J. Am. Chem. Soc. **1995,** *117,* 12801–12809

Intrinsic Coordination Properties of Iron in FeO^+: Kinetics at 294 ± 3 K for Gas-Phase Reactions of the Ground States of Fe^+ and FeO^+ with Inorganic Ligands Containing Hydrogen, Nitrogen, and Oxygen

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Received February 21, 1995®

Abstract: The coordination of the electronic ground states of Fe^+ (^6D) and FeO^+ ($^6\Sigma^+$) has been investigated in the gas phase with the inorganic molecules H_2, HD, D_2, H_2O, CO, NO, N_2, O_2, CO_2, NO_2, and N_2O. Reaction rate coefficients and product distributions were measured with the Selected-Ion Flow Tube (SIFT) technique operating at 294 ± 3 K and a helium buffer-gas pressure of 0.35 ± 0.01 Torr. Except with NO_2 and N_2O, Fe^+ was found to be unreactive: there was no evidence for the ligation of Fe^+ with H_2, HD, D_2, H_2O, CO, NO, N_2, O_2, and CO_2 under the conditions of the experiments, and Fe^+ was observed to react in a bimolecular fashion with NO_2 and N_2O by O-atom transfer to yield FeO^+. FeO^+ generally was observed to be much more reactive than Fe^+. While no reactions were seen to occur with NO and O_2, FeO^+ reacted with H_2, HD, D_2, and CO to produce Fe^+ and with NO_2 by O^- transfer to produce $NO^+ + FeO_2$. A very slow sequential addition of two molecules was seen with N_2. With N_2O, CO_2, and H_2O, FeO^+ was observed to add sequentially three ligand molecules; this corresponds to the availability of three coordination sites around iron in FeO^+. Rate coefficients were measured for each addition and structures have been proposed for the ligated FeO^+. Further addition, but at a much reduced rate, was observed with H_2O, but this was attributed to a second coordination shell involving hydrogen-bond formation. Also, experimental evidence is provided for the extension of the catalytic role of FeO^+ in the oxidation of CO to CO_2 to the ligated ions $FeO(N_2O)_n^+$ with $n = 1-3$.

Introduction

The gas-phase chemistry of Fe^+ and FeO^+ has attracted considerable attention in recent years. Much of the focus has been on the activation of CH/CC bonds or their oxidation by iron and iron oxide cations in the gas phase.[1] Also, catalytic properties of FeO^+ in the gas phase have been documented.[2-4] But at least two aspects of previous studies have motivated us to investigate the gas-phase chemistry of Fe^+ and FeO^+ further. First of all, it seemed to us that more emphasis should be given to the measurement of the room-temperature kinetics of gas-phase ligation reactions since gas-phase behavior can provide a useful benchmark for solution behavior and can provide insight into *intrinsic* aspects of ligation not accessible in solution. Experimental investigations of the kinetics of ligation have not been very common in the past, in part because of the low operating pressures ($<10^{-3}$ Torr) of the experimental mass-spectrometric techniques which have been used most often to investigate such reactions, viz. ICR,[2,5] FT-ICR,[3,4] and the guided ion beam technique.[6,7] These techniques do not afford effective collisional stabilization of ligated cations; higher operating pressures are required. A multicollision flow-tube technique has been used to investigate reactions of Fe^+ with small alkanes in helium buffer gas at 0.75 Torr,[8] and the newly-developed "chromatographic" technique employing a high-pressure drift cell containing 1.75 Torr of helium buffer gas has been used to investigate the reaction of Fe^+ with propane.[9] The Selected-Ion Flow Tube (SIFT) technique used in this study operates at a helium buffer-gas pressure of ca. 0.35 Torr so that an intermediate ligated cation can be collisionally stabilized before its unimolecular decomposition back to the separated reactants.

A second aspect of previous studies which motivated our investigation concerns the definition of reaction temperature, viz. both the internal and the kinetic energy distributions of the reactant Fe^+ and FeO^+ ions. The techniques most often used to date in the study of Fe^+ and FeO^+ chemistry, viz. ICR,[2,5] FT-ICR,[3,4] and the guided ion beam technique,[6,7] have not operated under strictly thermal equilibrium conditions. At the low operating pressures of these techniques there is some uncertainty regarding either the internal or the kinetic energy of reactant ions. It has been acknowledged and demonstrated that internal and kinetic energy can influence the kinetics and product distributions of reactions involving these ions.[2,3,6] Better definition of internal and kinetic energy distributions is achieved with multicollision techniques such as the flow-tube[8] and "chromatographic"[9] techniques used previously. In the latter technique the ions are thermalized by collisions with He and

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® Abstract published in *Advance ACS Abstracts,* December 1, 1995.

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drift field. The fields commonly employed do not perturb the ion translational temperature by more than a few degrees.[9,10] In the SIFT apparatus employed in the studies reported here, multiple collisions with helium buffer-gas atoms operate to thermalize reactant Fe^+ and FeO^+ ions to room temperature prior to entering the reaction region. They also thermalize product ions prior to secondary reaction. This allows the measurement of reaction kinetics and product distributions under thermal equilibrium conditions at a well-defined temperature.

Here we report the results of a systematic SIFT study of the kinetics of reactions of the electronic ground states of Fe^+ (^6D) and FeO^+ ($^6\Sigma^+$) with a variety of inorganic molecules proceeding at 294 ± 3 K in a helium bath gas at a moderate pressure of 0.35 ± 0.01 Torr. Both the reactions of FeO^+ and Fe^+ were investigated because the latter serves as a benchmark for an assessment of the influence of the O substituent on the Fe reactivity.[11] The inorganic reagent molecules chosen for study were H_2, HD, D_2, H_2O, CO, NO, N_2, O_2, CO_2, NO_2, and N_2O.

The molecules H_2O, N_2O, and CO_2 were chosen in view of the expected diversity in their modes of ligation. N_2O is important because it is the gas most commonly used in the generation of FeO^+ from Fe^+ ions.[1] Moreover, nitrous oxide is a monodentate ligand. Carbon dioxide was selected as an example of a weak and possibly bidentate or multi-electron donating ligand and it was expected that its coordination to FeO^+ would be complicated. H_2O can be expected to form adduct ions with FeO^+ not only by donating electrons and forming coordinate covalent O−Fe bonds but also by hydrogen bonding to the oxygen of FeO^+ and to coordinated water molecules. Reactions of FeO^+ with H_2O may, of course, also be relevant in an understanding of rust formation. The reactions with H_2, HD, and D_2 have previously drawn attention because of their low reactivity[4,7] with FeO^+ which has generated interest in theoretical aspects of these reactions.[12] CO and NO are "classic" ligands while N_2 is an example of a weak ligand. The reaction with O_2 is interesting, particularly in view of the previous observation of the addition of O_2 to neutral Fe atoms to form FeO_2.[13]

