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[14] a) Two different pathways, one of which proceeds by means of Li^1–R cleavage and the other by means of Li^2–R cleavage, are possible for **1b**. Only the former pathway is discussed here, since the energy profile of the latter was found to be essentially the same as that of the former. b) An isomer of **1c**, in which the CN group is oriented in the opposite direction, was also considered and was found to be energetically less favorable.

[15] The activation energies in series **a** and **b** calculated at the MP2/631A//B3LYP/631A level are 34.5 kcal mol^{-1} for series **a** and 30.9 kcal mol^{-1} for series **b**. Hence, the difference is 3.6 kcal mol^{-1}.

[16] This trend also holds when the solvent polarity and explicit solvent molecules (one Me$_2$O on each Li atom) are considered (Figure 1). The solvation of the Cu atom only takes place after the TS of the bromide displacement in which copper(I) becomes copper(III), and hence was not considered in the present discussion (see ref. [12a]).

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[19] A full optimization of the [LiCNLi]$^+$ moiety in **1b** afforded the structure below, with an energy gain of 22.6 kcal mol^{-1}. Such a linear geometry is found in many crystal structures of lithium cyanide compounds (see ref. [6b]).

[20] As in series **b**, the very small activation energy can be ascribed to the near-linear geometry of Li–NC moiety in **3c** (Figure 3b).

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Ionization of O_3 in Excess N_2: A New Route to N_2O via Intermediate $N_2O_3^+$ Complexes[**]

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The environmental impact of N_2O, the major source of stratospheric NO_x oxides responsible for ozone depletion, and a harmful greenhouse gas,[1–3] accounts for the active search of formation processes[4, 5] other than microbiological soil denitrification.[6] Inspired by the increasing recognition of the role played by ionic processes in the atmosphere[7] and by the ability of O_3^+ to transfer oxygen atoms to simple molecules,[8–10] we focused this study on the ionization of O_3 diluted in N_2 as a new route to atmospheric N_2O. Experiments based on Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry were performed, utilizing an instrument equipped with an external chemical ionization (CI) ion source, fed with an O_3/O_2 mixture. The ions formed were driven into the resonance cell, maintained at 300 K, where the $^{16}O_3^+$ ions, m/z 47.9847, were isolated by removing all other ions by "soft" RF pulses, and allowed to react with N_2, continuously admitted into the cell to reach stationary pressures ranging from 10^{-8} to 10^{-7} Torr. The results positively demonstrated the formation of N_2O^+ and O_2^+ as the primary reaction products [Eqs. (1) and (2)], through processes exothermic by 4.2 and 22.9 kcal mol^{-1}, respectively.[11]

$$O_3^+ + N_2 \rightarrow N_2O^+ + O_2 \tag{1}$$

$$O_3^+ + N_2 \rightarrow N_2O + O_2^+ \tag{2}$$

Although the nature of the experiments prevented accurate kinetic measurements,[12] we could roughly estimate $k_1 \sim 1.4 \times 10^{-11}$ and $k_2 \sim 1.6 \times 10^{-10}$ cm^3 s^{-1}. In any case, accurate kinetic measurements were outside the scope of the experiments, whose primary goal was to exploit the unique ability of FT-ICR spectrometry to establish a parent–daughter relationship between charged species, and hence to ascertain the reaction(s) responsible for the formation of the product of interest, N_2O^+. Next, CI experiments of N_2/O_3 mixtures, of composition adjusted to obtain the maximum reaction extent (roughly 5 mol% O_3), were performed at 373 K, 0.01–0.1 Torr. All experiments were carried out in duplicate, utilizing either $^{14}N_2$ or $^{15}N_2$ as a convenient way to simplify

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[**] This work was supported by the University of Rome "La Sapienza", the University of Perugia, the Italian National Research Council (CNR), and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST). The authors are grateful for the skilled help of F. Angelelli and A. Di Marzio.

the interpretation of the mass spectra and to exclude the interference of isobaric contaminants, as generally advisable when the species probed have a low abundance. Given the consistency of the results from the two sets of experiments, we shall discuss only those pertaining to the unlabeled species.

As shown in Figure 1, the CI spectrum displays a peak at *m*/*z* 44 (46 when working with $^{15}N_2$) assigned as N_2O^+, based on the comparison of its mass spectrometric features with those of the molecular ion of N_2O, henceforth denoted as the model ion. The collisionally activated dissociation (CAD) spectrum of the ion probed and the kinetic energy release (KER) of its metastable loss of a N atom correspond to those of the model ion.[13] Further support is provided by neutralization–reionization (NR) experiments.[14] Reionization of the uncharged species from the neutralization of the ion probed gives a cation of *m*/*z* 44, whose CAD spectrum corresponds to that obtained from the neutralization–reionization of the model N_2O^+ ion. The above results positively establish the formation of N_2O^+ according to Equation (1) in the N_2/O_3 plasma.

