Communication: Charge transfer dominates over proton transfer in the reaction of nitric acid with gas-phase hydrated electrons
Jozef Lengyel, Jakub Med, Petr Slavíček, and Martin K. Beyer

Citation: The Journal of Chemical Physics 147, 101101 (2017); doi: 10.1063/1.4999392
View online: http://dx.doi.org/10.1063/1.4999392
View Table of Contents: http://aip.scitation.org/toc/jcp/147/10
Published by the American Institute of Physics

Articles you may be interested in
Pair 2-electron reduced density matrix theory using localized orbitals
The Journal of Chemical Physics 147, 084101 (2017); 10.1063/1.4999423

Communication: Hypothetical ultralow-density ice polymorphs
The Journal of Chemical Physics 147, 091101 (2017); 10.1063/1.4994757

Perspective: Surface freezing in water: A nexus of experiments and simulations
The Journal of Chemical Physics 147, 060901 (2017); 10.1063/1.4985879

Perspective: Differential dynamic microscopy extracts multi-scale activity in complex fluids and biological systems
The Journal of Chemical Physics 147, 110901 (2017); 10.1063/1.5001027

Perspective: A controversial benchmark system for water-oxide interfaces: H2O/TiO2(110)
The Journal of Chemical Physics 147, 040901 (2017); 10.1063/1.4996116

Communication: A method to compute the transport coefficient of pure fluids diffusing through planar interfaces from equilibrium molecular dynamics simulations
The Journal of Chemical Physics 147, 101102 (2017); 10.1063/1.4997865
Communication: Charge transfer dominates over proton transfer in the reaction of nitric acid with gas-phase hydrated electrons

Jozef Lengyel, Jakub Med, Petr Slavíček, and Martin K. Beyer

1 Institut für Ionophysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria
2 Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, 16628 Prague, Czech Republic

(Received 8 August 2017; accepted 31 August 2017; published online 12 September 2017)

The reaction of HNO$_3$ with hydrated electrons (H$_2$O)$_n$$^-$ (n = 35–65) in the gas phase was studied using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and \textit{ab initio} molecular dynamics simulations. Kinetic analysis of the experimental data shows that OH$^+$ (H$_2$O)$_m$ is formed primarily via a reaction of the hydrated electron with HNO$_3$ inside the cluster, while proton transfer is not observed and NO$_2$$^+$ (H$_2$O)$_m$ is just a secondary product. The reaction enthalpy was determined using nanocalorimetry, revealing a quite exothermic charge transfer with $-241 \pm 69$ kJ mol$^{-1}$. \textit{Ab initio} molecular dynamics simulations indicate that proton transfer is an allowed reaction pathway, but the overall thermochemistry favors charge transfer. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4999392]

Charge transfer (CT) and proton transfer (PT) reactions form the basis for many important processes in chemistry, biology, and technology.\textsuperscript{1-4} The two processes can proceed independently, consecutively, or in parallel as proton coupled electron transfer.\textsuperscript{5,6} PT and CT processes can also compete: once proton transfer has taken place, electron transfer is no longer possible, and vice versa. Here we study the competition between PT and CT for the reaction of hydrated electrons in finite clusters (H$_2$O)$_n$$^-$ with gaseous nitric acid. Gas-phase hydrated electrons are quite convenient for such an exploration. First, the finite size allows for a direct observation of various molecular fragments formed in the reactions by mass spectrometry. Second, the energetics of the reaction can be probed using the concept of nanocalorimetry,\textsuperscript{7-9} i.e., by detecting the number of evaporating water molecules when the reaction takes place.