Experimental Section

The results reported here were obtained using a Selected-Ion Flow Tube (SIFT) apparatus which has been described previously.[14,15] All measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. The reactant Fe^+ ions were produced in a low-pressure ionization source either from $Fe(CO)_5$ by 35−50 eV electron bombardment or from ferrocene vapor at 60−70 eV, mass selected, injected into the flow tube, and allowed to thermalize by collisions (ca. 4×10^5) with He atoms before entering the reaction region. Both $Fe(CO)_5$ and ferrocene were introduced into the ion source in a large excess of helium (at a partial pressure of less than 5%). The ion signal showed a maximum with increasing pressure which is suggestive of ion/He collisions within the source and the occurrence of dissociative electron-transfer reactions of He^+ with the parent gas. Normally the ion signal was tuned at the maximum. We could not find any evidence for the presence of excited states of Fe^+ in our reacting Fe^+ population. Experimental evidence for the absence of excited states, although not conclusive, is provided by the linearity in the semilogarithmic decay of the Fe^+ signal observed over more than 3 orders of magnitude in the reactions with NO_2 and N_2O (the presence of excited states of different reactivity than the ground state would introduce curvature into the semilogarithmic decay). Also, the measured rate coefficient was independent of the electron energy and the nature of the parent gas. Finally, the rate coefficient for the reaction of Fe^+ with N_2O was found to be the same when Fe^+ was produced from the collisional dissociation of $Fe(C_5H_5)^+$ upon injection into the flow tube. These three observations taken together strongly suggest a contribution of excited states to the observed decays in the reactions of Fe^+ with N_2O and NO_2 less than the experimental error in the determination of their rate coefficients. It should be noted here that van Koppen et al. observed that 20 ± 3% of the Fe^+ produced from $Fe(CO)_5$ at 50 eV in their conventional ion source was in the ^4D second excited state and that this state was not measurably deactivated by collisions with helium.[9] However, there is no evidence for the production of significant amounts of a metastable excited Fe^+ state in our experiments, perhaps because of differences in ion source conditions.

In most experiments FeO^+ was produced in a high-pressure ion source containing a 1% mixture of $Fe(CO)_5$ in N_2O. Again, collisions with He atoms served to thermalize the ions before they entered the reaction region so that we are confident that the ground electronic $^6\Sigma^+$ state predominates among the FeO^+ ions entering the reaction region under our experimental conditions. Support for this contention comes from the observation that none of the measured semilogarithmic decays of the FeO^+ signal, some of which exceeded two orders of magnitude, showed curvature which could be attributed to the presence of excited states with different reactivities. Also, no differences were observed in the measured reaction kinetics using an entirely different mode of production for FeO^+: in the CO_2 and H_2O experiments FeO^+ was also produced from Fe^+ upstream in the flow tube by adding N_2O (1.5×10^{18} molecules s^{-1}) through the aspirator gas inlet together with the helium buffer gas.

Reactant neutrals were introduced into the reaction region either as a pure gas or, as in the case of H_2O, as a dilute (0.2−5%) mixture in helium. The H_2O was distilled and deionized before use. All other neutrals were obtained commercially and were of high purity (generally >99%). The rate coefficients for primary reactions reported here are estimated to have an absolute accuracy of ±30%. Higher-order rate coefficients were obtained by fitting the experimental data to the solution of the system of differential equations for a chain of successive reactions.

Results and Discussion

Table 1 summarizes the products and rate coefficients measured for the primary reactions of Fe^+ and FeO^+, while Table 2 lists the rate coefficients measured for the sequential addition reactions observed with FeO^+ at 294 ± 3 K in helium buffer gas at a total gas pressure of 0.35 ± 0.01 Torr. The standard enthalpy changes indicated for several reactions in the following section were derived from values found in the compilation of Lias et al.[17a] unless indicated otherwise.[17b−c,d] The standard enthalpy of formation of FeO^+ was taken to be 259 kcal mol^{-1},[17b] and $D_0(Fe^+{-}C)$ was taken as 94 ± 7 kcal mol^{-1}.[17d]

Reactions with H_2, HD, and D_2. No reactions were observed between Fe^+ and H_2, HD and D_2, $k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The failure to observe bimolecular products is not surprising given that H-atom transfer from H_2 is more than 50 kcal mol^{-1} endothermic. There has been a previous

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Table 1. Measured Products and Rate Coefficients for Reactions of the Ground States of FeO^+ and Bare Fe^+ with Selected Inorganic Ligands Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr. Reaction[a] and Collision[b] Rate Coefficients Are Given Beneath the Measured Products in Units of cm^3 $molecules^{-1}$ s^{-1}

reactant molecule	Fe^+	FeO^+
H_2	NR[c] $<10^{-14}$, 1.5×10^{-9}	$Fe^+ + H_2O$ $(8.75 \pm 0.2) \times 10^{-12}$, 1.50×10^{-9}
HD	NR $<10^{-13}$, 1.2×10^{-9}	$Fe^+ + HDO$ $(7.65 \pm 0.3) \times 10^{-12}$, 1.23×10^{-9}
D_2	NR $<10^{-13}$, 1.1×10^{-9}	$Fe^+ + D_2O$ $(4.2 \pm 0.3) \times 10^{-12}$, 1.1×10^{-9}
H_2O	NR $<10^{-13}$, 2.4×10^{-9}	$FeO(H_2O)^+$ $(1.8 \pm 0.2) \times 10^{-10}$, 2.4×10^{-9}
CO	NR $<10^{-14}$, 7.6×10^{-10}	$Fe^+ + CO_2$ $(2.05 \pm 0.2) \times 10^{-10}$, 7.3×10^{-10}
NO	NR $<10^{-11}$, 7.3×10^{-10}	NR $<10^{-11}$, 7.0×10^{-10}
N_2	NR $<10^{-14}$, 7.2×10^{-10}	$FeO(N_2)^+$ $(5 \pm 3) \times 10^{-14}$, 6.9×10^{-10}
O_2	NR $<10^{-14}$, 6.6×10^{-10}	NR $<2 \times 10^{-14}$, 6.3×10^{-10}
CO_2	NR $<10^{-15}$, 8.0×10^{-10}	$FeO(CO_2)^+$ $(4.9 \pm 0.4) \times 10^{-12}$, 7.6×10^{-10}
NO_2	$FeO^+ + NO$ $(4.8 \pm 0.4) \times 10^{-10}$, 8.9×10^{-10}	$NO^+ + FeO_2$ $(4.9 \pm 0.4) \times 10^{-10}$, 8.4×10^{-10}
N_2O	$FeO^+ + N_2$ $(3.1 \pm 0.1) \times 10^{-11}$, 8.6×10^{-10}	$FeO(N_2O)^+$ $(1.2 \pm 0.1) \times 10^{-11}$, 8.1×10^{-10}

[a] The reaction rate coefficient is given first along with the precision of the measurements, where appropriate. The relative uncertainty in all reaction rate coefficients does not exceed 10%; however, the absolute error may be as high as 30%. [b] The collision rate coefficient is given second and calculated using ADO theory.[16] [c] No reaction.

