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Catalyzed Reduction of N Oxides

Gas-Phase Reduction of Oxides of Nitrogen with CO Catalyzed by Atomic Transition-Metal Cations[**]

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Catalytic conversion of harmful gases, such as the oxides of nitrogen produced in fossil-fuel combustion into nitrogen and carbon dioxide, is of utmost importance, both environmentally and economically. CO was one of the first gases investigated for eliminating NO from automobile exhaust gas: the reaction of NO with CO [Eq. (1)] is one of the most

$$NO + CO \rightarrow {}^{1}\!/_{2}N_2 + CO_2 \qquad (1)$$

important reactions occurring in automotive catalytic converters where both reactants are undesirable pollutants.[1]

Base-metal oxides, mixed metal-oxide compounds such as perovskites, supported metal catalysts, metal zeolites, and alloys have all been investigated as heterogeneous catalysts for this reaction, which does not occur directly in the gas phase at room temperature to any measurable extent.[1] For example, copper in the +2 oxidation state has been found to be active both as a base-metal-oxide catalyst and in a metal-supported or perovskite form.

We report here the first example of homogeneous catalysis by the reaction described in Equation (1), which occurs in the gas phase with atomic transition-metal cations serving as catalysts. The catalysis occurs in two steps in which NO is first reduced to N_2O. An analogous three-step catalytic reduction of NO_2, in which NO_2 is first reduced to NO, was also discovered.

The overall catalytic scheme that was established in the study reported here consists of the three catalytic cycles shown in Figure 1. These three cycles were characterized with laboratory measurements of reactions of each of the three nitrogen oxides NO_2, NO, and N_2O with up to 29 different transition-metal cations M^+ [Eqs. (2)–(4)]:

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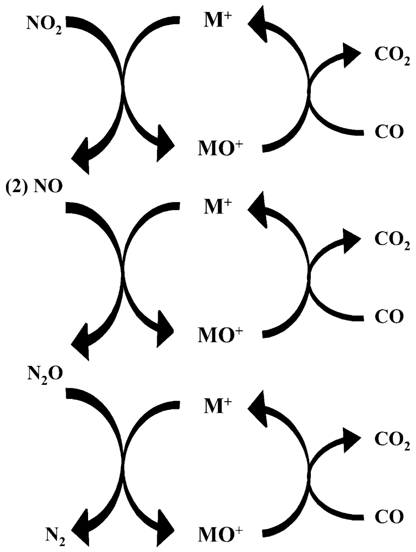

Figure 1. Catalytic cycles for the homogeneous reduction of nitrogen oxides by carbon monoxide, mediated by atomic transition-metal cations.

$$M^+ + NO_2 \rightarrow MO^+ + NO \qquad (2)$$

$$M^+ + NO + NO \rightarrow MO^+ + N_2O \qquad (3)$$

$$M^+ + N_2O \rightarrow MO^+ + N_2 \qquad (4)$$

These reactions lead to the reduction of the corresponding nitrogen oxide as well as the oxidation of M^+ to MO^+. Also, metal-oxide cations, MO^+, were reacted with CO. These reactions lead to the reduction of MO^+ to M^+ as well as the oxidation of CO to CO_2 according to Equation (5), where the catalyst

$$MO^+ + CO \rightarrow M^+ + CO_2 \qquad (5)$$

M^+, which reduces the three nitrogen oxides, is regenerated:

Two modes were observed for the reactions of M^+ with NO. M^+ ions with a high O-atom affinity, OA (M^+) > OA (N) = 151 kcal mol^{-1},[2] were found to abstract an O atom from NO exothermically according to Equation (6) with high efficiency, $k > 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$$M^+ + NO \rightarrow MO^+ + N \qquad (6)$$

The bimolecular reaction shown in Equation (6) was observed with $M^+ = Sc^+$, Ti^+, Y^+, Zr^+, Nb^+, La^+, Hf^+, Ta^+, and W^+ (see Table 1 for values of OA (M^+)). Second-order NO reactions of the type shown in Equation (3) were observed at high NO flows for $M^+ = V^+$, Cr^+, Mn^+, Fe^+, Co^+, Ni^+, Mo^+, Ru^+, Re^+, Os^+ and Ir^+. The reaction given in Equation (6) is endothermic for these latter ions (see Table 1) but that in Equation (3), driven by N–NO bond formation, is exothermic since OA (M^+) > OA (N) − D (N-NO) = 36 kcal mol^{-1}.[2] Figure 2 (top left) presents experimental data obtained for the second-order (in NO) reduction of NO by Fe^+. With V^+, Cr^+, Mn^+ and Mo^+, this reaction occurs in competition with the second-order ionization of NO [Eq. (7)], driven by the formation of the stable metal nitrosyl molecule MNO.