The analogous reaction of (H$_2$O)$_n$$^-$ with HCl was studied by Siu \textit{et al.}\textsuperscript{10} As HCl is a very strong acid, proton transfer prevails. Upon uptake of HCl by the (H$_2$O)$_n$$^-$ clusters (n = 30–70), HCl dissociates, and the electron recombines with the proton. The nascent H atom evaporates from the cluster and CT$^+$ (H$_2$O)$_n$ is observed in the mass spectrum. Since HNO$_3$ also is a strong acid, one might expect that the reaction of HNO$_3$ with hydrated electrons should result in NO$_2$$^+$ (H$_2$O)$_n$. On the other hand, HNO$_3$ is a slightly weaker acid than HCl and at the same time it reliably undergoes dissociative electron transfer in the gas phase.\textsuperscript{11-15} Charge transfer leading to NO$_2$$^+$ (H$_2$O)$_n$ or OH$^+$ (H$_2$O)$_n$ is therefore also conceivable. In fact, all three potential product species, NO$_2$$^+$ (H$_2$O)$_n$, NO$_2$$^-$ (H$_2$O)$_n$, and OH$^+$ (H$_2$O)$_n$, have been observed in our recent study,\textsuperscript{14} where low-energy free electrons were brought to interact with neutral mixed nitric acid–water clusters (HNO$_3$)$_m$(H$_2$O)$_n$, m $\approx$ 1–6, n $\approx$ 1–15.

The mechanism of the gas phase reaction between free electrons and HNO$_3$ was studied in detail using flowing afterglow techniques. Dissociative electron attachment to HNO$_3$ yields primarily NO$_2$$^+$ in a very efficient exothermic process with an energy release of around 13 kJ mol$^{-1}$,\textsuperscript{11-14} Shuman \textit{et al.}\textsuperscript{13} observed the formation of OH$^+$ as a minor channel, which is 30 kJ mol$^{-1}$ endothermic. The formation of NO$_2$$^+$ in the gas phase is even more endothermic with 43 kJ mol$^{-1}$ and has recently been observed using a crossed-beam experiment.\textsuperscript{14} However, electron driven processes often dramatically change upon solvation.\textsuperscript{15-18} Hydration affects the electronic structure of transient negative ions and enhances or suppresses reaction channels. Furthermore, HNO$_3$ has a strong affinity to ice,\textsuperscript{19} where it rapidly dissociates.\textsuperscript{20-22}

To experimentally resolve these issues, we studied the reaction of HNO$_3$ with (H$_2$O)$_n$$^-$ (n = 35–65) by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The measurements are complemented with \textit{ab initio} molecular dynamics simulations.

Figure 1 shows mass spectra of the reaction of HNO$_3$ with (H$_2$O)$_n$$^-$ at characteristic reaction delays. The reaction results in two intense product ions: OH$^+$ (H$_2$O)$_n$ and NO$_2$$^+$ (H$_2$O)$_n$. In addition, a small amount of NO$_2$$^-$ (H$_2$O)$_m$ is observed. At t = 0 s, [Fig. 1(a)], the mass spectrum is dominated by hydrated electrons. However, a significant amount of OH$^+$ (H$_2$O)$_n$ as well as traces of NO$_2$$^+$ (H$_2$O)$_n$ is present due to reactive collisions during the ion accumulation in the ICR cell, which takes 2 s. At t = 3 s, Fig. 1(b), roughly equal amounts of (H$_2$O)$_n$$^-$ and OH$^+$ (H$_2$O)$_n$ are present, and NO$_2$$^-$ (H$_2$O)$_m$ is catching up. The strong increase of the NO$_2$$^-$ (H$_2$O)$_m$ intensity between
molecule reactions involving HNO$_3$ naturally in the troposphere. Reaction (2) is the well-known acid–base reaction.

(2.8 ± 1.1) × 10^{-10} \text{ cm}^3 \text{s}^{-1}$ and $k(2) ≥ (2.4 ± 0.9) × 10^{-10} \text{ cm}^3 \text{s}^{-1}$, while the upper limits are given by the collision rates,

\[
\begin{align*}
\text{(H}_2\text{O)}_n^- + \text{HNO}_3 & \rightarrow \text{OH}^-(\text{H}_2\text{O})_m + \text{NO}_2^- + (n-m)\text{H}_2\text{O}, & (1) \\
\text{(H}_2\text{O)}_m\text{OH}^- + \text{HNO}_3 & \rightarrow \text{NO}_3^-\text{(H}_2\text{O)}_l + (m-l+1)\text{H}_2\text{O}. & (2)
\end{align*}
\]

Reaction (2) is the well-known acid–base reaction. The NO$_3^-$ anion is often seen as a terminal product in many ion-molecule reactions involving HNO$_3$ and also occurs naturally in the troposphere. NO$_3^-(\text{H}_2\text{O})_n$ undergoes ligand exchange reactions with additional HNO$_3$ molecules resulting in the formation of mixed NO$_3^-(\text{H}_2\text{O})_n$ cluster ions.