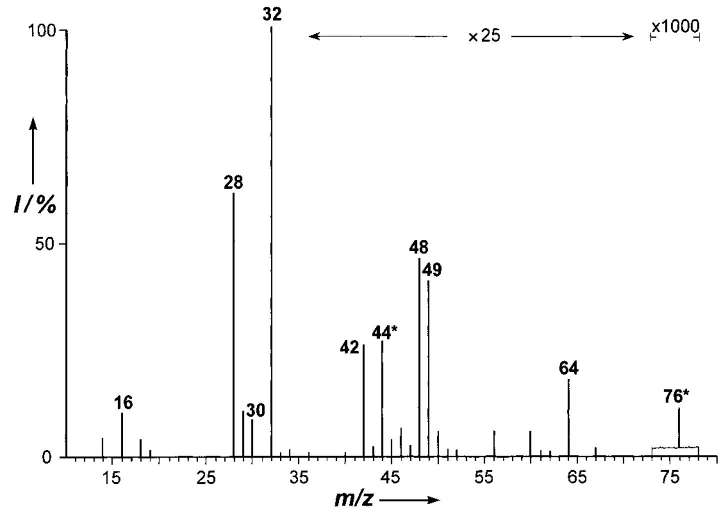


Figure 1. Typical N_2/O_3 CI mass spectrum displaying N_2^+ and O_2^+ as the major ions, together with much less abundant N^+, O^+, NO^+, O_3^+, $N_2O_2^+$, O_4^+, and N_n^+ ($n = 3-4$) ions. The ions at *m*/*z* 17, 29 and 49 are formed by reactions of adventitious water (see the *Experimental Section*). The peaks of the ions of interest, N_2O^+ and $N_2O_3^+$, are labeled.

As to the *direct* formation of neutral N_2O, according to Equation (2), particularly relevant to this study, detection of O_2^+, its charged product, in the CI experiments falls short of demonstrating the occurrence of the process, since other reactions, e.g. ionization of O_2 that invariably contaminates ozone, can also produce O_2^+. A clue to the problem, and valuable mechanistic insight are provided by the detection of a key intermediate, the ion of *m*/*z* 76, displayed by the CI spectrum (Figure 1) and positively identified as the adduct $N_2O_3^+$ by diagnostic mass spectrometric experiments. The most significant piece of evidence arises from the CAD spectrum (Figure 2), whose major peaks at *m*/*z* 32 and 44 are assigned to O_2^+ and N_2O^+, based on the comparison of their MS/MS spectra with those of the corresponding model ions. Remarkably, such fragmentation pattern denotes a $\mathrm{N{-}N{-}O\cdots O{-}O}$ connectivity, rather than the $\mathrm{N{-}N\cdots O{-}O{-}O}$ connectivity that characterizes the initial association of the monomers.

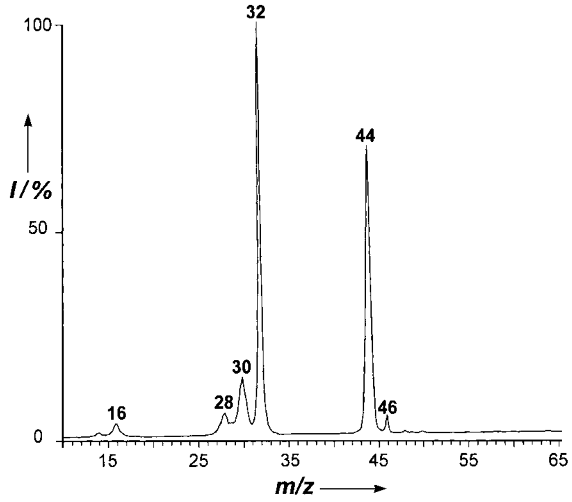


Figure 2. CAD spectrum of the adduct $N_2O_3^+$ (*m*/*z* 76). Ion energy: 8 keV, target gas: He.

Furthermore, the O_2^+ peak present in the CAD spectrum (Figure 2) indicates the loss of either N_2O or its neutral fragments, e.g. $N_2 + O$, $N + NO$, etc. To clarify this point, the neutral species from the CAD of $N_2O_3^+$ were separated from all charged species and reionized. The N_fR spectrum[14d] obtained in this way (Figure 3) displays an N_2O^+ peak at *m*/*z* 44, showing that at least a fraction of the CAD events undergone by $N_2O_3^+$ yields, rather than atoms and/or diatomic neutral molecules, a bound N_2O molecule, suggestive of its presence in the complex. Finally, the assignment of the peak at *m*/*z* 76 as $[\mathrm{N{-}N{-}O\cdots O{-}O}]^+$ is confirmed by the identical appearance of its CAD spectrum and that of a model obtained from O_2^+ and N_2O in O_2/N_2O CI experiments.

