

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231528008>

Oxygen Atom Transfer to Positive Ions: A Novel Reaction of Ozone in the Gas Phase

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JULY 1998

Impact Factor: 12.11 · DOI: 10.1021/ja971251j

CITATIONS

22

READS

16

6 AUTHORS, INCLUDING:



[Maria Anita Mendes](#)

University of São Paulo

69 PUBLICATIONS 1,308 CITATIONS

SEE PROFILE



[Luiz Alberto Moraes](#)

University of São Paulo

62 PUBLICATIONS 747 CITATIONS

SEE PROFILE

Oxygen Atom Transfer to Positive Ions: A Novel Reaction of Ozone in the Gas Phase

Maria Anita Mendes,[†] Luiz Alberto B. Moraes,[†] Regina Sparrapan,[†] Marcos N. Eberlin,^{*,†} Risto Kostiainen,[‡] and Tapio Kotiaho^{*,§}

Contribution from the Institute of Chemistry, State University of Campinas, UNICAMP CP6154, 13083-970 Campinas, SP Brazil, Department of Pharmacy, Division of Pharmaceutical Chemistry, P.O. Box 56 (Viikinkaari 5), 00014 University of Helsinki, Helsinki, Finland, and VTT Chemical Technology, P.O. Box 140, FIN-02044 VTT, Espoo, Finland

Received April 21, 1997

Abstract: In the gas phase, neutral ozone (O_3) transfers an oxygen atom to several positive ions, *i.e.* the radical cations of pyridines ($R-Py^+$; $R = H, CH_3, C_2H_5$, and Cl), pyrimidine (Pi^+), and alkyl halides (CH_3X^+ ; $X = Cl$ and I), and the halogen cations (X^+ ; $X = Cl, Br$, and I). Reactivity changes drastically within the halogen series ($Cl^+ \ll Br^+ \leq I^+$), whereas no O-transfer occurs to F^+ . The oxide derivatives $R-Py^+-O^+$, Pi^+-O^+ , $CH_3X^+-O^+$, and XO^+ are formed, as demonstrated by pentaquadrupole ($QqQqQ$) double- and triple-stage mass spectrometry. No oxygen atom transfer occurs, however, in “inverse” reactions, *i.e.*, those of ionized ozone (O_3^+) with the corresponding neutrals; and charge transfer dominates. *Ab initio* calculations suggest that O-transfer from ozone to ionized pyridine yields ionized pyridine *N*-oxide *via* simple nucleophilic addition of ozone as opposed to 1,3-dipolar cycloaddition. Similar nucleophilic addition followed by O_2 loss is also the most likely mechanism for O-transfer from ozone to the ionized alkyl halides and halogen cations. This novel O-transfer reaction to positive ions, which expands our knowledge of the rich chemistry of ozone, introduces a new pathway for the gas-phase oxidation of halogen atoms, pyridines, pyrimidines, alkyl halides, and analogues, and consequently for the gas-phase generation of their chemically interesting but difficult to access ionized oxides.

Introduction

Ozone (O_3), the less stable form of elemental oxygen, plays a key role in the upper atmosphere by acting as a vital ultraviolet light screen.¹ In solution, ozone acts as a strong oxidizing agent, an electrophile or nucleophile, and the diverse chemical behavior of ozone has been widely exploited in condensed-phase chemistry.² The accumulation of electronegative oxygen atoms in the ozone molecule makes it also a very electrophilic 1,3-dipole; hence it reacts promptly in concerted 1,3-dipolar cycloadditions with many olefins. Cycloaddition to olefins affords highly unstable trioxolanes, *i.e.* ozonides, the key intermediates in the cleavage of carbon–carbon double bonds by *ozonolysis*,³ an important reaction of ozone that is applied in synthetic and analytical procedures.

Because of its vital importance in atmospheric and condensed-phase chemistry, the physical and chemical properties of ozone in both its neutral and ionized forms have been studied extensively.^{1,4} The neutral/neutral and negative ion/neutral reactions of ozone have been studied thoroughly, but its positive ion/neutral reactions (O_3^+/M or M^+/O_3) have received much

less attention. Few examples are reported, such as the reaction of neutral ozone with metal cations,^{1a} and with strong Brønsted acids.⁵ The reactions of ozone with CH_5^+ , for instance, allowed the first experimental detection of the elusive protonated ozone (O_3H^+), the estimation of its proton affinity, and the study of the reactions of O_3H^+ with methane.⁵

In the present study, ion/molecule reactions of neutral ozone with positive ions, *i.e.* ionized organic molecules (M^+) and halogen cations (X^+), have been investigated in the gas phase by double- (MS^2) and triple-stage (MS^3)⁶ pentaquadrupole ($QqQqQ$) mass spectrometry,⁷ as well as those of ionized ozone with the corresponding neutrals (O_3^+/M). Neutral ozone was observed to transfer readily an oxygen atom to several positive

[†] State University of Campinas.

[‡] University of Helsinki.

[§] VTT Chemical Technology.

(1) (a) McEwan, M. J.; Phillips, L. F. *Chemistry of the Atmosphere*; Edward Arnold Ltd., London, 1975. (b) Molina, M. J. *Pure Appl. Chem.* **1996**, 68, 1749. (c) Slinger, T. G. *Science* **1994**, 265, 1817.

(2) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985. (b) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984.

(3) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1.