$$M^+ + NO + NO \rightarrow NO^+ + MNO \qquad (7)$$

Cu^+, Rh^+, Pd^+, Ag^+, Cd^+, and Pt^+ ions were observed to react only by second-order ionization of NO (as well as by NO addition in some cases). Reactions of the metal-oxide MO^+ ions with CO [Eq. (5)] are exothermic if OA (M^+) < OA (CO) = 127 kcal mol^{-1}.[2] Of those ions with OA (M^+) < 127 kcal mol^{-1} (see Table 1) that have been observed to react measurably with N_2O according to Equation (4), only Fe^+, Os^+, and Ir^+ have been observed to undergo the reaction given in Equation (5), with $k > 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Figure 2 (top right) shows experimental data obtained for the reduction of FeO^+ by CO, which is exothermic by 47 kcal mol^{-1}.

The reactions described by Equations (3) and (5) taken together in principle constitute the catalytic cycle shown in Scheme 1 (and the middle of Figure 1), which leads to the reduction of NO to N_2O and requires that 36 < OA (M^+) < 127 kcal mol^{-1}. Also, the ionization energy of the metal and metal oxide must be less than that of NO, E_i (M) and E_i (MO) < E_i (NO) = 9.26 eV,[2] to avoid competition with

Table 1: O-atom affinities, $OA = D_0$ (M^+-O) [kcal mol^{-1}],[3] and ionization energies, E_i (M) and E_i (MO) [eV],[2] for transition-metal cations.

First Row				Second Row				Third Row			
M^+	OA (M^+)	E_i (M)	E_i (MO)	M^+	OA (M^+)	E_i (M)	E_i (MO)	M^+	OA (M^+)	E_i (M)	E_i (MO)
Sc^+	164.6 ± 1.4	6.56		Y^+	167.0 ± 4.2	6.22	5.85	La^+	206 ± 4	5.58	4.9
Ti^+	158.6 ± 1.6	6.75	6.56	Zr^+	178.9 ± 2.5	6.63	6.1	Hf^+	173 ± 5	6.83	7.55
V^+	134.9 ± 3.5	6.77	7.5	Nb^+	164.4 ± 2.5	6.76	6.1	Ta^+	188 ± 15	7.55	7.92
Cr^+	85.8 ± 2.8	7.43	7.85	Mo^+	116.7 ± 0.5	7.09	8	W^+	126 ± 10[a]	7.86	9.1
Mn^+	68.0 ± 3.0	7.43	8.65					Re^+	115 ± 15	7.83	
Fe^+	80.0 ± 1.4	7.9	8.9	Ru^+	87.9 ± 1.2	7.36	8.7	Os^+	100 ± 12	8.44	
Co^+	74.9 ± 1.2	7.88	8.9	Rh^+	69.6 ± 1.4	7.46	9.3	Ir^+	59[b]	8.97	10.1
Ni^+	63.2 ± 1.2	7.64	9.5	Pd^+	33.7 ± 2.5	8.34	9.1	Pt^+	77	8.96	10.1
Cu^+	37.4 ± 3.5	7.72		Ag^+	28.4 ± 1.2	7.58		Au^+		9.23	
Zn^+	38.5 ± 1.2	9.39		Cd^+		8.99		Hg^+		10.4	

[a] This value for OA (W^+) is too low according to our observation of the fast reaction $W^+ + NO \rightarrow WO^+ + N$, $k = 5.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. [b] This value for OA (Ir^+) is also too low according to our observation of the reaction $Ir^+ + NO_2 \rightarrow IrO^+ + NO$ (see Table 2).

