Energy resonance in electron transfer from nitric oxide to atomic metal cations at room temperature

Michael J.Y. Jarvis, Voislav Blagojevic, Gregory K. Koyanagi, Diethard K. Bohme *

*Department of Chemistry and Centre for Research in Mass Spectrometry, York University, 4700 Keele Street, North York, Toronto, Ont., Canada M3J 1P3*

Abstract

Rate coefficients have been measured for the spin-allowed transfer of an electron from $NO(X^2\Pi)$ to $Au^+(^1S)$, $Zn^+(^2S)$, $Se^+(^4S)$, $As^+(^3P)$ and $Hg^+(^2S)$ at room temperature using an inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. The observed range of a factor of 3 in the corresponding reaction efficiencies can be accounted for qualitatively by invoking energy resonance and Franck–Condon factors in the formation of $NO^+(X^1\Sigma^+, v)$. The electron transfer to $Se^+(^4S)$ may leave the neutral Se product atom in an excited $Se^*(4p^4, {}^3P)$ state.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Several simple models for low-energy (thermal) electron transfer reactions in the gas phase have been discussed in the literature [1,2]. For electron transfer from diatomic molecules these include the Franck–Condon model (in which ionization is controlled by Franck–Condon factors), the energy resonance model (in which the exothermicity of electron transfer is deposited maximally into vibrational and rotational excitation of the diatomic product ion [3–6]), and a statistical model involving the formation of a long-lived complex (in which excess energy is distributed statistically between translation, rotation and vibration). No one of these models can explain the experimental results obtained for electron transfer reactions generally and the experimental database available for the assessment of these models is limited. Here, we report experimental results that we have obtained recently for the thermal-energy electron transfer from NO to five atomic metal cations that significantly add to this database and allow a further evaluation of the available models for electron transfer.

We have measured the efficiencies for electron-transfer reactions of type (1) at room temperature with the atomic metal cations, $M^+ = Au^+$, Zn^+, Hg^+, As^+ and Se^+.

$$M^+ + NO(X^2\Pi) \rightarrow NO^+(X^1\Sigma^+, v) + M \qquad (1)$$
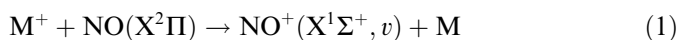
The measurements indicate a striking range in the efficiency of electron transfer (a factor of 3) and so provide a good opportunity to assess the importance of the role of energy resonance and Franck–Condon factors in determining this efficiency.

An early application of the charge-exchange mass spectrometry (CEMS) technique has provided measurements of the electron-transfer cross-sections for 33 positive ground-state *molecular* cations (with ground-state recombination energies ranging from 9.12 to 10.87 eV) projected at thermal NO with 10 eV kinetic energy [7]. The positions of the maxima in the measured dependence of the absolute electron-transfer cross-sections on the recombination energies of the positive ions exhibit remarkable resonances with the first five vibrational energy levels of $NO^+(X^1\Sigma^+, v)$. Furthermore, the normalized peak heights correspond qualitatively with the relative magnitudes of the respective Franck–Condon factors for $NO(X^2\Pi, v = 0) \rightarrow NO^+(X^1\Sigma^+, v = 0$–$4)$. These results provide a striking demonstration of the role of energy resonance and Franck–Condon

---

* Corresponding author. Fax: +1 416 736 5936.
  E-mail address: dkbohme@yorku.ca (D.K. Bohme).

Table 1
(Evaluated) ionization energies in eV [8]

Au	9.22567
NO($X^2\Pi$)	9.2642 ± 0.0002
Zn	9.39405
Se	9.75238
As	9.8152
Hg	10.43750

factors in determining the efficiency of electron transfer from NO to *molecular* cations.

Here, we focus on electron transfer from NO to *atomic* cations. The recombination energies of the electronic ground states of the five atomic metal cations investigated range from 9.22 to 10.44 eV [8] (see Table 1) and so, in principle, also can 'sample' the five lowest vibrational states of $NO^+(X^1\Sigma^+, v)$. A much more exothermic electron transfer from NO has been studied previously with several atomic non-metal cations. The electron transfer to $O^+(^4S)$(IE(O) = 13.6 eV) to give the spin-allowed ground-state products has been shown to require an 'extreme position hop' while the very favorable resonance and Franck–Condon conditions for the formation of nearly resonant $O(^1S) + NO^+(X^1\Sigma^+, v = 0)$ is spin forbidden [6]. Electron transfer from NO to $O^+(^4S)$ has been reported to be slow at room temperature, $k < 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [9,10], but shows an onset at 0.2 eV which has been attributed to the spin-forbidden formation of the excited atom $O(^1D)$ [11]. A detailed resonance and Franck–Condon analysis also has been reported for the even more exothermic electron transfer to $N^+(^3P)$ (IE(N) = 14.5 eV) which has three exothermic and spin-allowed channels and has been shown by several groups to be quite fast at room temperature, $k \approx 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [12].