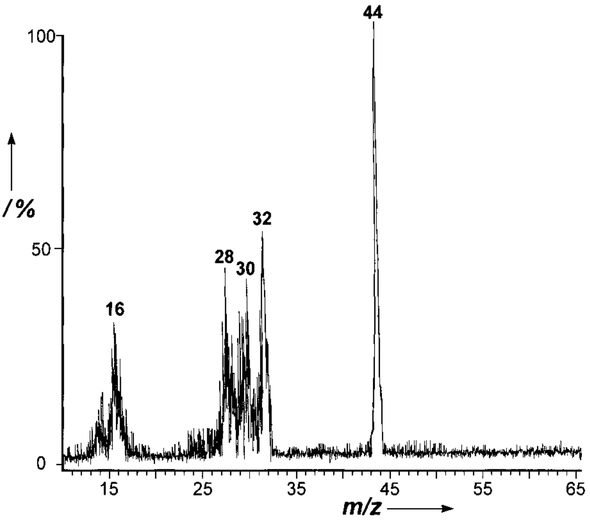
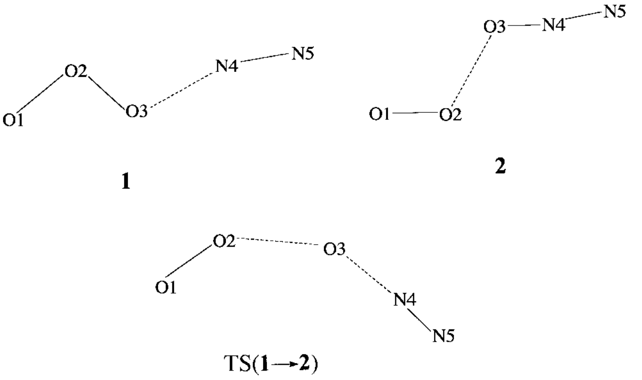


Figure 3. N_fR spectrum of the neutral species from the CAD of the adduct $N_2O_3^+$.

Density functional (DF) calculation using the hybrid[15] functional[16–18] was utilized to locate the stationary points of the investigated systems and to evaluate the vibrational frequencies. Transition states were located using the method of Schlegel and coworkers.[19] The 6-311 + G(3d) basis set was used.[20] The 0 K total energies were corrected to 298 K by standard procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311 + G(3d)-optimized geometries. All calculations were performed using Gaussian 98.[21] The optimized structures of the stationary points on the doublet potential energy surface[22] of $N_2O_3^+$ are shown in Scheme 1, whereas their total energies, frequencies and geometrical parameters are reported in Table 1. Species **1**, formed by the exothermic (11.0 kcal mol^{-1}) addition of the reagents can evolve (overcoming a barrier of 10.6 kcal mol^{-1} (TS(**1**→**2**)) into **2**, more stable by 47.2 kcal mol^{-1}, whose dissociation into N_2O and O_2^+ is endothermic by 28.8 kcal mol^{-1}. The accurate theoretical description of O_3 and related species is notoriously difficult and would require a prohibitively complex multireference approach. The accuracy of the present results can roughly be estimated by summing up the ΔH° changes computed for the formation of **1**, its conversion into **2**, and the dissociation of the latter, which gives $\Delta H_2^\circ = -29.4$ kcal mol^{-1}, vs. the tabulated value of -22.9 kcal mol^{-1}.[11]



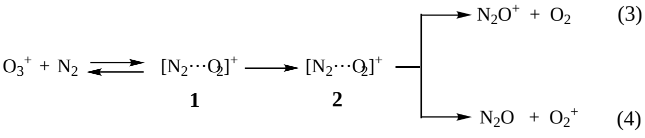
Scheme 1. Optimized geometries of relevant stationary points localized on the $[N_2, O_3]^+$ potential energy surface.

Table 1. Calculated bond lengths [Å], angles [°], total energies [Hartree], and vibrational frequencies [cm^{-1}] (intensities [km mol^{-1}]) of the structures of the stationary points on the doublet potential energy surface of $N_2O_3^+$.