(4) (a) Smith, D.; Spanel, P. *Mass Spectrom. Rev.* **1995**, 14, 255. (b) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, 84, 437. (c) Steinfeld, J. I.; Adler-Golden, S. M.; Gallagher, J. W. *J. Phys. Chem. Ref. Data* **1987**, 16, 911. (d) Wang, N. S.; Howard, C. J. *J. Phys. Chem.* **1990**, 94, 8787. (e) Schmelz, T.; Chamblaud, G.; Rosmus, P.; Köppel, H.; Cederbaum, L.; Werner, H.-J. *Chem. Phys. Lett.* **1991**, 183, 209. (f) Dominé, F.; Ravishankara, A. R.; Howard, C. J. *J. Phys. Chem.* **1992**, 96, 2171. (g) Viggiano, A. A. *Mass Spectrom. Rev.* **1993**, 12, 115. (h) Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, 18, 75. (i) Fedchak, J. A.; Peko, B. L.; Champion, R. L. *J. Chem. Phys.* **1995**, 103, 981. (j) Li, Z.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1995**, 99, 13445. (k) Arnold, S. T.; Morris, R. A.; Viggiano, A. A. *J. Chem. Phys.* **1995**, 103, 2454. (l) Huey, L. G.; Hanson, D. R.; Howard, C. J. *J. Phys. Chem.* **1995**, 99, 5001. (m) Newson, K. A.; Luc, S. M.; Price, S. D.; Mason, N. J. *Int. J. Mass Spectrom. Ion Processes* **1995**, 148, 203. (n) Newson, K. A.; Price, S. D. *Int. J. Mass Spectrom. Ion Processes* **1996**, 153, 151. (o) Garner, M. C.; Sherwood, C. R.; Hanold, K. A.; Continetti, R. E. *Chem. Phys. Lett.* **1996**, 248, 20.

(5) Cacace, F.; Speranza, M. *Science* **1994**, 265, 208.

(6) Schwartz, J. C.; Wade, A. P.; Enke, C. G.; Cooks, R. G. *Anal. Chem.* **1990**, 62, 1809.

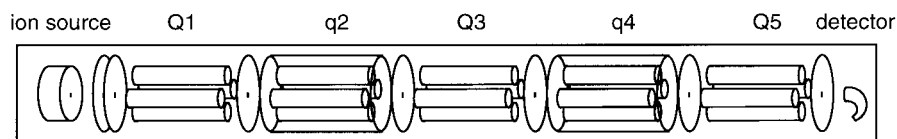


Figure 1. A diagram of the pentaquadrupole mass spectrometer. Q1, Q3, and Q5 are mass-analyzer quadrupoles whereas q2 and q4 function as ion-focusing reaction chambers. In a typical ion/molecule reaction experiment, ions are generated in the ion source, purified (mass-selected) by Q1, and further reacted under controlled conditions (collision energy and pressure) with a neutral gas introduced in q2. Product ions of interest are then mass selected by Q3, and structurally analyzed by collision-induced dissociation or structurally diagnostic ion/molecule reactions in q4, while Q5 is scanned to acquire the triple-stage mass spectra. For more details see ref 7f.

ions ($M^{+•}$, X^{+}) in a novel gas-phase oxidation reaction that affords the ionized *N*-oxide derivatives ($M^{+•}\text{-O}^{•}$, XO^{+}) as the main ionic products.

Methods

The study was carried out via MS^2 and MS^3 experiments⁶ performed in an Extrel [Pittsburgh, PA] pentaquadrupole (QqQqQ) mass spectrometer, a versatile instrument for studying of ion/molecule reactions in the gas phase.⁷ In the QqQqQ⁸ (Figure 1) three mass analyzing (Q1, Q3, Q5) and two "rf-only" reaction quadrupoles (q2, q4) are placed sequentially. Ions are formed in the ion source, each desired ion is "purified" one at a time via mass selection in Q1, and their reactions are performed in q2 with selected neutrals at controlled conditions such as collision energy and concentration (neutral gas pressure). Product ions produced in q2 are mass selected one at a time by Q3 for further structural investigation in q4 via either structurally diagnostic collision-induced dissociation (CID)⁹ or ion/molecule reactions, whereas Q5 is scanned to collect the triple-stage (MS^3) product spectra. Collision energies of 1 eV (calculated by the m/z 39:41 ratio in neutral ethylene/ionized ethylene reactions¹⁰) were applied for ion/molecule reactions in q2, whereas 15 eV CID with argon were performed in q4. The total pressures inside each differentially pumped region were typically 2×10^{-6} (ion-source), 8×10^{-6} (q2), and 8×10^{-5} (q4) Torr.

(7) (a) Gozzo, F. C.; Eberlin, M. N. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 554. (b) Moraes, L. A. B.; Pimpim, R. S.; Eberlin, M. N. *J. Org. Chem.* **1996**, *61*, 8726. (c) Eberlin, M. N.; Sorilha, A. E. P. M.; Gozzo, F. C.; Pimpim, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 3550. (d) Moraes, L. A. B.; Gozzo, F. C.; Eberlin, M. N.; Vaniootalo, P. *J. Org. Chem.* **1997**, *62*, 5096. (e) Carvalho, M.; Moraes, L. A. B.; Kascheres, C.; Eberlin, M. N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2347. (f) Eberlin, M. N. *Mass Spectrom. Rev.* **1997**, *16*, 113.

(8) Juliano, V. F.; Gozzo, F. C.; Eberlin, M. N.; Kascheres, C.; Lago, C. L. *Anal. Chem.* **1996**, *68*, 1328.