The minor product series NO$_2^-(\text{H}_2\text{O})_m$ may be formed via reaction (3) in competition with reaction (1). However, the presence of traces of HONO as a decomposition product of HNO$_3$ on the apparatus walls has to be taken into account, which would afford reactions (4) and (5). Unfortunately, the kinetic fits are ambiguous, due to the low intensity of this product. However, the overall shape of the kinetics curve over all six different experiments is most consistent with NO$_2^-(\text{H}_2\text{O})_m$ formation in the second reaction step, i.e., reaction (5),

\[
\text{(H}_2\text{O)}_m^- + \text{HNO}_3 \rightarrow \text{NO}_2^-\text{(H}_2\text{O})_m + \text{OH} + (n-m)\text{H}_2\text{O}. & (3)
\]
(H₂O)ₙ⁻ + HONO → NO₂⁻(H₂O)ₙ + H + (n − m)H₂O. 

The plot of average cluster sizes as a function of time, Fig. 2(b), shows that the OH⁻(H₂O)ₙ⁻ ion distribution is significantly shifted to smaller cluster sizes relative to that of the hydrated electrons (H₂O)ₙ⁺. The loss of water molecules indicates an exothermic reaction. We therefore applied the nanocalorimetry approach, in which the exothermicity of the reaction is determined via the average number of evaporated water molecules. The mean cluster sizes for reactants and products as well as their difference are plotted as a function of time, Figs. 2(b) and 2(c), and fitted with a set of differential equations that account for the water loss due to reaction as well as BIRD.² Note that the time dependence of the difference in Fig. 2(c) is due to a complex interplay of BIRD, reaction kinetics and the 2 s long fill cycle of the cell. Since the product ions present at 0 s arise from ions residing for longer times in the cell, they are smaller than expected, and the difference seems artificially large. As shown before, the differential equations used for the fit describe these effects faithfully.³ A nanocalorimetric fit reveals a result of 5.7 ± 1.6 and 2.3 ± 0.2 evaporated water molecules for reactions (1) and (2), respectively. With the energy required to evaporate a single water molecule from the cluster, ΔE_vap = 43.3 ± 3.1 kJ mol⁻¹,³¹,³² and thermal corrections as detailed in the supplementary material,³³,³⁴ this translates to ΔH_exp(298 K) = −241 ± 69 kJ mol⁻¹ for reaction (1) and −94 ± 11 kJ mol⁻¹ for reaction (2).

Table I summarizes the measured reaction enthalpy in comparison with ab initio calculation and literature thermochemical data from bulk aqueous solution. The measured energy release of the CT reaction agrees within error limits with the literature value for the room temperature reaction enthalpy in the condensed phase. The thermochemistry also makes it plausible that no NO₂⁻ formation is observed in the first reaction step. The bulk value for the formation of NO₂⁻, reaction (3), is only slightly less exothermic than for reaction (1), which would be consistent with its occurrence as a minor primary reaction pathway, as well as with the average cluster size of NO₂⁻(H₂O)ₙ [Fig. 2(b)]. However, since we know from other experiments,¹⁴,²⁹ that traces of HONO are inevitably present in the reactant gas, formation of NO₂⁻(H₂O)ₙ is most likely due to collisions with HONO.

To get a mechanistic understanding of the primary reaction, we performed ab initio molecular dynamics simulations on small model systems. We started the simulations with equilibrated hydrated electrons with 15 water molecules, the hydrated electrons (H₂O)₁⁵⁻.