Table 2. Measured Rate Coefficients[a] for the Sequential Ligation Reactions of FeO^+ with N_2O, CO_2, and H_2O of the Type $FeO^+(\text{ligand})_{n-1} + \text{Ligand} \rightarrow FeO^+(\text{ligand})_n$ Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr

n	N_2O	CO_2	H_2O
1	1.2×10^{-11}	4.9×10^{-12}	1.8×10^{-10}
2	1.2×10^{-11}	3.7×10^{-12}	2.8×10^{-10}
3	1.4×10^{-11}	2.0×10^{-13}	2.0×10^{-10}
4	$<10^{-14}$	$<10^{-15}$	5×10^{-11}
5			5×10^{-11}

[a] In units of cm^3 $molecule^{-1}$ s^{-1}.

report that Fe^+ does not react with H_2, HD, and D_2 under guided-ion beam conditions at low energies.[18] The absence of an association channel under our SIFT conditions is consistent with weak bonding between Fe^+ and H_2 and/or a short lifetime of the intermediate complex. The ^6D $3d^64s^1$ ground electronic state of Fe^+ has a large 4s orbital which contributes to repulsive interaction with H_2.[18] It seems likely that the interaction between ground-state Fe^+ (^6D) and H_2 is at best only weakly attractive and that there is a surface crossing from a sextet to a quartet surface which allows the Fe^+ ground state to enter a $(^4F\ 3d^7)Fe(H_2)^+$ potential well where the adduct is more strongly bound. This is in a manner analogous to that described for the interaction of Fe^+ and propane.[9] Our results suggest that the lifetime of the intermediate $Fe(H_2)^+$ complex may be insufficient for curve-crossing and subsequent stabilization, in spite of the significant bond energy of 10.8 ± 0.6 kcal mol^{-1} which has recently been reported for $(^4F)Fe(H_2)^+$.[19] In this context we may compare our result for $Fe^+ + H_2$, $k < 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 0.35 Torr of He, with the effective bimolecular rate coefficient obtained for the reaction of $Fe^+ + CH_4$, $k = (1.1 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, using the flow-tube technique at 300 K and 0.75 Torr of He.[8] The difference in *k*, >100, can be rationalized, in our opinion, on the basis of the lower operating pressure of our experiments, a stronger interaction between Fe^+ and CH_4, $D_0(Fe^+-CH_4) = 13.7 \pm 0.8$ kcal mol^{-1},[20a] and a longer lifetime of the intermediate $Fe-CH_4$ complex due to its larger number of degrees of freedom. The importance of degrees of freedom in determining the lifetime of an intermediate complex can be appreciated by comparing the result for the reaction of Fe^+ with methane with the much larger rate coefficients of $(5.9 \pm 1.8) \times 10^{-11}$ and $(6.2 \pm 1.9) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} measured for the reactions with ethane and propane in the flow-tube study.[8] $Fe^+-C_2H_6$ and $Fe^+-C_3H_8$ have binding energies at 0 K of 15.2 ± 1.4 and 18.0 ± 0.9 kcal mol^{-1}, respectively, which are both not much larger than $D_0(Fe^+-CH_4)$.[20b,c]

FeO^+ was observed to react slowly with H_2, HD, and D_2 to produce Fe^+ as the only product ion. Production of both the ground (^6D) and the first excited (^4F) electronic state of Fe^+ along with H_2O, HOD, and D_2O, respectively, is substantially exothermic.[7,12] Measured product ratios for other product ions, e.g. FeH^+ and $FeOH^+$, were <1%. Experimental results with HD are shown in Figure 1. The measured rate coefficients are given in Table 1 and correspond to reaction efficiencies along with their precision of $(5.8 \pm 0.2) \times 10^{-3}$, $(6.2 \pm 0.3) \times 10^{-3}$, and $(3.9 \pm 0.3) \times 10^{-3}$, respectively, with an estimated absolute accuracy of ±30%. The reaction efficiency, RE, is taken to be equal to the ratio of the measured reaction rate coefficient to the calculated collision rate coefficient, k_{exp}/k_c. The Langevin collision theory[16a] is used to calculate k_c with polarizabilities for H_2, HD, and D_2 of 0.8023, 0.7976, and 0.7921, respectively.[16b] The isotope effects are small: in terms of rate coefficients they are $k(H_2)/k(HD) = 1.1 \pm 0.1$ and $k(H_2)/k(D_2) = 2.1 \pm 0.1$, and in terms of reaction efficiency they are $RE(H_2)/RE(HD) = 0.94 \pm 0.08$ and $RE(H_2)/RE(D_2) = 1.5 \pm 0.1$.

Our results are qualitatively in agreement with a recent FT-ICR study, but our rate coefficients are consistently lower by about a factor of 2: the FT-ICR rate coefficients are 1.6 ± 10^{-11}, 1.3×10^{-11}, and 1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} with a reported uncertainty of ±40%.[4] The high values obtained in

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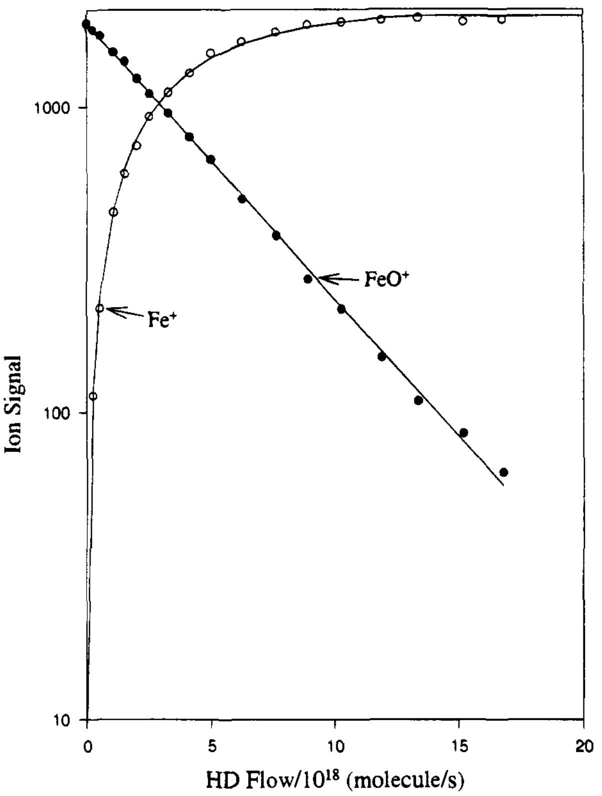

Figure 1. Experimental data for the reaction of FeO^+ with HD. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. FeO^+ was formed in a mixture of $Fe(CO)_5$ and N_2O in a high-pressure ionization source exposed to 20–60 eV electrons. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate for this reaction.

the FT-ICR experiments have been attributed by others to insufficient collisional cooling of the FeO^+ ions,[7] but perhaps also can be attributed to a calibration error. The more recent published value of 1.5×10^{-12} cm^3 molecule^{-1} s^{-1} (no uncertainty given) reported for the rate coefficient of the reaction of FeO^+ with D_2 occurring in a guided-ion beam tandem mass spectrometer[5b] is more than a factor of 2 lower than our value of 4.2 (± 30%) × 10^{-12} cm^3 molecule^{-1} s^{-1}. An updated value for the guided ion-beam results of 2.5×10^{-12} cm^3 molecule^{-1} s^{-1} is higher than the published value and leads to agreement between the two techniques, at least within the experimental uncertainties of the two techniques.[21]

Explanations for the observed inefficiencies of the reactions of FeO^+ with H_2, HD, and D_2 and the small isotope effects have proven to be challenging.[7,12] The potential-energy surface for the reaction of FeO^+ with H_2 has received theoretical attention: one plausible explanation for the observed low reactivity of this reaction involves a transition from the sextet surface of the entrance channel to an intermediate quartet surface which requires 6 kcal mol^{-1} of energy.[7,12] This energy requirement is roughly in agreement with the value of 3 kcal mol^{-1} which can be estimated from the efficiency determined in our experiments, viz. from the relation $k = k_c e^{-E/RT}$. Here it should be recognized that an Arrhenius activation energy of course is not strictly equivalent to the barrier height on a potential energy surface.