(9) (a) McLafferty, F. W. *Tandem Mass Spectrometry*; Wiley: New York, 1983. (b) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (c) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169. (d) Cooks, R. G.; Beynon, J. H.; Caprioli, C.; Lestes, J. R. *Metastable Ions*; Elsevier: New York, 1973. (e) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*; VHC: New York, 1988.

(10) Tiernan, T. O.; Futrell, J. H. *J. Phys. Chem.* **1968**, *72*, 3080.

(11) Newson, K. A.; Luc, S. M.; Price, S. D.; Mason, N. J. *Int. J. Mass Spectrom. Ion Processes* **1995**, *148*, 203.

(12) Gaussian 94, Revision B.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomper, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *72*, 650.

(14) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(15) Dissociation occurs even under the low energy collision conditions used for the ion/molecule reactions likely owing to the high efficiency of transfer of translational to internal energy that occurs in quadrupole collision cells, see: Douglas, D. J. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 101.

(16) Considering that very similar q2 collision conditions were applied for all reactions, the ratios of the sum of the abundance of ionic products to that of surviving reactant ion were used as estimates of both reaction yields and relative reactivities.

Table 1. Ionic Products [m/z (Relative Abundance)^a] of Reactions between Several Positive Ions and the O_3/O_2 Mixture

ion ($M^{+•}$ or X^{+})	O-transfer	charge transfer ($\text{O}_2^{+•}$)	dissociation products of $M^{+•}$
pyridine ^{+•} ^b	95 (100)	none	52(2), 39(2)
3-chloropyridine ^{+•} ^b	129(100)	none	78(8)
2-methylpyridine ^{+•}	109(14)	none	65, 66, 67(3)
3-methylpyridine ^{+•}	109(27)	none	65, 66, 67(8)
4-methylpyridine ^{+•}	109(34)	none	65, 66, 67(9)
pyrimidine ^{+•}	96(100)	none	53(5)
4-ethylpyridine ^{+•}	123 (42)	none	106(12)
pyrazole ^{+•}	none	none	41(2)
thiophene ^{+•}	none	none	none
benzene ^{+•}	none	none	52(4), 51(1)
bromobenzene ^{+•}	none	none	77(28)
benzyl bromide ^{+•}	none	none	91(7)
ethylene ^{+•}	none	none	27(22)
isoprene ^{+•}	none	none	67(8), 53(1)
$\text{CH}_3\text{CN}^{+•}$	none	32(100)	40(6)
$\text{CH}_3\text{Cl}^{+•}$ ^b	66(100)	32(12)	49(12)
$\text{CH}_3\text{I}^{+•}$ ^b	158(100)	none	none
$\text{NH}_2\text{Cl}^{+•}$ ^c	none	none	none
$\text{CH}_4^{+•}$	none	32(100)	15(19)
F^{+} ^b	none	32(100)	
Cl^{+} ^b	51(3)	32(100)	
$^{79}\text{Br}^{+}$ ^b	95(100)	none	
I^{+} ^b	143(100)	none	

^a When no signal of 100% relative abundance is reported, the base signal was the surviving reactant ion. ^b Spectrum shown as a figure, see text. ^c Chloramine was sampled via membrane introduction mass spectrometry, see ref 19.

The ionized neutrals were generated by 70 eV electron ionization (EI) of their neutral counterparts, whereas the halogen cations were formed by dissociative 70 eV EI of CF_3Cl , CH_3Cl , CH_3Br , and CH_3I . Ozone was made from high-purity dried O_2 in a custom-made ozonator and trapped on silica gel at -72°C .¹¹ The enriched O_3/O_2 mixture was introduced in q2 to obtain an instrument overall pressure of approximately 8×10^{-6} Torr (the actual pressure inside the collision cell is estimated to be close to 0.1 mTorr). Maximum yields of products were observed after 1–2 h of continuous flow of the gas mixture probably because of initial reactions of ozone with background compounds present in the gas lines.

Ab initio molecular orbital calculations were carried out by Gaussian94.¹² The species were optimized at the (HF) Hartree–Fock level of theory by employing the polarization 6-31G(d,p) basis set.¹³ Improved energies were obtained by single-point calculations at the HF/6-31G(d,p) level and incorporating valence electron correlation calculated by second-order Møller–Plesset (MP2) perturbation theory.¹⁴ Harmonic vibrational frequencies were calculated at the HF/6-31G(d,p) level and used to characterize the stationary points and to obtain the zero-point vibrational energies (ZPE).

Results and Discussion

Several chemical species (mostly organic molecules), both in their neutral and ionized forms, were reacted with ionized or neutral ozone, respectively, via double-stage (MS^2) experiments. The resulting product spectra display therefore the ionic products arising from collisions of the mass-selected ion with the neutral reactant.