TABLE I. Reaction energetics for reactions of HNO₃ with (H₂O)ₙ⁻ and OH⁻(H₂O)ₙ in units of kJ mol⁻¹.

| Reaction      | Experimental | Experimental | Calculation | Calculation |
|---------------|--------------|--------------|-------------|-------------|
|               | cluster      | bulk         | n = 15      | n = 6       |
| Reaction (1)  | −241 ± 69    | −258 ± 11¹⁳,³⁵,³⁶ | −248 ± 7    | −278        |
| Reaction (2)  | −94 ± 11     | −129¹⁷       | 164 ± 6     | 158         |
| Reaction (3)  | −246 ± 11¹³,³⁵,³⁶ | −177 ± 9     | −212        |
| Reaction (6)  | −99 ± 11¹³,³⁵,³⁶ | −82 ± 8      | −95         |

where the vertical detachment energy (VDE) is above 1 eV.³⁸ The calculated values are slightly larger than the measured data for somewhat larger finite size clusters (see the supplementary material for details).³⁹ Then we let react a neutral HNO₃ molecule placed randomly at a distance of 7.5 Å from the center of mass of the water cluster. Figure 3 shows the evolution of quantities characterizing structures and charge distribution along two selected MD trajectories. Panel A displays a trajectory in which the CT takes place and the non-planar radical anion of nitric acid is formed. The vertical ionization energy of the isolated anionic water oscillates above 1 eV while the (adiabatic) electron affinity for HNO₃ was measured to be 0.6 eV.⁴⁰,⁴¹ The charge transfer reaction is facilitated by solvation of the nitric acid molecule. Indeed, the CT is exothermic for larger clusters (see the supplementary material), yet an energy barrier is expected for this process. In our simulations, the CT reaction was typically observed in tens of picoseconds after the HNO₃ molecule and the anionic cluster get in contact.

The nascent HNO₃⁻ dissociates (again on the picosecond time scale) upon interaction with water. For about 1 ps, the negative charge is localized on the NO₂⁻ moiety. Unlike for the unsolvated reaction, the dissociation into NO₂⁻ is not observed in the MD simulations. In the presence of a hydration shell, the electron is instead transferred from NO₂⁻ to OH,
yielding OH\(^-\) and NO\(_2\). Interestingly, dissociation of the N–O bond takes place concomitantly with charge localization on the OH moiety, and the oscillations in the charge distribution are mirrored in the oscillations of the N–O distance. The NO\(_2\) molecule then typically leaves the cluster, [reaction (1)], in line with the experimentally observed reaction (1). Although not observed in the trajectory calculations, the relatively long localization of the negative charge on the NO\(_2\) moiety suggests that the formation of NO\(_2\)\(^-(\text{H}_2\text{O})_m\) via reaction (3), which would require N–O bond cleavage and OH evaporation before charge transfer from NO\(_2\)\(^-\) to OH can take place, is a plausible scenario. The difference in thermochemistry between the two pathways is relatively small, therefore the detailed hydration environment of the two product species will be crucial for ultimate charge localization. Minor changes in the hydrogen-bonded network may thus favor one or the other. Besides bond breaking, evaporation of water molecules was observed in some trajectories already on the picosecond time scale.

The simulations, however, also yield trajectories where the proton transfer takes place first and, subsequently, the hydrated electron recombines with H\(_2\)O\(^+\), leading to H\(_2\)O + H units, with the H atom leaving the cluster,

\[
\text{(H}_2\text{O})_m^- + \text{HNO}_3 \rightarrow \text{(H}_2\text{O})_m\text{NO}_3^- + \text{H} + (n - m)\text{H}_2\text{O}. \tag{6}
\]

The trajectory presented in Fig. 1(b) displays a proton transfer taking place in 1.5 ps. The proton then hops several times before the H\(_2\)O\(^+\) accepts the electron and forms free neutral hydrogen at about 8 ps. In this particular case, the hydrogen atom remains trapped in the cluster for another 2.5 ps before it leaves.