Our failure to observe association reactions between FeO^+ and hydrogen is consistent with the theoretical prediction of a binding energy of only 5 kcal mol^{-1}.[12]

Reactions with CO, NO, N₂, and O₂. No reactions were observed between Fe^+ and CO, NO, N_2, and O_2. Table 1 provides upper limits to the measured rate coefficients: the higher upper limit for the reaction with NO is due to the higher impurity level in this gas. Thermodynamics predicts that bimolecular reactions involving all of these molecules are kinetically unfavorable. The ionization energy of Fe (IE = 7.9024 eV)[17c] is too low for electron transfer to be exothermic. Also, formation of FeO^+ is endothermic in each case, as is the formation of FeC^+ from CO and probably also the formation of FeN^+ from NO and N_2, although the standard enthalpy of formation for FeN^+ does not seem to be available. Previous reports have shown that Fe^+ is unreactive toward CO and O_2 under low-energy and low-pressure ICR[2] and guided-ion beam mass spectrometer conditions.[6] The absence of measurable association reactions at the much higher pressures of our SIFT experiments with helium as the stabilizing third body again would suggest weak bonding between Fe^+ and the ligand and/or a short lifetime of the intermediate $Fe(X)^+$ complex. We are not aware of previous determinations of the binding energy for $Fe^+{-}NO$, but $Fe(N_2)^+$ and $Fe(CO)^+$ have been investigated both theoretically and experimentally.[22,23] Theory indicates that $Fe(N_2)^+$ prefers an end-on structure resulting in a $^4\Sigma^-$ state with an adiabatic binding energy of only 11.9 ± 2.3 kcal mol^{-1}. $Fe(CO)^+$ is also predicted to have a linear geometry and a $^4\Sigma^-$ electronic ground state, but it has more than twice the binding energy: the most recent experimental results[23a] suggest a bond-dissociation energy of 32 kcal mol^{-1} for $Fe^+{-}CO$ which is comparable to, but larger than, the computed adiabatic dissociation energy.[24] The situation with O_2 seems different. According to theory, Fe^+ and triplet oxygen molecule can form a side-on peroxo complex, $Fe(O_2)^+$ ($^6A_1$), without curve crossing which easily isomerizes to the high-valent iron(V) dioxide, $OFeO^+$ ($^6A_1$).[25] The calculations predict a bond-dissociation energy of 24 kcal mol^{-1} for the side-on complex and of 29 kcal mol^{-1} for the dissociation of $OFeO^+$ into Fe^+ and O_2.[25] These bond-dissociation energies are perhaps large enough to expect observable addition but, again, the lifetime of the intermediate complex involving this diatomic ligand will be relatively short because of the small number of internal degrees of freedom expected to be effective in the energy dispersal.

It is interesting to note that the addition of O_2 has been observed with neutral Fe atoms in a nitrogen bath at much higher pressures ranging from 8.4 to 40.0 Torr.[13] The reaction was measured to have a positive temperature dependence which was attributed to a barrier in the entrance channel to the potential-energy surface of the adduct. According to these results, the effective bimolecular rate coefficient for this addition reaction proceeding under our conditions of temperature and pressure would be 8×10^{-17} cm^3 molecule^{-1} s^{-1} (assuming that N_2 and He are equally effective as stabilizing third bodies). Our upper limit for the corresponding reaction with Fe cations is $< 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

FeO^+ also was observed to be unreactive in our SIFT experiments with NO, N_2, and O_2 but did react with CO by O-atom abstraction as shown in reaction 1.

$$FeO^+ + CO \rightarrow Fe^+ + CO_2 \qquad (1)$$

This reaction is exothermic by more than 40 kcal mol^{-1}, while

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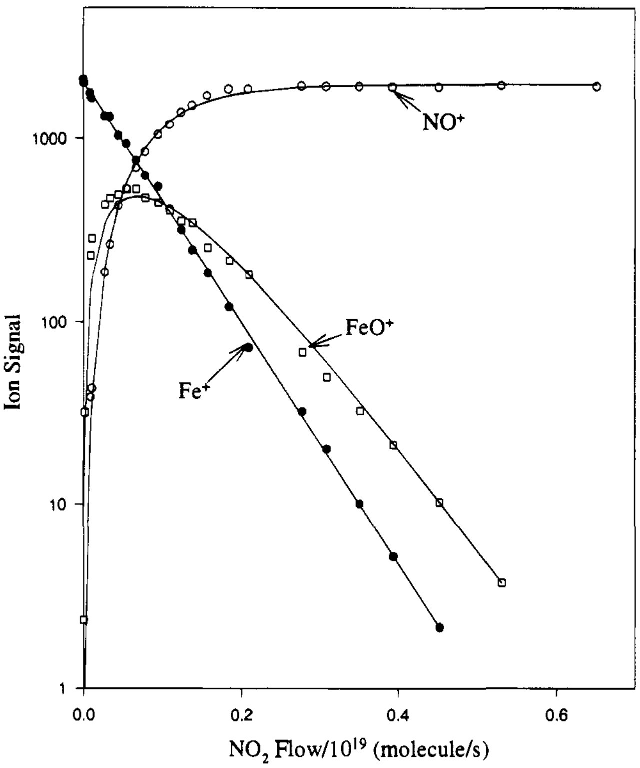

Figure 2. Experimental data for the reaction of Fe^+ with nitrogen dioxide, NO_2. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. Fe^+ was formed initially by electron-impact ionization of $Fe(CO)_5$. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. Rate coefficients derived from this fit are given in Table 1.

the analogous reactions with NO, N_2, and O_2 are endothermic by 8, 42, and 56 kcal mol^{-1}, respectively. The rate coefficient of reaction 1 determined under our SIFT conditions, $k = 2.05$ (± 30%) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, is considerably smaller than a previously reported value of 9 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (no uncertainty given) obtained with ICR spectroscopy.[2] The difference may be due to the possible presence of excited FeO^+ in the ICR experiments which has been discussed,[2] and/or due to a kinetic energy effect. The reaction of FeO^+ with N_2 was observed in our experiments to produce the adduct $FeO(N_2)^+$, but only very slowly, $k = 5 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. Trace amounts of a second adduct, $FeO(N_2)_2{}^+$, were also observed. We have discussed elsewhere the nature of the bonding of N_2 to FeO^+.[26] There was no evidence in our experiments for adduct formation between FeO^+ and NO or O_2.

Reactions with NO_2. Figure 2 shows that both Fe^+ and FeO^+ react with NO_2. The O-atom transfer reaction 2 was the

$$Fe^+ + NO_2 \rightarrow FeO^+ + NO \qquad (2)$$

only reaction observed with Fe^+ and was found to occur rapidly under our experimental conditions, $k_2 = 4.8 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Reaction 2 corresponds to the reverse of the non-reaction between FeO^+ and NO observed in this study, and so is 8 kcal mol^{-1} exothermic. This exothermicity is insufficient for the production of the excited $^4\Phi$ electronic state of FeO^+ which, according to the most recent calculations,[12] lies 19 kcal mol^{-1} above the $^6\Sigma^+$ ground state. The production of NO^+ + FeO in reaction 2 is less exothermic by about 8 kcal mol^{-1} since IE(FeO) < IE(NO) by 0.36 eV, and so is approximately thermoneutral.