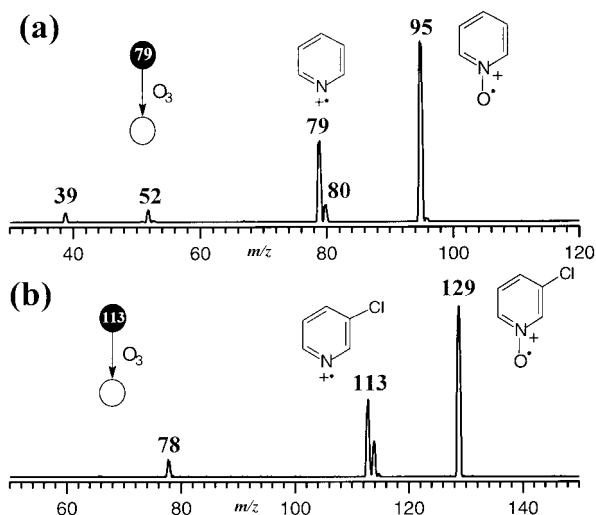
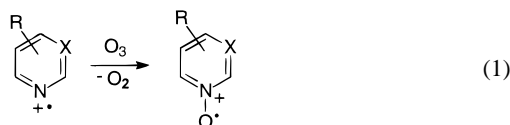


Figure 2. Pentaquadrupole double-stage (MS²) product spectra for reactions of (a) ionized pyridine and (b) ionized 2-chloropyridine with neutral ozone. Note the O-transfer products of *m/z* 95 and 129.

M⁺/O₃ reactions. Most of the positively charged species react with neutral ozone (Table 1) mainly by charge transfer or undergo collision-induced dissociation,¹⁵ or both. However, several ionized pyridines, alkyl halides, and halogen atoms react with neutral ozone to yield mainly product ions of a formal O-transfer reaction, i.e. the ionic products display *m/z* ratios 16 units higher than that of the reactant ion.

Ionized Pyridines. O-transfer from ozone to ionized pyridine occurs in high yield,¹⁶ and the product of *m/z* 95 represents more than 95% of the total product ion current (Figure 2a). The O-transfer product of ionized pyridine is best rationalized as ionized pyridine *N*-oxide (eq 1, R = H, X = CH). O-transfer from ozone also occurs in high to medium yields to several ionized pyridine derivatives, i.e. 2-, 3-, and 4-methylpyridine, 4-ethylpyridine (Table 1), 3-chloropyridine (Figure 2b), and the ionized 1,3-dinitrogen analogue pyrimidine (Table 1, eq 1, R = H, X = N).



Ionized Halogen Atoms. Figure 3 shows the product spectra for reactions of X⁺ (X = F, Cl, Br, I) with neutral ozone. O-transfer to X⁺ is not general, and a drastic change in reactivity occurs. Note in Figure 3 that the higher the atomic number of the halogen atom the higher the yield¹⁶ of the O-transfer product XO⁺. In fact, no product of O-transfer to F⁺, i.e. FO⁺ of *m/z* 35, is formed (Figure 3a), and O₂⁺ of *m/z* 32 dominates. Several pathways may account for formation of O₂⁺ in the F⁺/O₃(O₂) reactions. F⁺ may undergo charge transfer with O₃, and O₃⁺ may dissociate subsequently to O₂⁺ or undergo charge transfer with O₂ present in the reaction mixture. Charge transfer may, however, occur directly from F⁺ to O₂. Charge transfer of F⁺ to both O₃ and O₂ is expected to be highly favored owing to the high ionization potential (IP) of the F atom (17.42 eV) when compared to that of O₃ (12.43 eV) and O₂ (12.07 eV).¹⁷

O-transfer may in fact occur from ozone to F⁺, but FO⁺ could be consumed rapidly owing to favorable charge transfer to O₃ or O₂ [the FO• radical (12.77 eV) has a slightly greater ionization

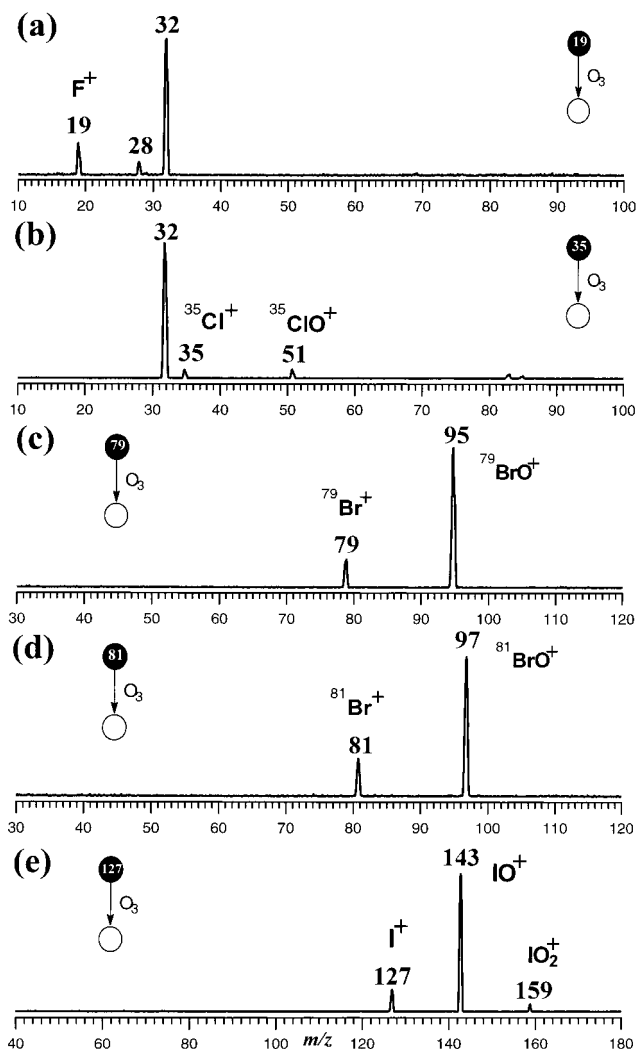


Figure 3. Pentaquadrupole double-stage (MS²) product spectra for reactions of (a) F⁺, (b) ³⁵Cl⁺, (c) ⁷⁹Br⁺, (d) ⁸¹Br⁺, and (e) I⁺ with neutral ozone. Note that no O-transfer occurs to F⁺, whereas increasing yields of the XO⁺ product ions are observed in the following order: Cl⁺ ≪ Br⁺ ≤ I⁺.

