for about 14% of the reactivity and it is 21 kJ mol^{-1} endothermic if the peroxide acid (ONOOH) is formed [12,19]. Formation of the more stable HNO$_3$ makes the reaction exothermic by over 80 kJ mol^{-1}. Finally, NO$_2^-$ was produced in about 12% of the reactions and, again, this reaction is very exothermic. This channel differs from the CNO$^-$ channel by the location of the proton.

The fast proton transfer to HCl indicates that HCl is a stronger acid than ONOOH. Similarly, the slow proton transfer to HCN may indicate that the acidities of ONOOH and HCN are similar [31]. However, the recent calculations of the heats of formation of ONOO$^-$ and ONOOH indicate that the reaction with HCN should be endothermic by a substantial amount. Therefore, the observation of proton transfer in the reaction with HCN indicates that either the calculated heat of formation of one of the peroxide species is incorrect or that isomerization to HNO$_3$ occurs.

As discussed earlier, charge transfer occurred from ONOO$^-$ to both O$_3$ and NO$_2$, indicating that the electron affinity (EA) of ONOO is less than the EA of those two molecules. The recent G3 calculations concur [12], but the EA for O$_3$ is just barely larger. Thus, in order for the O$_3$ reaction to be exothermic, the heat of formation of ONOO$^-$ can only be raised and not lowered. However, the HCN results would indicate that the heat of formation should be lowered. Therefore, the HCN reaction indicates that the heat of formation of ONOOH is incorrect.

4. Conclusions

Rate constants and product distributions have been measured for a number of small molecules reacting with ONOO$^-$ at 200 and 300 K. NO, CO, H$_2$, CH$_4$, N$_2$O, and H$_2$O did not react. HCl and HCN underwent proton transfer; although other competing channels were observed. Charge transfer was observed exclusively for O$_3$ and NO$_2$. SO$_2$ and HCl underwent exchange of an NO in ONOO$^-$. HCN was the only substance to show substantial chemistry, producing CNO$^-$ and NO$_2^-$ in addition to the proton transfer channel. The rate constants for the reactive molecules were generally rapid, occurring with an efficiency of >10% of the collision rate constant.

We had hoped to check for isomerization of $ONOO^-$ to the lower energy D_{3h} NO_3^- form. The current results intimate that isomerization was never a major process, but the experimental issues described above prevented the observation of a small amount of isomerization. A better experimental determination could be made by using a flowing afterglow source [32]. With such an instrument, $ONOO^-$ could be made by the same chemistry as used here, and then injected into the flow tube. Assuming that significant breakup did not occur upon injection, the kinetics measurements would be greatly simplified. Product identification could also be made more definitive and it would be possible to search for the *cis* and *trans* isomers of $ONOO^-$. In terms of atmospheric chemistry, the present results show that $ONOO^-$ will probably react with either CO_2 or O_3 to lead eventually to the more stable species, CO_3^- and NO_3^-. Furthermore, we found NO does not react with $ONOO^-$, in contrast to a previous result [2].

Acknowledgements

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