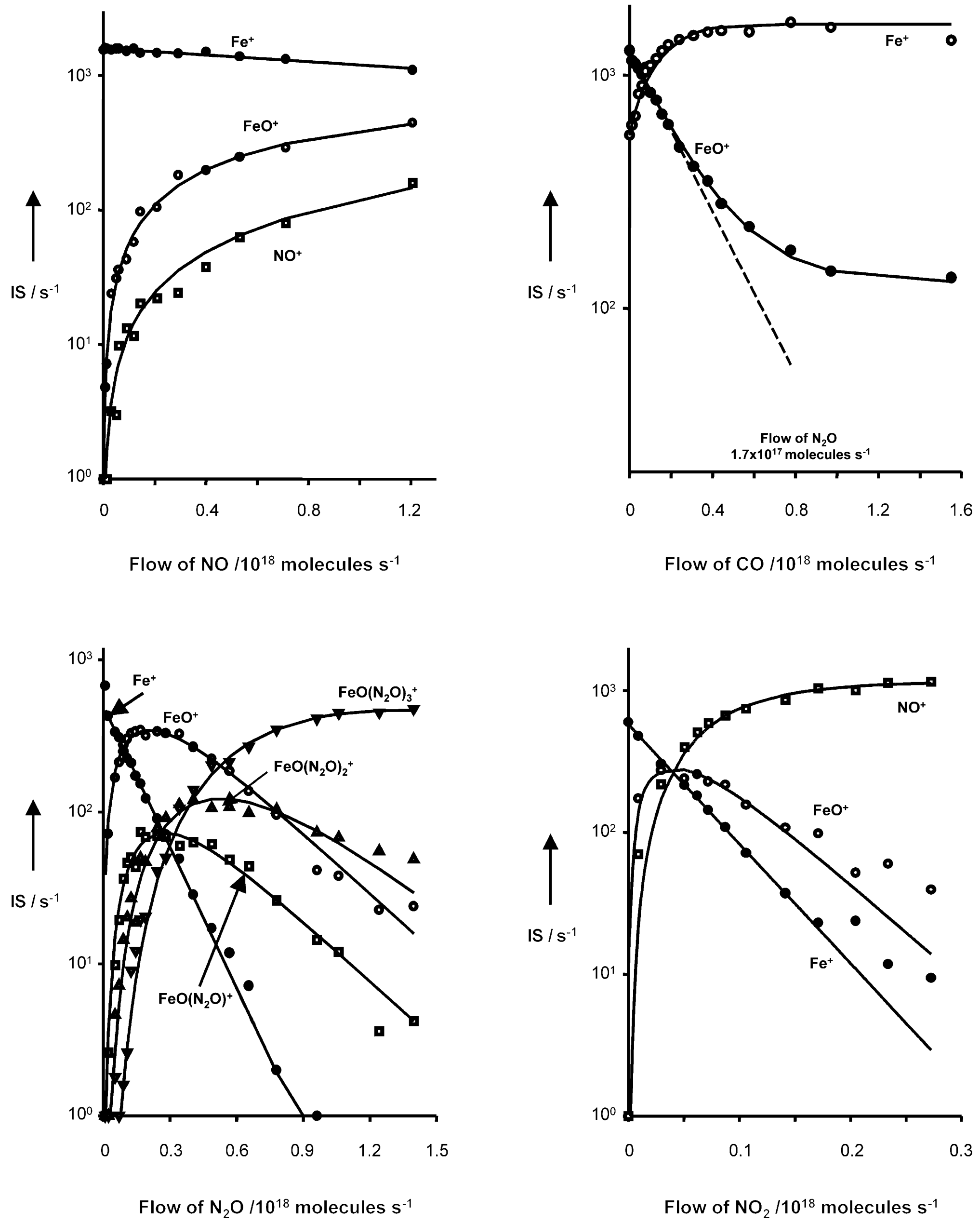

Figure 2. Top left: Experimental data for the second-order (in NO) reduction of NO by Fe^+ ions. The product FeO^+ reacts further in this case with NO by electron transfer. Top right: Data for the reduction of FeO^+ by CO. The decay of FeO^+ (solid line) is slowed down due to the reoxidation of Fe^+ by N_2O added upstream into the flow tube. Bottom left: Data for the reduction of N_2O by Fe^+ ions. The FeO^+ product adds to N_2O sequentially at high flows of N_2O. Bottom right: Data for the reduction of NO_2 by Fe^+ ions. The FeO^+ product reacts further to produce $NO^+ + FeO_2$. IS = Ion signal.

$$\begin{array}{c} 2\,NO + M^+ \longrightarrow MO^+ + N_2O \\ \underline{MO^+ + CO \longrightarrow M^+ + CO_2} \\ 2\,NO + CO \longrightarrow N_2O + CO_2 \end{array}$$

Scheme 1. Catalytic cycle for the homogeneous reduction of nitric oxide by carbon monoxide, mediated by atomic transition-metal cations.

bimolecular electron transfer, which we have observed to predominate in exothermic reactions.