energy than O₂ (12.07 eV) and O₃ (12.43 eV)¹⁷). To investigate this possibility, reactions of F⁺ with the O₃/O₂ mixture were performed under mainly single collision conditions by using much lower pressures in q2. The secondary reaction of FO⁺ with O₃ or O₂ should be disfavored under single collision conditions; hence, if indeed FO⁺ is formed as the primary product, it should be detected in the low-pressure product spectra. No FO⁺ was detected, however, when working on a range of low-pressure conditions. This finding suggests that if O₂⁺ is formed by charge transfer, it must occur directly from the primary F⁺ reactant ion. An alternative remains for a process suppressing O-transfer from O₃ to F⁺, i.e. the highly electrophilic F⁺ may abstract O• from ozone (oxygen anion transfer), a reaction that would yield O₂⁺ and the FO• radical.

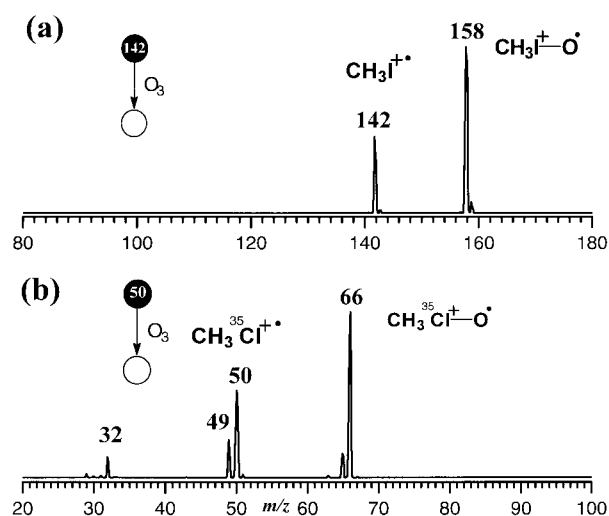
The IP of the chlorine radical (12.97 eV) is just slightly higher than that of O₃ and O₂; hence reactions of Cl⁺ with the O₃/O₂ mixture occur predominantly by charge transfer or alternatively by oxygen anion transfer (O₂⁺ of *m/z* 32), but also modestly by O-transfer yielding ClO⁺ of *m/z* 51 (Figure 3b). Note that secondary charge transfer of ClO⁺ to O₃/O₂ is not expected because the ionization energy of the ClO• radical (10.95 eV)¹⁷ is considerably lower than that of O₃ and O₂.

(17) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

Table 2. Ionic Products [m/z (Relative Abundance)] of Reactions between Ionized Ozone (O_3^{+*}) and Several Neutral Compounds

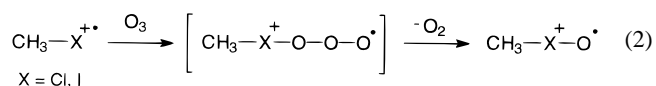
neutral reactant (M)	charge transfer (M^{+*})	O_2^{+*}	M^{+*} dissociation products	other products
$CH_2=CH_2$	28(100)	32(58)	none	41(100), 69(18) ^a
$CH_2=CH-CH_2-Cl$	76, 78(100)	32(20)	41(57)	81(57)
isoprene	68(10)	32(18)	67(100)	81, 95, 107, 135 (23) ^b
benzene	78(100)	32(8)	none	none
styrene	104(100)	32(4)	none	none
furan	68(100)	32(3)	none	none
thiophene	84(100)	32(3)	none	none
pyridine	79(47)	32(68)	none	80(100) ^c
pyrimidine	80(100)	32(45)	none	81(82) ^c
anisole	108(100)	32(34)	none	none
3-chlorothiophene	118, 120(100)	32(5)	none	none
CH_3-S-CH_3	62(100)	32(15)	61(98), 49(8)	none
$C_2H_5-S-S-C_2H_5$	122(100)	32(28)	94, 66(3)	none
CH_3I	142(100)	32(1)	none	157(32) ^d
CH_3Cl	50(100)	32(7)	49(25)	none
CO	none	32(100)	none	none
CO_2	none	32(100)	none	none

^a Secondary products of ionized ethylene. ^b Secondary products of ionized isoprene, see ref 20. ^c Protonated Neutral. ^d The secondary $CH_3-I^+-CH_3$ product.

**Figure 4.** Pentaquadrupole double-stage (MS^2) product spectra for reactions of (a) CH_3I^{+*} and (b) CH_3Cl^{+*} with neutral ozone. Note the O-transfer product of m/z 158 and 66.

The Br (11.81 eV) and I (10.45 eV) atoms display IP's considerably lower than that of O_3 ; hence, in reactions of Br^{+*} (Figure 3c,d) and I^{+*} (Figure 3e) with O_3 , the O-transfer products $^{79}BrO^+$ of m/z 95 and IO^+ of m/z 143 are formed in high yields,¹⁶ i.e. they constitute practically 100% of the product ion current. O-transfer from O_3 to $^{79}Br^{+*}$ (Figure 3c) was confirmed by reacting $^{81}Br^{+*}$ (Figure 3d) and noting formation of $^{81}BrO^+$ of m/z 97.