2. Experimental method

The experimental results reported here were obtained using the inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer in the Ion-Chemistry Laboratory at York University, described in detail elsewhere [13,14]. The atomic metal cations were generated in an inductively-coupled argon plasma ion source at ca. 5500 K. Solutions containing the metal salt of interest having concentration of ca. 5 μg l^{-1} were peristaltically pumped via a nebulizer into the plasma. The atomic metal ions emerging from the ICP are largely in their ground electronic states: the ground-state populations at the ICP temperature of 5500 K have been calculated to be 97.0% for $Au^+(^1S)$, 100% for $Zn^+(^2S)$, 94% for $Se^+(^4S)$, 98.6% for $As^+(^3P)$ and 100% for $Hg^+(^2S)$ [15]. After extraction from the ICP, the plasma ions may experience both radiative electronic-state relaxation and collisional electronic-state relaxation. The latter may occur with argon as the extracted plasma cools upon sampling and then by collisions with He atoms in the flow tube (ca. 4×10^5 collisions) prior to the reaction region. The large number of collisions with Ar and He should be sufficient to ensure that the atomic

ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region. In the case of Se^+, the minor isotopes of $^{76}Se^+$ and $^{78}Se^+$ were selected upstream and monitored downstream to avoid obfuscation by $^{80}Se^+$ that overlaps with Ar_2^+ generated in the ICP.

The NO reagent gas had a nominal purity of 99.5% (BOC gases). Reaction rate coefficients were determined in the usual manner [16,17]. Primary rate coefficients are determined from the observed semi-logarithmic decay of the primary reactant ion intensity using pseudo-first order kinetics. The rate coefficients for the primary reported herein have an absolute accuracy of $\pm 30\%$.

3. Results and discussion

The results of the rate coefficient measurements are summarized in Table 2. Also included are calculated reaction efficiencies expressed as k/k_c. The collision rate coefficients, k_c, are calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich [18] with $\alpha(NO) = 1.70 \times 10^{-24}$ cm^3 and $\mu_D = 0.161$ Debye [19]. Fig. 1 shows data for two of the five reactions that were investigated. For the most part,

Table 2
Rate coefficients (in units of cm^3 molecule^{-1} s^{-1}) and reaction efficiencies (k/k_c) measured for reactions of metal cations with nitric oxide in helium at 0.35 ± 0.01 Torr and 295 ± 2 K

Reaction	k^a	k_c^b	k/k_c
$Zn^+ + NO \rightarrow NO^+ + Zn$	9.7×10^{-11}	7.1×10^{-10}	0.14
$As^+ + NO \rightarrow NO^+ + As$	3.2×10^{-10}	7.0×10^{-10}	0.46
$Se^+ + NO \rightarrow NO^+ + Se$	3.0×10^{-10}	6.9×10^{-10}	0.43
$Au^+ + NO \rightarrow NO^+ + Au$	1.0×10^{-10}	6.3×10^{-10}	0.16
$Hg^+ + NO \rightarrow NO^+ + Hg$	1.2×10^{-10}	6.3×10^{-10}	0.19

[a] The estimated uncertainty is $\pm 30\%$.
[b] Collision rate coefficient calculated using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich [18].
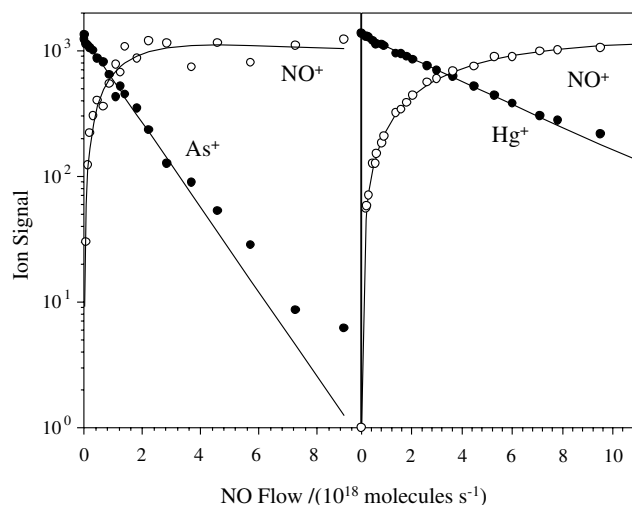

Fig. 1. Experimental data for the electron-transfer reactions of As^+ and Hg^+ with NO in helium buffer gas at 0.35 Torr and 295 K.

these electron-transfer reactions are fairly rapid when exothermic with $k \geqslant 9.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} but do not have unit efficiency with $k/k_c \leqslant 0.46$. To the best of our knowledge, none of these rate coefficients and efficiencies has been reported previously.