The further reduction of N_2O to N_2 [Eq. (4)] can be achieved with transition-metal ions with $OA\ (M^+) > OA\ (N_2) = 40\ kcal\,mol^{-1}$.[2] We have surveyed the transition-metal cations in the periodic table and, of the M^+ ions observed to undergo the reaction in Equation (3), we have observed the reaction described in Equation (4) with $k > 1\times10^{-12}\ cm^3\,molecule^{-1}\,s^{-1}$ for $M^+ = V^+, Fe^+, Co^+, Os^+$, and Ir^+. Experimental data obtained for the reduction of N_2O by Fe^+ ions are shown in Figure 2 (bottom left). FeO^+ is seen to add N_2O at high concentrations of N_2O in sequential N_2O addition reactions.

The reactions described by Equations (4) and (5) taken together in principle constitute the catalytic cycle shown in Scheme 2 (and the bottom of Figure 1), which leads to the

$$\begin{array}{l} M^+ + N_2O \longrightarrow MO^+ + N_2 \\ MO^+ + CO \longrightarrow M^+ + CO_2 \\ \hline N_2O + CO \longrightarrow N_2 + CO_2 \end{array}$$

Scheme 2. Catalytic cycle for the homogeneous reduction of nitrous oxide by carbon monoxide, mediated by atomic transition-metal cations.

reduction of N_2O to N_2 and requires that $40 < OA$ (M^+) < 127 kcal mol^{-1} and E_i (M) and E_i (MO) $< E_i$ (N_2O) $= 12.886$ eV.[3] Figure 2 (top right) shows catalytic data for M = Fe.

The reaction shown in Equation (4) has commonly been used in the gas phase to produce transition-metal oxide cations[4] and previous measurements using ion cyclotron resonance (ICR) spectroscopy actually have demonstrated that Fe^+ ions will catalyze the oxidation of CO to CO_2 by N_2O under ICR conditions according to Scheme 2 (and that the five transition-metal cations Ti^+, Zr^+, V^+, Nb^+, and Cr^+ fail to do so).[5]

Scheme 1 and Scheme 2 taken together lead to the conversion of NO and CO to N_2 and CO_2 according to the overall reaction [Eq. (8)], which is the equivalent of Equation (1):

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2 \tag{8}$$

The M^+ catalyst must satisfy the thermodynamic requirements that $40 < OA$ (M^+) < 127 kcal mol^{-1} and E_i (M) and E_i (MO) $< E_i$ (NO) $= 9.26$ eV. This requirement is met (see Table 1) by the transition metals Fe, Os, and Ir, all of which have been observed to undergo the reactions given in Equations (3), (4), and (5) with $k > 1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Table 2). Mo^+ and Ru^+ ions meet this requirement, but their reaction with N_2O gives only addition (no MO^+ formation). Co^+ and Cr^+ ions also meet this requirement but the reaction in Equation (4) was too slow to produce enough MO^+ species to measure the results of the following reaction [Eq. (5)].

Finally, NO_2 has also been observed to be reduced by certain transition-metal ions according to Equation (2), often in competition with formation of NO^+ (see Table 2). Figure 2 (bottom right) shows experimental data for the reduction of NO_2 by Fe^+ [Eq. (9)], followed by Equation (10):

$$Fe^+ + NO_2 \rightarrow FeO^+ + NO \tag{9}$$

$$FeO^+ + NO_2 \rightarrow NO^+ + FeO_2 \tag{10}$$

The reactions described in Equations (2) and (5) taken together in principle constitute the catalytic cycle shown in Scheme 3 (and the top of Figure 1), which leads to the reduction of NO_2 to NO.

$$\begin{array}{l} M^+ + NO_2 \longrightarrow MO^+ + NO \\ MO^+ + CO \longrightarrow M^+ + CO_2 \\ \hline NO_2 + CO \longrightarrow NO + CO_2 \end{array}$$

Scheme 3. Catalytic cycle for the homogeneous reduction of nitrogen dioxide by carbon monoxide, mediated by atomic transition-metal cations.