Ionized Alkyl Halides. O-transfer is also a major reaction of ozone with ionized methyl iodide (Figure 4a) and methyl chloride (Figure 4b). Simple mechanistic considerations suggest the corresponding oxides $CH_3X^+-O^{\bullet}$ ($X = Cl, I$) to be the most likely products (eq 2).



"Inverse" M/O_3^{+*} Reactions. Ionized ozone (O_3^{+*}) was also reacted with some neutrals, including pyridine, pyrimidine, methyl chloride, and methyl iodide (Table 2). However, no O-transfer products were formed, and charge transfer dominates. Both the lack of O-transfer and the dominance of charge transfer for the M/O_3^{+*} reactions are rationalized in terms of the lower

IP's of the neutrals (for instance, IP of pyridine = 9.25 eV) when compared to that of ozone (12.43 eV).¹⁷

After charge transfer, however, the ion/neutral complexes in the "inverse" reactions are the same as those in the "direct" reactions [$M + O_3^{+*} \rightarrow M^{+*}/O_3 \leftarrow M^{+*} + O_3$]. An obvious difference between the ion/neutral complexes from both reactions is their internal-energy content. Therefore, even the "inverse" reaction could become efficient in promoting O-transfer if the energy content of the ion/neutral complex is reduced. Quenching of the ion/neutral complex could be achieved, for instance, by varying the translational energy of the O_3^{+*} reactant or via collisional deactivation. Thus, the reactions of O_3^{+*} with all the neutrals reported in Table 2 were performed in the whole range of translational energies in which reactions occur, i.e. from nominal -1 eV to 3 eV.¹⁰ In another effort to promote collisional quenching of the ion/neutral complexes, the neutral gas pressures in the collision cell (q2) were varied to cause depletion of the O_3^{+*} current from 5% to 95%. No O-transfer products were detected in any of these conditions. Hence, either the nascent neutral ozone is much too "hot" and dissociates rapidly after exothermic charge transfer (for instance reaction of O_3^{+*} with neutral pyridine gives 3.18 eV¹⁷ excess energy after charge transfer) or the ion/neutral complexes M^{+*}/O_3 formed in the "inverse" reactions are too short-lived for collisional quenching.

The Neutral Reactant: O_3 or O_2 ? Owing to incomplete conversion of O_2 to O_3 and possible degradation of O_3 in the q2 gas lines, a considerable amount of O_2 is present in the reaction mixture.¹¹ Thus, O_2 could participate in the O-transfer reaction. To verify this possibility, the ions for which O-transfer occurs were reacted with pure O_2 under the same experimental conditions applied to the reactions with the O_3/O_2 mixture. Conditions were adjusted to maximize O-transfer with the O_3/O_2 mixture; then this mixture was replaced by pure O_2 . No O-transfer products remained, which confirms that O-transfer occurs from O_3 alone.

The Structures of the O-Transfer Products. The multiple ion-selection/reaction capabilities of the pentaquadrupole mass spectrometer⁸ (Figure 1) permitted "on-line" access to structural information of the O-transfer products via the recording of their

(18) Stevenson, D. P. *Discuss. Faraday Soc.* **1951**, 10, 35.

(19) (a) Kotiaho, T.; Eberlin, M. N.; Shay, B. J.; Cooks, R. G. *J. Am. Chem. Soc.* **1993**, 115, 1004. (b) Eberlin, M. N.; Kotiaho, T.; Cooks, R. G. *J. Am. Chem. Soc.* **1994**, 116, 2457.

(20) Eberlin, M. N.; Cooks, R. G. *J. Am. Chem. Soc.* **1993**, 115, 9226.

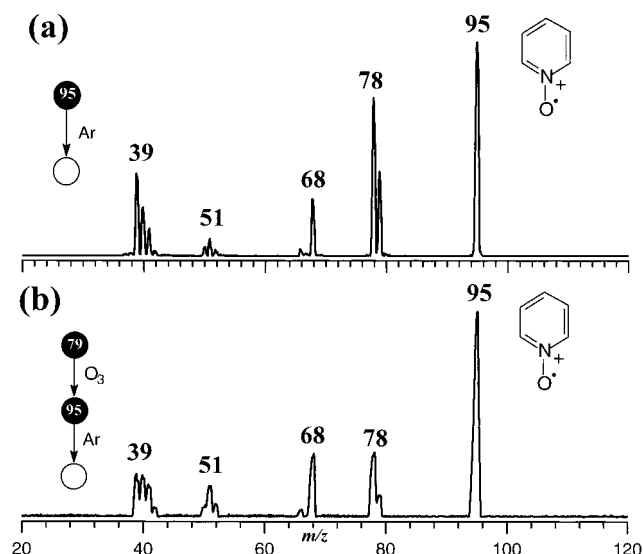


Figure 5. Pentaquadrupole (a) double-stage (MS²) dissociation product spectrum of ionized pyridine *N*-oxide generated by 70 eV EI of the neutral and (b) triple-stage (MS³) sequential product spectra of the O-transfer products arising from reactions of neutral ozone with ionized pyridine. The similarity of both spectra suggests O-transfer to the pyridine nitrogen.

sequential product spectra,⁶ typical examples of which are presented in Figures 5 and 6. To acquire these triple-stage (MS³) mass spectra, the O-transfer products were mass selected by Q3 and then subject to 15 eV dissociative collisions with argon in q4, whereas Q5 was scanned across the appropriate *m/z* range.