The extent of the matches (or resonances) in the recombination energies of the reacting atomic cations and the vibrational manifold of NO$^+$(X$^1\Sigma^+$, $v = 1$–4) is evident in Fig. 2. The adiabatic ionization energy of NO is known accurately to be 9.2642 ± 0.0002 eV [8]. The energies of the vibrational levels of NO$^+$(X$^1\Sigma^+$, $v = 1$–4) were calculated using the Morse function $G(v) = \omega_e(v + 1/2) - x_e\omega_e(v + 1/2)^2$ with values of $\omega_e = 2376.42$ and $x_e\omega_e = 16.262$ cm^{-1} [8]. They are 9.555 eV ($v = 1$), 9.842 eV ($v = 2$), 10.125 eV ($v = 3$) and 10.404 eV ($v = 4$). The Franck–Condon factors for the transitions NO(X$^2\Pi$, $v = 0$) $\rightarrow$ NO$^+$(X$^1\Sigma^+$, $v = 0$ to 4) are, respectively, 0.48, 1.0, 0.92, 0.48 and 0.16 [7,20].

Fig. 2 shows that the closest energy resonance exists for the reaction of As$^+$(^{3}P) which also exhibits the highest electron-transfer efficiency. Also of note is the electron transfer to Au$^+$(^{1}S) that is very slightly endothermic (by 0.034 eV or 0.78 kcal mol^{-1}) but within thermal energy of $v = 0$ and so has a substantial efficiency of 0.16. An efficiency of 0.13 can be derived if the endothermicity is used in $\exp(-\Delta H/RT)$ and the Franck–Condon factor (0.48) is taken as the maximum probability for electron transfer.

The recombination energy of Hg$^+$, RE Hg$^+$(^{2}S), is nearly energy resonant with $v = 4$ but the low Franck–Condon (FC) factor appears to reduce the electron-transfer efficiency.

Zn$^+$(^{2}S) and Se$^+$(^{4}S) are furthest away from energy resonance with the nearest exothermic vibrational level, viz.

$v = 0$ and 1, respectively. This may explain why the electron transfer to Zn$^+$(^{2}S) is measured to have the lowest reaction efficiency. However, electron transfer to Se$^+$(^{4}S), furthest away (distance being measured only to the nearest exothermic outcome) from energy resonance (0.20 eV from $v = 1$), has an efficiency as high as As$^+$(^{3}P), within experimental error. Perhaps this is a consequence of the availability of the first excited state of Se, Se (4p^4, ^{3}P, $J = 1$), which lies 0.247 eV above the ground-state of Se [21]. If this is the case, then we have observed the electron-transfer reaction (2).

$$Se^+(^4S) + NO(X^2\Pi) \rightarrow NO^+(X^1\Sigma^+, v = 1)$$
$$+ Se^*(4p^4, {}^3P, J = 1) \qquad (2)$$
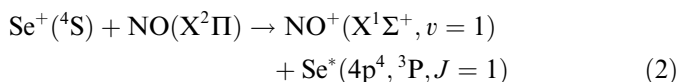
The first excited states of the other metal atoms Zn, Hg and As are too high to lead to alternative resonances in the electron transfer from NO(X$^2\Pi$) to their cations. Their formation is endothermic since the lowest excited energy levels for the metals are at 4.0 eV for Zn(4s^1 4p^1, ^{3}P), 1.3 eV for As(4s^2 4p^3, ^{2}D), 0.247 and 0.314 eV for Se(4p^4, ^{3}P, $J = 1$, 0), and 4.7 eV for Hg(5d^{10} 6s^1 6p^1, ^{3}P).