Altogether, we have performed 25 simulations lasting up to 25 ps [the simulations were stopped once either the reaction (1) or (6) took place]. Within that time, we have seen 16 times charge transfer (in 10 cases, the reaction was followed by the subsequent decomposition reaction within the 25 ps time window) and 6 times the proton transfer reaction. No reactive event occurred within the first 25 ps in the three remaining trajectories. We thus observe that both the CT and PT processes are very fast; the fast PT is consistent with previous studies on trajectories. We thus observe that both the CT and PT processes event occurred within the first 25 ps in the three remaining trajectories. We thus observe that both the CT and PT processes are very fast; the fast PT is consistent with previous studies on trajectories. The two pathways is relatively small, therefore the detailed hydration environment of the two product species will be crucial for ultimate charge localization. Minor changes in the hydrogen-bonded network may thus favor one or the other. Besides bond breaking, evaporation of water molecules was observed in some trajectories already on the picosecond time scale.

In summary, we have demonstrated that the charge transfer reaction between hydrated electron and HNO\(_3\) is an ultrafast process taking place on the picosecond time scale in finite-size water particles. The transient negative ion HNO\(_2\)\(^-\) is formed faster than the ionic dissociation of the acid molecule in the water cluster can occur. The excess electron destabilizes the HO–NO\(_2\) bond. The competition between OH and NO\(_2\) for the electron is won by OH due to the high hydration enthalpy of OH\(^-\).

See supplementary material for experimental and theoretical details; conversion of \(\Delta E_{\text{raw}}\) to \(\Delta H_0\); thermochemistry of bulk analogues for reactions (1)–(3) and (6); further calculation details; and benchmark calculations.

J.L. acknowledges support through the Lise-Meitner Programme of the Austrian Science Fund (FWF): Project No. M1983-N34. P.S. and J.M. thank Czech Science Foundation, Grant Nos. 14-08937S and 17-04068S.

1 R. A. Marcus, Rev. Mod. Phys. 65, 599–610 (1993).
2 D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley, and X. Zhu, J. Phys. Chem. B 107, 6668–6697 (2003).
3 J. T. Hynes, J. P. Kliman, H.-H. Limbach, and R. L. Schowen, Hydrogen-Transfer Reactions (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007).
4 J. Blumberger, Chem. Rev. 115, 11191–11128 (2015).
5 R. I. Cukier and D. G. Nocera, Annu. Rev. Phys. Chem. 49, 337–369 (1998).
6 M. H. V. Huynh and T. J. Meyer, Chem. Rev. 107, 5004–5064 (2007).
7 W. A. Donald, R. D. Leib, J. T. O’Brien, A. I. S. Holm, and E. R. Williams, Proc. Natl. Acad. Sci. U. S. A. 105, 18102–18107 (2008).
8 R. F. Höckendorf, O. P. Balaj, C. van der Linde, and M. K. Beyer, Phys. Chem. Chem. Phys. 12, 3772–3779 (2010).
9 A. Akhgaransch, W. K. Tang, H. Zhang, C.-K. Siu, and M. K. Beyer, Phys. Chem. Chem. Phys. 18, 23528–23537 (2016).
10 C.-K. Siu, O. P. Balaj, V. E. Bondybay, and M. K. Beyer, J. Am. Chem. Soc. 129, 3238–3246 (2007).
11 F. C. Fehsenfeld, C. J. Howard, and A. L. Schmeltekopf, J. Phys. Chem. 63, 2835–2841 (1975).
12 N. G. Adams, D. Smith, A. A. Viggiano, J. F. Paulson, and M. J. Henchman, J. Chem. Phys. 54, 6728–6731 (1986).
13 N. S. Shuman, T. M. Miller, and A. A. Viggiano, J. Chem. Phys. 136, 124307 (2012).
14 J. Lengyel, M. Ončík, J. Feder, J. Kočíšek, A. Pysanenko, M. K. Beyer, and M. Färnik, Phys. Chem. Chem. Phys. 19, 11753–11758 (2017).
15 G. Niedner-Schatteburg and V. E. Bondybay, Chem. Rev. 100, 4059–4086 (2000).
16 V. E. Bondybay and M. K. Beyer, Int. Rev. Phys. Chem. 21, 277–306 (2002).
17 O. P. Balaj, C.-K. Siu, I. Balteanu, M. K. Beyer, and V. E. Bondybay, Int. J. Mass Spectrom. 238, 65–74 (2004).
A. A. Viggiano, S. T. Arnold, and R. A. Morris, Int. Rev. Phys. Chem. 17, 147–184 (2010).