The triple-stage mass spectrum of the product of O-transfer to ionized pyridine is shown in Figure 5b, whereas Figure 5a shows the double-stage spectrum of an authentic ion, i.e. ionized pyridine *N*-oxide formed by direct ionization of the corresponding neutral. Both spectra are nearly identical, which provides solid evidence that Py⁺–O• is formed as the primary O-transfer product.

⁷⁹BrO⁺ (Figure 6a) and IO⁺ (Figure 6b) dissociate exclusively to ⁷⁹Br⁺ of *m/z* 79 and I⁺ of *m/z* 127, respectively, as predicted by the Stevenson's rule.¹⁸ This classic rule of ion dissociation states that the fragment ion of lower IP is formed preferentially. Hence, Br⁺ and I⁺ are the expected fragments considering the following IP's: O (13.62 eV), Br• (11.81), and I• (10.45).¹⁷

CH₃I⁺–O• of *m/z* 158 (Figure 6c) dissociates upon collision activation mainly by CH₃• loss to afford IO⁺ of *m/z* 143 (Figure 3d), whereas IO⁺ apparently dissociates in turn to I⁺ of *m/z* 127. In contrast, CH₃Cl⁺–O• of *m/z* 66 dissociates predomi-

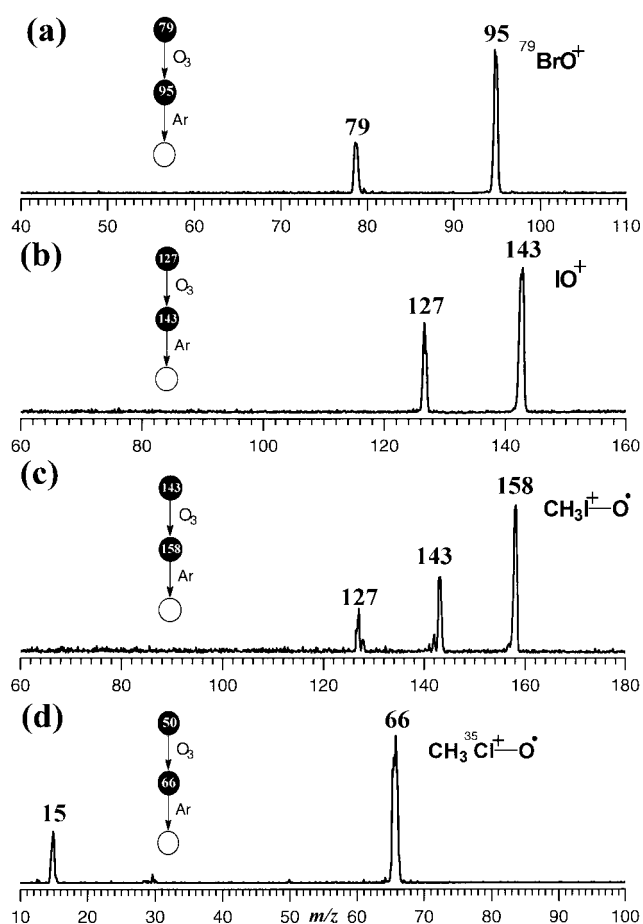


Figure 6. Pentaquadrupole triple-stage (MS³) sequential product spectra of the oxygen atom transfer products (a) ⁷⁹BrO⁺, (b) IO⁺ (c) CH₃IO⁺, and (d) CH₃ClO⁺.

nantly by ClO• loss (Figure 6d) to yield CH₃⁺ of *m/z* 15, as expected from the lower IP of the methyl radical [ClO• (10.95 eV) and CH₃• (9.84 eV)].

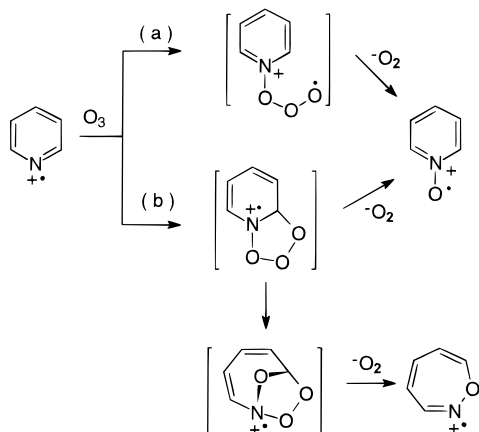
Ab Initio Calculations. Mechanism of O-Transfer to Pyridine. O-transfer of ozone to ionized pyridine could proceed via (a) a simple nucleophilic addition followed by O₂ loss to afford ionized pyridine *N*-oxide or (b) 1,3-dipolar cycloaddition forming primarily an 1,2,3-trioxolane bicyclic intermediate (Scheme 1). Direct dissociation by O₂ loss of the bicyclic intermediate would also yield ionized pyridine *N*-oxide, whereas prior isomerization via ring expansion to the corresponding 1,2,4-trioxolane bicyclic ring system (a process normally

Table 3. Total Energies from Structure Optimization MP2/6-31G(d,p)//6-31G(d,p) +ZPE ab Initio Calculations

species	MP2/6-31G(d,p)//6-31G(d,p) energy (hartree)	ZPE (hartree) ^a	MP2/6-31G(d,p)//6-31G(d,p)+ZPE ^a energy (hartree)
a	–247.19081	0.08201	–247.10880
O₃^b	–224.79448	0.00603	–224.78844
O₂^b	–149.94681	0.00405	–149.94276
b	–472.10457	0.09550	–472.00908
c	–472.06540	0.09538	–471.97002
d	–472.05317	0.09697	–471.95621
e	–322.12024	0.08280	–322.03744
f	–322.14345	0.08552	–322.05793

^a ZPE energies were scaled by 0.89. ^b Energies of the most stable triplet state.