Schemes 1, 2, and 3 taken together lead to the conversion of NO_2 and CO to N_2 and CO_2 according to Equation (11):

$$2\,NO_2 + 4\,CO \rightarrow N_2 + 4\,CO_2 \tag{11}$$

The M^+ catalyst must satisfy the thermodynamic requirements that $73.5 < OA(M^+) < 127$ kcal mol^{-1} and E_i (M) and E_i (MO) $< E_i$ (NO) $=$ 9.26 eV. Of the 29 transition-metal ions that were surveyed only Fe, Os, and Ir[2] meet this requirement (see Table 1) and have been observed to undergo all the reactions in Equations (2)–(5), with $k > 1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Table 2).

Os^+ and Ir^+ ions produce higher oxides in sequential reactions with NO_2 and N_2O (but not NO) according to the reactions given in Equations (12 a,b) and (13) up to $n = 3$ and

$$MO_n^+ + NO_2 \rightarrow MO_{n+1}^+ + NO \quad (n = 0-3) \tag{12a}$$

$$\rightarrow NO^+ + MO_{n+1} \quad (n = 0) \tag{12b}$$

$$MO_n^+ + N_2O \rightarrow MO_{n+1}^+ + N_2 \quad (n = 0-3) \tag{13}$$

$n = 2$ for M = Os and Ir, respectively. Figure 3 shows results for Os^+ in which NO^+ is produced primarily by the reaction of OsO^+ with NO_2 in competition with OsO_2^+ formation.

Os^+ and Ir^+ ions react sequentially with N_2O according to Equation (13). The bare metal cation is recovered by sequential reactions with CO molecules according to Equation (14) as shown in Figure 3 for OsO_n^+:

$$MO_n^+ + CO \rightarrow MO_{n-1}^+ + CO_2 \quad (n = 1-4) \tag{14}$$

This demonstrates that the catalytic cycle will not be inhibited if higher oxides are formed, that is, the transition-metal oxide cations MO_n^+ formed in each step of the catalytic cycle are reverted back to bare metal cations by reaction with CO.

In conclusion, we have reported a detailed and comprehensive thermodynamic and kinetic investigation of a novel role for transition-metal cations in the homogeneous catalytic conversion of nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide. Fe^+, $Os^{+,}$ and Ir^+ ions are

Table 2: Rate coefficients, k [cm^3 molecule^{-1} s^{-1}], and products observed for reactions with M = Fe, Os, and Ir at room temperature in helium buffer at 0.35 Torr.

Reaction	Fe		Os		Ir	
	Products	k[a]	Products	k[a]	Products	k[a]
$M^+ + NO + NO$	$FeO^+ + N_2O$	1.6×10^{-11}	$OsO^+ + N_2O$	1.5×10^{-11}	$IrO^+ + N_2O$	1.5×10^{-11}
$M^+ + N_2O$	$FeO^+ + N_2$	3.7×10^{-11}	$OsO^+ + N_2$	5.8×10^{-11}	$IrO^+ + N_2$	2.9×10^{-10}
$M^+ + NO_2$	$FeO^+ + NO$	9.1×10^{-10}	$OsO^+ + NO$ (0.8) $NO^+ + OsO$ (0.2)	7.3×10^{-10}	$IrO^+ + NO$ (0.6) $NO^+ + IrO$ (0.4)	7.9×10^{-10}
$MO^{+[b]} + CO$	$Fe^+ + CO_2$	$> 3.7\times10^{-10}$	$Os^+ + CO_2$	$> 4.6\times10^{-11}$[c]	$Ir^+ + CO_2$	$> 2.6\times10^{-11}$[c]

[a] Apparent bimolecular rate coefficient with an estimated accuracy of ±30%. [b] Produced from the reaction of M^+ with N_2O (M = Fe, Os, Ir) and of MO_2^+ with CO (M = Os, Ir). [c] Determined from a fit to the production and loss of MO^+.