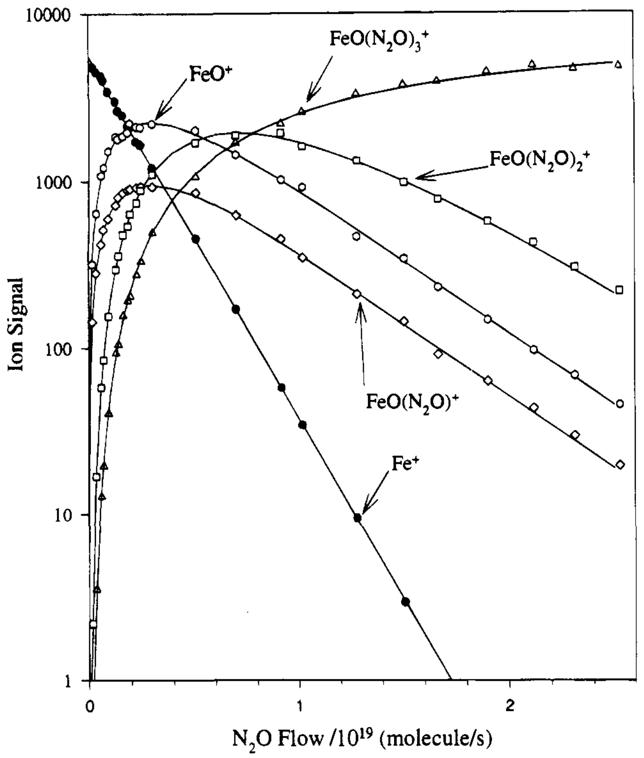

Figure 3. Experimental data for the reaction of Fe^+ with nitrous oxide, N_2O. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. Fe^+ was formed initially by electron-impact ionization of $Fe(CO)_5$. The solid lines represent a fit to the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. Rate coefficients derived from this fit are given in Tables 1 and 2.

FeO^+ reacts equally quickly with NO_2 to produce NO^+ as shown in Figure 2 and eq 3, $k_3 = 4.9 \times 10^{-10}$ cm^3 $molecule^{-1}$

$$FeO^+ + NO_2 \rightarrow NO^+ + FeO_2 \qquad (3)$$

s^{-1}. Of course the neutral product was not observed, but it is interesting to establish its identity since this might provide some insight into a likely mechanism: possible neutral products include FeO_2, FeO + O, and Fe + O_2. Thermodynamics predicts that the production of Fe + O_2 and FeO + O is endothermic by 67 and 88 kcal mol^{-1}, respectively. This leaves FeO_2 as the only possible neutral product and points toward O^- transfer, rather than say dissociative electron transfer, as a likely reaction mechanism. It is mechanistically possible that the O^- initially attaches to the Fe site in FeO^+ (as in reaction 2) to produce O−Fe−O, or that Fe−O−O or cyclic FeO_2 is produced. In any case, the energy for the dissociation of whichever of these FeO_2 species is produced into Fe + O_2 must exceed 67 kcal mol^{-1} for reaction 3 to be exothermic and proceed rapidly in the gas phase. It is interesting to note that low-level ab initio calculations (HF/STO-3G*) reported very recently predict the lowest-energy state of FeO_2 to have an isosceles triangle superoxide ($^7A_1$) geometry with a bond energy, $D_0(Fe-O_2)$, of 43 ± 12 kcal mol^{-1}.[13]

The production of $FeO_2{}^+$ + NO in reaction 3, which might be considered the analogue of reaction 2 but which was not observed in our experiments, is less exothermic by 6 kcal mol^{-1} than reaction 3 since IE(FeO_2) > IE(NO) by 0.24 eV. Here we have taken IE (FeO_2) = 9.5 eV.[27]

Reactions with N_2O. Experimental results for the reaction of FeO^+ with N_2O are shown in Figure 3. The observed

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[26] Baranov, V.; Bohme, D. K. *Chem. Phys. Lett.* **1995**, *239*, 339.

[27] Hildenbrand, D. L. *Chem. Phys. Lett.* **1975**, *34*, 352.

chemistry is initiated by the bimolecular reaction 4 which

$$Fe^+ + N_2O \rightarrow FeO^+ + N_2 \qquad (4)$$

produces FeO^+. It is not known to what extent reaction 4 produces the electronically excited $^4\Phi$ state of FeO^+; its production is exothermic by about 23 kcal mol^{-1} since it lies 19 kcal mol^{-1} above the $^6\Sigma^+$ ground state.[12] The primary decay of Fe^+ shown in Figure 3 provides a rate coefficient of (3.1 ± 0.9) × 10^{-11} cm^3 molecule^{-1} s^{-1} for this reaction at 294 ± 3 K. This value is lower than a previously reported value of 7 × 10^{-11} cm^3 molecule^{-1} s^{-1} (no uncertainty given) obtained using ICR spectroscopy.[2] Again the ICR result is higher, suggesting that it does not correspond to complete thermalization of the reactant ions or a calibration error. Reaction 4 has also been observed to proceed in an ion-beam apparatus with a cross section about 1/10 of the collision cross section and with a negative dependence on collision energy typical of reactions proceeding without an activation energy.[28] Our result indicates a reaction efficiency of less than 1/25. We do not completely understand why this O-atom transfer reaction is so inefficient. Armentrout et al. have discussed qualitatively the nature of the surface for reactions of atomic metal ions generally with N_2O and have rationalized the low observed efficiency of such reactions in terms of a singlet−triplet N_2O surface crossing, but this model does not seem to account for the observed absence of an activation energy for reaction 4.[28]

Under our SIFT conditions FeO^+ produced in reaction 4 continues to react with nitrous oxide in the flow tube and sequentially forms the ligated FeO^+ cations $FeO(N_2O)^+$, $FeO(N_2O)_2^+$, and $FeO(N_2O)_3^+$ according to reactions 5−7, respectively (see Figure 3).

$$FeO^+ + N_2O \rightarrow FeO(N_2O)^+ \qquad (5)$$

$$FeO(N_2O)^+ + N_2O \rightarrow FeO(N_2O)_2^+ \qquad (6)$$

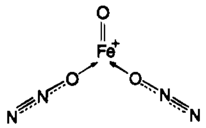
$$FeO(N_2O)_2^+ + N_2O \rightarrow FeO(N_2O)_3^+ \qquad (7)$$

The failure of reaction 5 to produce $FeO_2^+ + N_2$, the analogue of reaction 4 with Fe^+, is noteworthy. This bimolecular reaction appears to be exothermic by 26 kcal mol^{-1} based on the known O-atom affinity[17] for N_2 of 40 kcal mol^{-1} and the energy of 66.0 kcal mol^{-1} recently computed for the dissociation of $O{-}Fe{-}O^+$ ($^6A_1$) into FeO^+ ($^6\Sigma^+$) + O (^3P).[25] However, our experiments indicate that this bimolecular channel is pre-empted by collisional association. Perhaps the lifetime of the intermediate complex against bimolecular decomposition is sufficiently long for collisional stabilization to predominate. The relatively low efficiency of the analogous reaction 4 may be consistent with this view.