	1 $^2A'$	**2** $^2A''$	TS(**1**→**2**) ^2A
O2-O1	1.209	1.144	1.183
O3-O2	1.358	2.241	1.542
O3-O2-O1	113.8	108.6	123.6
N4-O3	2.245	1.204	1.977
N4-O3-O2	100.3	119.1	152.7
N4-O3-O2-O1	180.0	180.0	– 70.0
N5-N4	1.094	1.119	1.094
N5-N4-O3	167.7	178.6	176.6
N5-N4-O3-O2	180.0	180.0	– 175.1
E_{B3LYP}	– 334.608436	– 334.686027	– 334.590241
ZPE[a]	0.012877	0.015745	0.011652
	88.5 (0.3)	47.1 (0.2)	418.2*i*
	108.3 (0.1)	80.1 (0.7)	50.5
	138.7 (1.2)	147.6 (0.7)	109.4
	183.0 (0.7)	315.9 (0.1)	143.8
	239.0 (23.7)	551.1 (3.5)	231.2
	557.6 (15.2)	563.1 (2.0)	294.0
	706.9 (111.3)	1228.7 (72.3)	419.8
	1209.7 (129.9)	1773.2 (1059.9)	1450.8
	2420.7 (110.1)	2204.5 (27.3)	2415.1

[a] Zero point energy.

Combining the experimental and computational results, one obtains a satisfactory picture: adduct **1** from the electrostatic association of the reagents can undergo back dissociation or evolve into **2**, which can dissociate by two processes [Eqs. (3) and (4)]. However, back dissociation is entropically



favored, which accounts for the low combined efficiency (ca. 10 %) of the reactions, as well as for the failure to detect $N_2O_3^+$ adducts in the FT-ICR experiments. At the higher pressure of CI experiments a larger fraction of **1** escapes back dissociation and evolves into **2**. This, and the more efficient collisional stabilization of $N_2O_3^+$ increase its steady-state concentration and make its detection in the CI spectrum possible. Furthermore, the more efficient collisional cooling of **2** is expected to affect the branching ratio of processes (3) and (4) in favor of the latter, less endothermic by 18.4 kcal mol^{-1}.[11, 23] In summary, this study demonstrates a reaction sequence yielding N_2O upon ionisation of O_3 diluted in N_2. Owing to the higher ionization potential of nitrogen compared to ozone, even initial ionization of N_2 would produce O_3^+ by fast charge exchange. In air, reaction (3) is expected to also produce *neutral* N_2O by fast charge exchange with O_2.[24]

To assess the relevance of the present results to atmospheric chemistry, one has to identify the specific environments where ionization of air enriched in ozone does occur. Such requirements are met near power lines and especially in thunderstorms. Indeed, the atmospheric relevance of lightning and corona discharges as the source of 10 to 15 % of tropospheric NO is well established.[25] It is also long known[26] that ozone is produced by thunderstorms, and recent laboratory simulations show that actually the O_3 yield ($(4 \pm 1) \times 10^{17}$ molecules per Joule), far exceeds that of NO_2 ($(1.4 \pm 0.7) \times 10^{16}$ molecules per Joule).[27] These results, and the intense ionization of air by lightning, coronas, and other phenomena associated with thunderstorms, suggest that the process reported in this study is a likely source of tropospheric nitrous oxide and that the present results provide a sound fundamental support to previous studies and theories, which, based on an extensive body of experimental data, postulated the formation of N_2O as a consequence of the ionization of air by natural or anthropogenic phenomena.[28–31]

Experimental Section

The experiments were performed with a multisector mass spectrometer of the EBE-TOF configuration (ZAB Specoa-TOF from VG Micromass Ltd., Manchester, UK), modified by addition of two pairs of collision gas cells and a low-temperature CI source equipped with a thoriated filament. Typical CI source conditions were as follows: source temperature 100°C; repeller voltage 0.0 V; ion extraction voltage 8 kV; source pressure 0.05–0.1 Torr. The CAD spectra were recorded with helium as collision gas, admitted into the cell to such a pressure as to reduce the beam intensity by 30%. The NR experiments were performed in the first pair of collision cells positioned between the magnet and the second electrostatic analyzer, reionization being achieved with O_2 as the collider. Any ions leaving the first collision cell were removed using a high-voltage (1 kV) deflector whose efficiency was checked by control experiments. The NR spectra were averaged over 20 to 50 acquisitions to achieve a satisfactory signal-to-noise ratio. The gases, research-grade products from commercial sources with a stated purity exceeding 99.95 mol%, were used as such. Ozone was prepared from dry O_2 in a commercial ozonizer, collected in a silica trap at 77 K and recovered by controlled warming. Some of the initially pure O_3 desorbed from the trap undergoes dissociation into O_2 in the transfer line and/or in the ion source. Furthermore, trace impurities such as H_2O and CO_2 are produced by unspecified reactions of O_3 with the transfer line and the source materials. $^{15}N_2$ (98 atom%) was obtained from Aldrich Chemical Co., Inc.

Received: December 7, 2000
Revised: March 7, 2001 [Z16237]

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Preorganization of the Bioactive Conformation of Sialyl Lewis^X Analogues Correlates with Their Affinity to E-Selectin

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Excessive infiltration of leukocytes from blood vessels into surrounding tissues can cause acute or chronic reactions as observed in reperfusion injuries, stroke, psoriasis, rheumatoid

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