Scheme 1



postulated for ozonolysis³) could produce an isomeric O-transfer product, *i.e.* ionized 1,2-oxazepine (Scheme 1).

To compare the energetics of these two alternative reaction pathways, an *ab initio* potential energy surface diagram (Figure 7) was elaborated (Table 3). Simple nucleophilic addition of ozone to ionized pyridine is shown to be far more exothermic (-70.1 kcal/mol) than cycloaddition (-45.7 kcal/mol). The less favorable 1,2,3-trioxolane cycloadduct, if formed to any extent, is predicted to dissociate directly by O_2 loss to yield also ionized pyridine *N*-oxide in a -6.3 kcal/mol exothermic process. Although the alternative isomerization of the 1,2,3-trioxolane to the 1,2,4-trioxolane cycloadduct, and further O_2 dissociation, would generate the more stable O-transfer product, *i.e.* ionized 1,2-oxazepine (Figure 7), both the endothermicity of the initial isomerization (8.7 kcal/mol) and the substantial high energy barrier expected for the isomerization process must suppress this reaction pathway.

Therefore, from the calculations summarized in Figure 7, O-transfer from ozone to pyridine proceeds mainly via simple nucleophilic addition of ozone and generates, upon O_2 loss, ionized pyridine *N*-oxide as the main ionic product. This theoretical prediction agrees with the MS^3 experiments that, as already discussed, also suggest formation of ionized pyridine *N*-oxide. Note that isomerization of ionized pyridine *N*-oxide to the more stable 1,2-oxazepine isomer is expected to be hampered by a substantial energy barrier for ring expansion. This isomerization may occur to some extent, however, under collisional activation, as the HCN loss that occurs for both the O-transfer product of pyridine and the authentic ionized pyridine *N*-oxide (the fragment of m/z 68 in Figure 5) is best rationalized from the isomeric 1,2-oxazepine structure.

Concluding Remarks

Oxygen anion (O^-) and O-transfer are commonly observed in negative ion–neutral reactions and neutral–neutral reactions

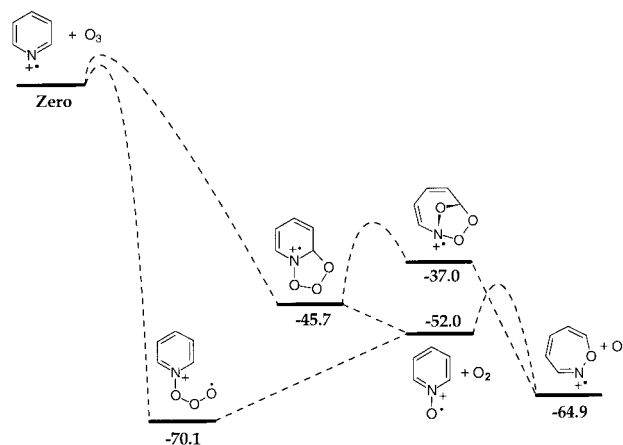


Figure 7. *Ab initio* MP2/6-31G(d,p)//6-31G(d,p) + ZPE potential energy surface diagram for reactions of ionized pyridine with neutral ozone. Energy barriers were not estimated. Energies are given in kcal/mol. The less energetic reaction pathway is represented by simple nucleophilic addition followed by O_2 loss that yields ionized pyridine *N*-oxide.

of ozone.⁴ For example, it has been observed that neutral ozone transfers an oxygen atom to $\text{CH}_3\text{S}^\bullet$, $\text{CH}_3\text{SS}^\bullet$,^{4f} and HS^\bullet ^{4d} and to NO_2^- .^{4c} It has also been reported that O_3^\bullet transfers an oxygen anion (O^-) to CO_2 ^{4a} and NO_2 .^{4k} Therefore, the reactivity of $\text{O}_3^{+\bullet}$ described herein contrasts to that of its negative counterpart $\text{O}_3^{\bullet-}$, *i.e.* $\text{O}_3^{+\bullet}$ reacts with a variety of neutral species exclusively by charge transfer whereas O-transfer is common for O^- . The present results show, however, that O-transfer is achieved when the reaction is performed with *neutral ozone* and some selected positively charged species.

In the 70's it was reported that O-transfer occurs from O_3 to inorganic ions such as NO^+ , K^+ , Fe^+ , Mg^+ , and Cu^+ .^{1a} For the first time, therefore, neutral ozone is shown to transfer efficiently an oxygen atom to halogen cations, most efficiently to Br^+ and I^+ , and two classes of organic ions, *i.e.* ionized alkyl halides and ionized nitrogenated aromatic compounds. This novel O-transfer reaction, which reveals a new pathway by which ozone acts as a strong oxidizing agent, opens a new route to generate and study several ionized oxides in the gas phase. They include ionized pyridine and pyrimidine *N*-oxides, and some difficult to access but chemically fascinating species such as $\text{CH}_3\text{X}^+-\text{O}^\bullet$ and the oxohalogen cations XO^+ .

Acknowledgment. This work was supported by the Research Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq). T.K. acknowledges FAPESP for a visiting researcher scholarship.

JA971251J