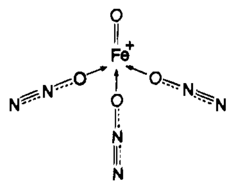
The solid curves in Figure 3 fit the experimental data to solutions of the system of differential equations for a chain of successive reactions and provide effective bimolecular rate coefficients of 1.1, 1.1, and 1.4 × 10^{-11} cm^3 molecule^{-1} s^{-1} for reactions 5, 6, and 7, respectively. The pressure dependence of these rate coefficients was not determined, but presumably these reactions proceed by termolecular association with He acting as the third body under the operating conditions of the experiments. These rate coefficients are quite large and so are more consistent with ligand−bond formation rather than with weaker, purely electrostatic bonding, viz. solvation. It is also important to note that the $FeO(N_2O)_3^+$ does not react further, $k < 10^{-14}$ cm^3 molecule^{-1} s^{-1}, suggesting a special stability for this ion.

The observation that the rate coefficients for reactions 5, 6, and 7 are practically identical indicates that the sequential addition of N_2O molecules is not significantly influenced by previous additions. Such a behavior points toward structures **I**, **II**, and **III** for the three adducts observed. We propose that these structures result from the filling of three coordination sites on iron in FeO^+($^6\Sigma^+$). The remaining six valence-shell orbitals of iron are occupied by five unpaired electrons and one lone pair donated from O^{2-} (thereby preserving the multiplicity of 6). The failure of $FeO(N_2O)_3^+$, which we presume to have C_{3v} symmetry, to react further can then be attributed to the occupation of all the orbitals of iron available for coordination.

I



II



III

Our observations of the addition reactions 5−7 have implications for the proposed role of FeO^+ as a catalyst in the oxidation of CO to CO_2 and analogous oxidation reactions.[2,3] N_2O is the most widely used reagent in the production of FeO^+. Our experiments show that at sufficiently high pressures (either of pure N_2O or of a buffer gas/N_2O mixture) N_2O will ligate FeO^+ with up to three N_2O molecules and the question arises whether ligation will act to "poison" the catalyst by reducing the reactivity of FeO^+. The answer to this question was resolved in separate SIFT experiments in our laboratory in which FeO^+ was ligated with N_2O upstream of the flow tube and CO was added downstream. The results of one such experiment are shown in Figure 4. These experiments indicated that the ligated $FeO(N_2O)_n^+$ ions (n = 1−3) react with CO with a rate coefficient close to the unligated FeO^+, $k \approx 10^{-10}$ cm^3 molecule^{-1} s^{-1}, presumably according to the following reaction (neutral products were not identified):

$$FeO(N_2O)_n^+ + CO \rightarrow Fe^+ + nN_2O + CO_2 \qquad (8)$$

So it appears that the catalytic role of FeO^+ in the oxidation of CO to CO_2 can be extended to FeO^+ ligated with up to three molecules of N_2O as illustrated in Figure 5. This result is interesting but perhaps not surprising since the unligated reaction is exothermic by 40 kcal mol^{-1} and the sum of the three N_2O ligation bond energies is not likely to exceed 40 kcal mol^{-1}. It should be noted also that the thermodynamics for other analogous oxidation reactions catalyzed by FeO^+ may not be as favorable so that ligation may indeed "poison" other similar catalysis reactions.

Reactions with CO_2. Fe^+ was found not to react with CO_2 under our SIFT conditions, $k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The failure to form $Fe(CO_2)^+$ is interesting, particularly with a view to the reported production of a loosely-bound $Fe^+{\cdot}CO_2$ ion−dipole adduct from the reaction of Fe^+ with β-butyrolactone (with the elimination of C_3H_6) in an FT-ICR mass spectrometer.[29] The latter study was able to establish a bond-dissociation energy for $Fe^+{-}(CO_2)$ of only 8 ± 2 kcal mol^{-1}. The failure to observe the direct formation of $Fe(CO_2)^+$ from Fe^+ and CO_2

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(28) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

(29) Schwarz, J.; Schwarz, H. *Organometallics* **1994**, *13*, 1518.

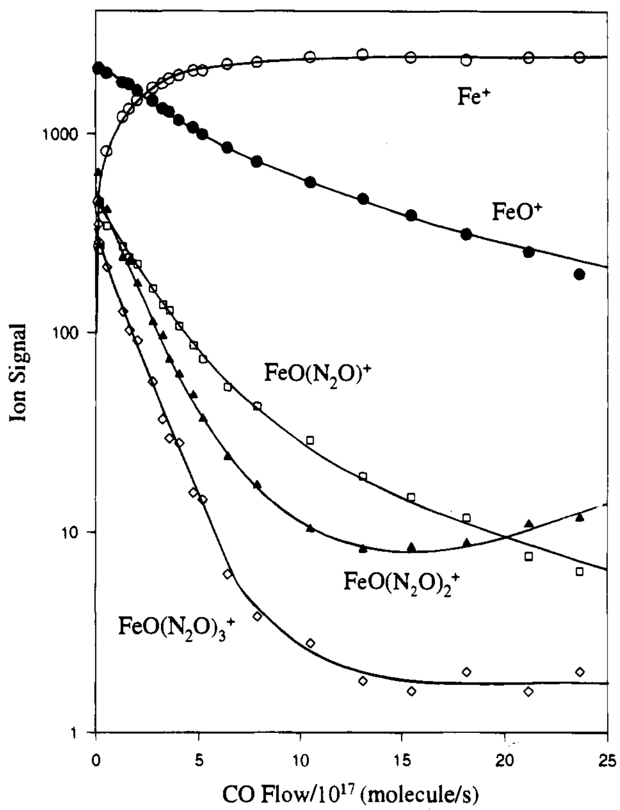


Figure 4. Experimental data for the reaction of FeO$^+$ and FeO(N$_2$O)$_n$$^+$ (n = 1−3) with carbon monoxide. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. FeO$^+$ was produced in a high-pressure ion source containing a 1% mixture of Fe(CO)$_5$ in N$_2$O. The FeO(N$_2$O)$_n$$^+$ ions were produced from FeO$^+$ upstream in the flow tube by adding N$_2$O (4 × 10^{18} molecules s^{-1}) through the aspirator gas inlet together with the helium buffer gas. The flow was selected to provide a predominant FeO$^+$ ion signal and approximately equal amounts of the FeO(N$_2$O)$_n$$^+$ adduct ions. The effective reaction length was 47 cm.

under our operating conditions is consistent with an intermediate complex lifetime too short for collisional stabilization due to a low binding energy for the complex.

Experiments in which FeO$^+$ is initially established as the dominant reactant ion upstream in the flow tube indicated the occurrence of the following sequence of addition reactions as shown in Figure 6:

$$FeO^+ + CO_2 \rightarrow FeO(CO_2)^+ \qquad (9)$$

$$FeO(CO_2)^+ + CO_2 \rightarrow FeO(CO_2)_2^+ \qquad (10)$$

$$FeO(CO_2)_2^+ + CO_2 \rightarrow FeO(CO_2)_3^+ \qquad (11)$$

The solid lines in Figure 6 are based on a numerical solution of the respective differential equations using values for k_9, k_{10}, and k_{11} given in Table 1.