T. Huthwelker, M. Ammann, and T. Peter, Chem. Rev. 106, 1375–1444 (2006).

B. D. Kay, V. Hermann, and A. W. Castleman, Jr., Chem. Phys. Lett. 80, 469–474 (1981).

P. R. McCurdy, W. P. Hess, and S. S. Xantheas, J. Phys. Chem. A 106, 7628–7635 (2002).

J. Lengyel, A. Pysanenko, J. Kočíšek, V. Poterya, C. C. Pradzynski, T. Zeuch, P. Slavíček, and M. Fárník, J. Phys. Chem. Lett. 3, 3096–3101 (2012).

R. C. Dunbar, Mass Spectrom. Rev. 23, 127–158 (2004).

J. A. Davidson, F. C. Feihensfeld, and C. J. Howard, Int. J. Chem. Kinet. 9, 17–29 (1977).

A. A. Viggiano, F. Dale, and J. F. Paulson, J. Geophys. Res. 90, 7977–7984, doi:10.1029/jd090id05p07977 (1985).

H. Wincel, E. Mareand, and A. W. Castleman, Jr., J. Phys. Chem. 100, 7488–7493 (1996).

N. Heine, T. I. Yacovitch, F. Schubert, C. Brieger, D. M. Neumark, and K. R. Asmis, J. Phys. Chem. A 118, 7613–7622 (2014).

O. Möhler and F. Arnold, J. Atmos. Chem. 13, 33–61 (1991).

J. Lengyel, C. van der Linde, A. Akhgarnusch, and M. K. Beyer, Int. J. Mass Spectrom. 418, 101–106 (2017).

G. Beig and G. P. Brasseur, J. Geophys. Res.: Atmos. 105, 22671–22684, doi:10.1029/2000jd900119 (2000).

C. Hock, M. Schmidt, R. Kuhnen, C. Bartels, L. Ma, H. Haberland, and B. von Issendorff, Phys. Rev. Lett. 103, 073401 (2009).

W. A. Donald, R. D. Leib, M. Demireva, B. Negru, D. M. Neumark, and E. R. Williams, J. Phys. Chem. A 115, 2–12 (2011).

A. Akhgarnusch, R. F. Höckendorf, and M. K. Beyer, J. Phys. Chem. A 119, 9978–9985 (2015).

J. Lengyel, C. van der Linde, M. Fárník, and M. K. Beyer, Phys. Chem. Chem. Phys. 18, 23910–23915 (2016).

D. W. Smith, J. Chem. Educ. 54, 540 (1977).

H. Shiraishi, G. R. Sunaryo, and K. Ishigure, J. Phys. Chem. 98, 5164–5173 (1994).

Handbook of Chemistry and Physics, 78th ed., edited by D. R. Lide (CRC Press, Boca Raton, 1997).

J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, and D. R. Worsnop, J. Chem. Phys. 92, 3980 (1990).

L. Ma, K. Majer, F. Chirot, and B. von Issendorff, J. Chem. Phys. 131, 144303 (2009).

B. P. Mathur, E. W. Rothe, S. Y. Tang, K. Mahajan, and G. P. Reck, J. Chem. Phys. 64, 1247–1248 (1976).

J. F. Paulson and F. Dale, J. Chem. Phys. 77, 4006–4008 (1982).

S. Riikonen, P. Parkkinen, L. Halonen, and R. B. Gerber, J. Chem. Phys. Lett. 4, 1850–1855 (2013).

S. T. Arnold, R. A. Morris, and A. A. Viggiano, J. Chem. Phys. 103, 9242 (1995).

M. K. Beyer, B. S. Fox, B. M. Reinhard, and V. E. Bondybey, J. Phys. Chem. B 115, 9288–9297 (2001).

A. Kumar, J. A. Walker, D. M. Bartels, and M. D. Sevilla, J. Phys. Chem. A 119, 9148–9159 (2015).