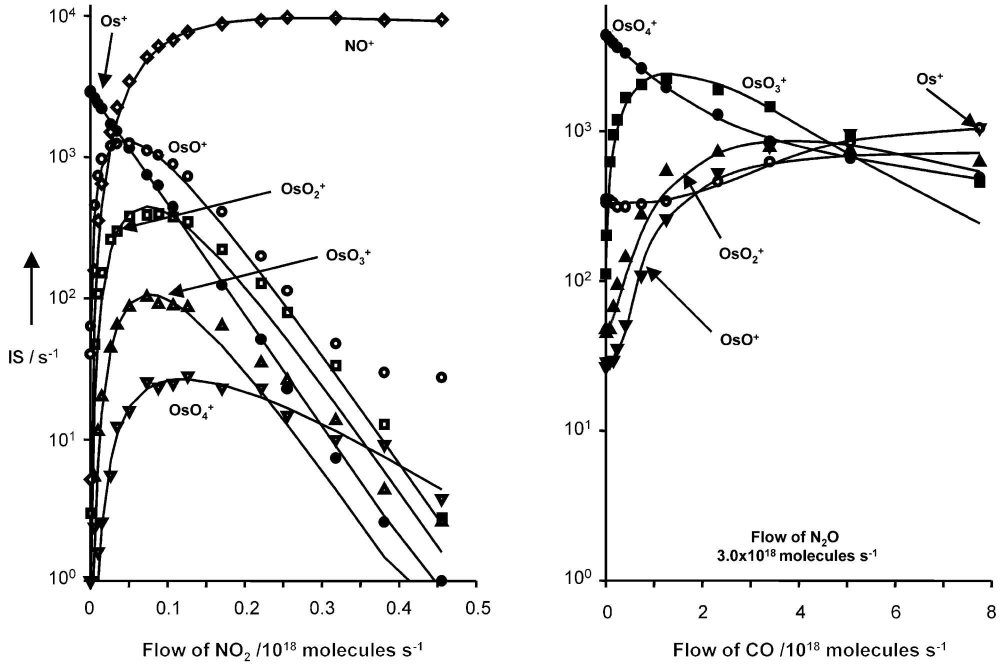

Figure 3. Experimental data for the sequential oxidation of Os^+ ions by NO_2 (left) and the reduction of oxides of Os^+ by CO (right). The NO^+ formation (left) competes with the further oxidation of OsO^+. IS = Ion signal.

shown to be most effective. The catalytic conversion has been demonstrated in principle but it remains to be seen whether the catalytic cycles shown in Figure 1 have applications in practical catalysis; they may provide the basis of new designs of catalytic converters in automobiles through the use, for example, of cold cathode discharges. For the most part the reactions measured are clean (single-channel) reactions so that the specific catalytic cycles that are proposed in principle have a turnover number of infinity. The two exceptions are the NO_2 cycles involving Ir^+ and Os^+ ions that show both MO^+ and NO^+ production in their reactions with NO_2 (60% and 80% MO^+ production for Ir^+ and Os^+, respectively). These two cycles have turnover numbers of 1.5 and 4, respectively. Of course in a practical device that exploits the catalytic cycles that we have proposed, the turnover numbers can be further reduced by secondary reactions, competing reactions with impurities or surfaces, or other losses.

Experimental Section

The reactions were investigated in an inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer.[6] The transition-metal ions were produced from their metal-salt solutions, which were sprayed into an argon plasma operating at atmospheric pressure and ≈5500 K. The ions are then mass selected by a quadrupole mass filter and injected into a flow tube flushed with He buffer gas at 0.35 Torr and 294 ± 3 K. The ions cool by radiation and collision with argon and helium from their point of origin to the entrance of the reaction region.[7] The reagent gas (NO, NO_2, or N_2O) was added into the reaction region downstream into the flow tube and the reacting mixture was sampled by a second quadrupole mass spectrometer. Reaction-rate coefficients were derived from the measured variation of the ion signal intensities with the reagent flow with an estimated accuracy of ±30%. In the study of metal-oxide cation chemistry, the metal-oxide cation was produced upstream from the reaction of the metal ion with N_2O. CO was introduced into the reaction region further downstream into the flow tube.

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