The rate coefficients for addition of CO$_2$ to FeO$^+$ are lower than those for the addition of N$_2$O and so suggest lower binding energies for the addition of CO$_2$. The lower binding energies may be attributed to the lower electron-donor properties of carbon dioxide in comparison with nitrous oxide. As was the case with N$_2$O, the rate coefficient for addition is nearly independent of the number of ligands added, at least up to n = 2, and becomes immeasurably small for the addition of the fourth ligand. Curiously, the rate coefficient, k_{11}, for the addition of the third molecule of CO$_2$ is approximately 1.5 orders of magnitude lower than those for the primary and secondary ligand-addition reactions. We believe that this behavior may be understood in terms of the pattern of coordination of CO$_2$ to FeO$^+$ shown in structures **IV**, **V**, **VI**, and **VII**.

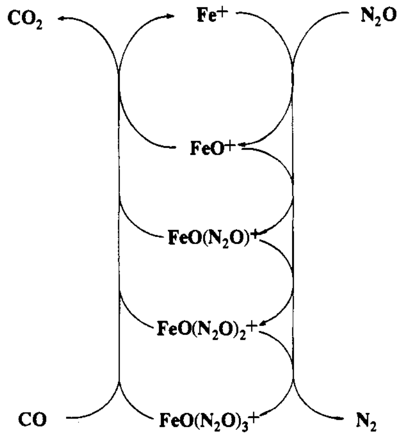
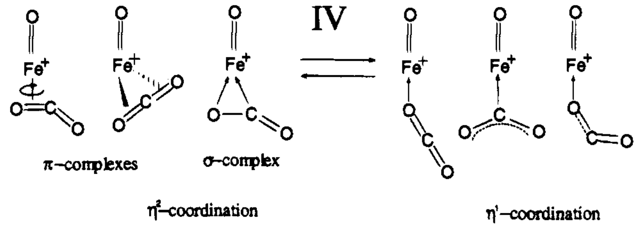
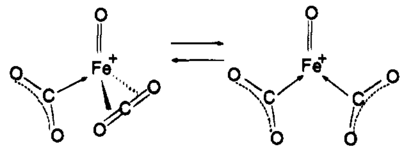
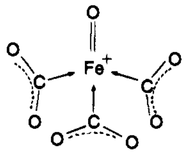


Figure 5. Schematic of the catalytic role of FeO$^+$ and ligated FeO$^+$ in the oxidation of CO to CO$_2$.


IV

V

VI


VII

CO$_2$ can act as a monodentate, as a bidentate, or as a π-electron donating ligand, as has been observed in the condensed phase.[30] Accordingly, various types of ligation, as those shown in **IV**, may occur in the FeO(CO$_2$)$^+$ adduct which we have observed. Some insight into the structure of the second adduct, FeO(CO$_2$)$_2$$^+$, is provided, in part, by its relatively low rate of ligation of a third CO$_2$ molecule. For example, a comparison with the observations for the ligation of FeO$^+$ with N$_2$O, which indicate three equally rapid additions of N$_2$O, excludes a structure analogous to **III** as the only structure for FeO(CO$_2$)$_3$$^+$. Structures of type **V** in which two different modes of coordination fully occupy the three available sites of coordination, and **VI** which has one available site of coordination but which is sterically hindered, would reasonably account for the lower reactivity of FeO(CO$_2$)$_2$$^+$. Structure **VII** is one of several possible structures for FeO(CO$_2$)$_3$$^+$ in which all three ligands should be monodentate.

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(30) For an overview, see: Aresta, M.; Quaranta, E.; Tommasi, I. *New J. Chem.* **1994**, *18*, 133.

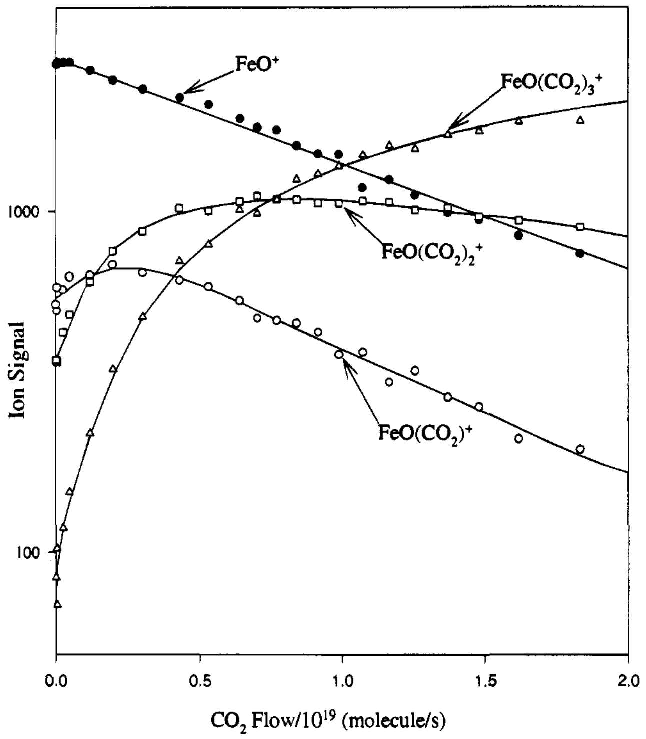

Figure 6. Experimental data for the reaction of FeO^+ with carbon dioxide. The measurements were performed at 294 ± 3 K and at helium buffer-gas pressure of 0.35 ± 0.01 Torr. FeO^+ was formed initially from the reaction of Fe^+ with N_2O (see Experimental Section). The solid lines represent a fit the experimental data with the solution of the system of differential equations for a chain of successive addition reactions. Rate coefficients derived from this fit are given in Table 2.

Reactions with H_2O. Fe^+ was observed to be unreactive also with H_2O, $k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The bimolecular formations of FeO^+, $FeOH^+$, and FeH^+ are all clearly endothermic and so are not expected to occur. The failure to observe association to form $Fe(H_2O)^+$ is perhaps unexpected. Previous experimental[19,31,32] and theoretical studies[24,33] of the binding energy of Fe^+-H_2O indicate values of 30.6 ± 1.2,[19] 28.8 ± 3,[31] 32.8 ± 4,[32] and 32.5[33] kcal mol^{-1}. Such a high binding energy might be expected to lead to a measurable reaction rate coefficient for this association reaction with a triatomic ligand under our experimental operating conditions in helium buffer gas, but this was not the case. It is known from theory that Fe^+-H_2O can bond from the $3d^64s^1$ Fe^+ ground state and that the $^6A_1$ ground state of $Fe(H_2O)^+$ reduces the repulsion between the 4s electron of Fe^+ and H_2O by 4s−4p hybridization of the Fe^+ and polarization.[33] Since a change in spin is not required in the association reaction of Fe^+ with H_2O, and the ion−dipole interaction should be strong enough to induce the hybridization necessary for strong bonding, the low efficiency observed should be determined by the lifetime of the collision complex. Apparently the lifetime of the collision complex is too short for stabilization by He.

It should be noted that the gas-phase generation of hydrated Fe^+ ions, $Fe(H_2O)_n^+$ with $n = 1-4$, has been reported previously by several research groups.[19,31,32] However, the addition of H_2O to Fe^+ was not unequivocally demonstrated in these experiments. Formation of $Fe(H_2O)^+$ has been achieved by the ligand-exchange reaction[19] of $Fe(CO)^+$ with H_2O and by sputtering a frosted iron surface.[31] In the flowing-afterglow study,[32] hydration of Fe^+ proceeds in the presence of ionized iron carbonyl and the termolecular association of H_2O to Fe^+, which was presumed to occur under these conditions, was not demonstrated. However, a recently published guided-ion beam study reports evidence for the collisional stabilization of $Fe(D_2O)^+$ by D_2O at the rather low operating pressure of ca. 0.4 mTorr.[34] D_2O is expected to be much more effective in stabilizing an intermediate $Fe(D_2O)^+$ complex than He atoms.