We conclude that the variations in the efficiencies for the five exothermic electron transfer reactions that were investigated, all of which are spin allowed, can be accounted for by noteworthy and intriguing combinations of energy resonance and Franck–Condon effects. Possibly we have identified another example of an electron-transfer from NO to an atomic cation, other than the electron transfer to O$^+$(^{4}S) at hyperthermal energies [11], that leaves the neutral atom in an excited state. However, we have not yet analysed the role of the rotational states of NO$^+$(X$^1\Sigma^+$, v) that also may lead to accidental energy resonances [3]. Finally, we note that NO is the only common diatomic species with an ionization energy that aligns well with the recombination energies of a series of metal cations.
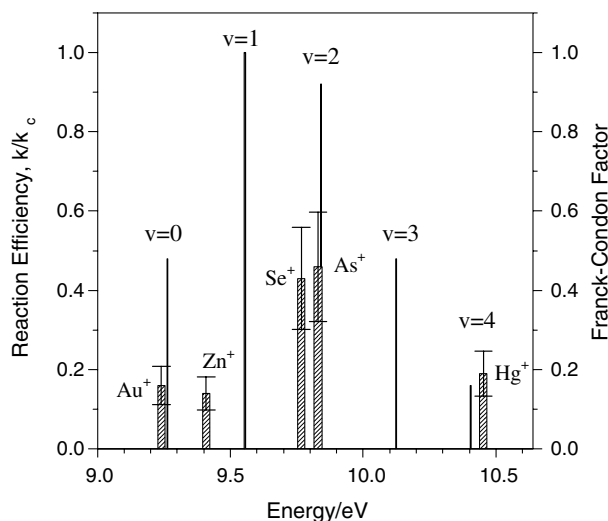
Acknowledgments

Fig. 2. Energy resonance diagram showing the positions of the recombination energies *RE* of the atomic ions investigated with respect to the vibrational energy levels of NO$^+$(X$^1\Sigma^+$, v). The heights of the lines designating the vibrational energy levels are proportional to the Franck–Condon factors for the transitions into these levels (normalized to the Franck–Condon factor for $v = 0$). The heights of the (hatched) bars (drawn with a thickness = *RT* and an onset at *RE*) represent the efficiencies of the electron-transfer reactions.

References

[1] V.M. Bierbaum, S.R. Leone, in: P. Ausloos, S.G. Lias (Eds.), Structure/Reactivity and Thermochemistry of Ions, D. Reidel, Dortrecht, The Netherlands, 1987, pp. 23–55.

[2] S. Kato, in: M.L. Gross, R. Caprioli (Eds.), The Encyclopedia of Mass Spectrometry, Theory and Ion Chemistry, vol. 1, Elsevier, Amsterdam, 2003, p. 276.

[3] D.K. Bohme, J.B. Hasted, P.P. Ong, J. Phys. B (Proc. Phys. Soc.) 1 (1968) 879.

[4] F.A. Houle, S.L. Anderson, D. Gerlich, T. Turner, Y.T. Lee, Chem. Phys. Lett. 82 (1981) 392.

[5] E.A. Gislason, G. Parlant, Comment. At. Mol. Phys. 19 (1987) 157.

[6] R.A. Dressler, D.J. Levandier, S. Williams, E. Murad, Comment. At. Mol. Phys. 34 (1998) 43.

[7] J.M. Tedder, P.H. Viddaud, Chem. Phys. Lett. 76 (1980) 380.

[8] P.J. Linstrom, W.G. Mallard, (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899. Available from: <http://webbook.nist.gov/chemistry/>.

[9] M. McFarland, D.L. Albritton, F.C. Fehsenfeld, A.L. Schmeltekopf, E.E. Ferguson, J. Geophys. Res. 79 (1974) 2005.

[10] J. Glosik, A.B. Rakshit, N.D. Twiddy, N.G. Adams, D. Smith, J. Phys. B 11 (1978) 3365.

[11] D.J. Levandier, Y. Chiu, R.A. Dressler, J. Chem. Phys. 112 (2000) 122.

[12] Y. Ikezoe, S. Matsuoka, M. Takebe, A. Viggiano, Gas-phase Ion–Molecule Reaction Rate Constants through 1986, Maruzen Co. Ltd., Tokyo, Japan, 1987.

[13] G.K. Koyanagi, V.V. Lavrov, V.I. Baranov, D. Bandura, S.D. Tanner, J.W. McLaren, D.K. Bohme, Int. J. Mass Spectrom. 194 (2000) L1.

[14] G.K. Koyanagi, V.I. Baranov, S.D. Tanner, D.K. Bohme, J. Anal. At. Spectrom. 15 (2000) 1207.

[15] V.V. Lavrov, V. Blagojevic, G.K. Koyanagi, D.K. Bohme, J. Phys. Chem. A 108 (2004) 5610.

[16] G.I. Mackay, G.D. Vlachos, D.K. Bohme, H.I. Schiff, Int. J. Mass Spectrom. Ion Phys. 36 (1980) 259.

[17] A.B. Raksit, D.K. Bohme, Int. J. Mass Spectrom. Ion Processes 55 (1983/1984) 69.

[18] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.

[19] Handbook of Chemistry and Physics, 78th ed., CRC Press, Boca Raton, 1997.

[20] M.E. Wicks, J. Phys. Chem. 41 (1964) 930.

[21] NIST Atomic Spectra Database. Available from: <http://physics.nist.gov/PhysRefData/ASD/index.html>.