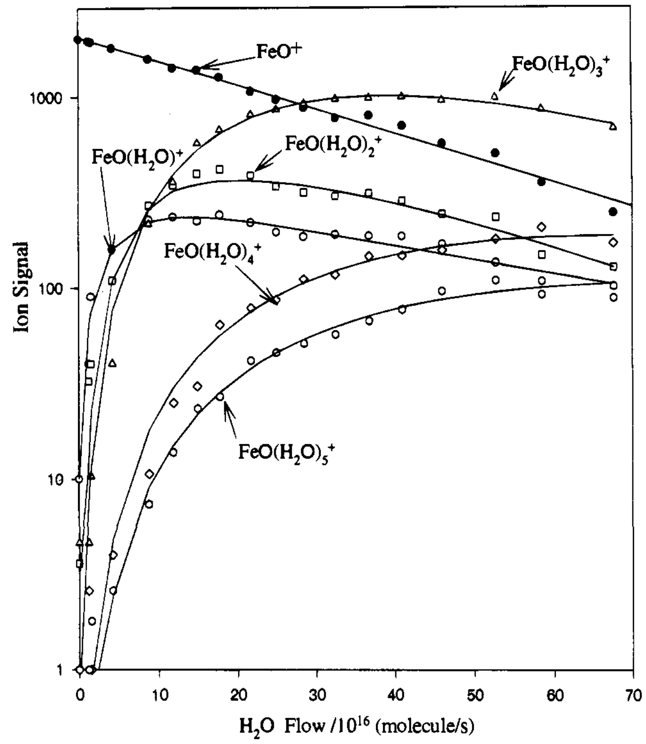

Figure 7. Experimental data for the reaction of FeO^+ with water molecules. The measurements were taken at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. FeO^+ was formed initially from the reaction of Fe^+ with N_2O (see Experimental Section). The solid lines represent a fit to the experimental data with the solution of the system of differential equations for a chain of successive addition reactions. Rate coefficients derived from this fit are given in Table 2.

The observed sequential chemistry initiated by FeO^+ with H_2O under our SIFT conditions is shown in Figure 7. This chemistry can be described by the association reactions 12−16, all of which are presumably termolecular at the conditions

$$FeO^+ + H_2O \rightarrow FeO(H_2O)^+ \qquad (12)$$

$$FeO(H_2O)^+ + H_2O \rightarrow FeO(H_2O)_2^+ \qquad (13)$$

$$FeO(H_2O)_2^+ + H_2O \rightarrow FeO(H_2O)_3^+ \qquad (14)$$

$$FeO(H_2O)_3^+ + H_2O \rightarrow FeO(H_2O)_4^+ \qquad (15)$$

$$FeO(H_2O)_n^+ + H_2O \rightarrow FeO(H_2O)_{n+1}^+ \qquad (16)$$

of our experiment and so involve collisional stabilization of the intermediate complex by collisions with buffer-gas He atoms. The effective bimolecular rate coefficients deduced from the experimental data are summarized in Table 2. Up to eight water molecules were observed to add in total.

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(31) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 5036.

(32) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

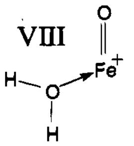
(33) (a) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1989**, *90*, 7264. (b) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876.

(34) Clemmer, D. E.; Yu-Min, C.; Khan, F. A.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 6522.

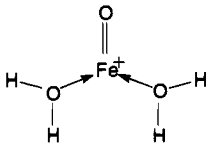
The observed addition of at least eight molecules of H_2O to FeO^+ is in sharp contrast with the maximum addition of three molecules observed with N_2O and CO_2 as shown graphically in Figure 8.

The results in Figure 8 for H_2O can be accounted for in terms of more than one coordination shell. The inner shell can be expected to be similar to those proposed for the coordination of N_2O and CO_2 to FeO^+ for which the coordination number is 3. This is consistent with the trend in the magnitude of the rate coefficients with the addition of up to three molecules of H_2O. The adduct ions $FeO(H_2O)_n^+$ with $n = 1-3$ can therefore be expected to have the structures **VIII** to **X**, respectively. We interpret the drop in the measured rate coefficient by a factor of 4 upon the addition of the fourth molecule of H_2O to signify a change in the nature of bonding. We suggest that the fourth and higher H_2O molecules bond by hydrogen bonding in a second coordination shell as is illustrated in structures **XI** and **XII** for $Fe(H_2O)_4^+$ and $FeO(H_2O)_6^+$, respectively.

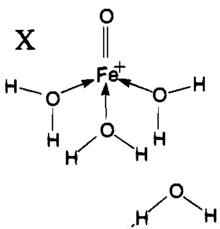
VIII



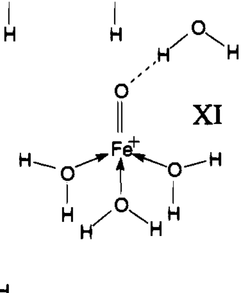
IX



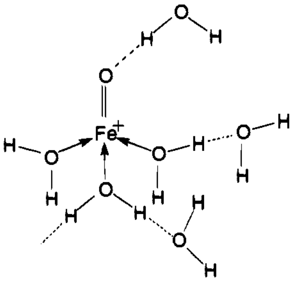
X



XI



XII



Conclusions

The results of the SIFT experiments reported here provide the first truly thermal rate coefficients for reactions of Fe^+ and FeO^+ with inorganic ligands at 294 ± 3 K.

Multiple ligation of FeO^+ by sequential ion–molecule association reactions has been observed with N_2O, CO_2, and H_2O in the gas phase at room temperature in helium at 0.35 Torr. Rate coefficients for the successive addition of these molecules to FeO^+ have been measured, and these have provided insight into the coordination number of Fe in FeO^+. In contrast, Fe^+ itself was observed not to undergo ligation under similar operating conditions (but N_2O reacts with Fe^+ to produce FeO^+ with the elimination of N_2). This difference in reactivity can be attributed to electronic effects associated with overcoming the repulsion between the 4s electron of Fe^+ and incoming ligands, and a higher ligation energy with FeO^+ due to a higher formal charge on the iron which arises from electron withdrawal by the atomic oxygen.

We suggest that the iron occupies a central position in the structures of the ligated cations investigated in this study and that the symmetry of the coordination compounds $FeO(N_2O)_3^+$, $FeO(CO_2)_3^+$, and $FeO(H_2O)_3^+$ is likely to be C_{3v}. We have demonstrated from measurements of the ligation-reaction kinetics that the coordination number of the FeO^+ ion in the gas phase equals 3 with the monodentate ligands N_2O and H_2O. Even though the ligation of FeO^+ with CO_2 is different because of the bidentate nature of CO_2, our experimental observations also suggest a coordination number of 3 with this molecule. The rate of addition of the third CO_2 ligand may be suppressed when two-point attachment of one of the previously ligated CO_2 molecules has taken place. The observation in the case of water of the formation of adduct ions with as many as eight molecules, viz. $FeO(H_2O)_8^+$, demonstrates the importance of hydrogen bonding to the oxygen of FeO^+ and the formation of a second coordination shell dominated by hydrogen bonding to the water molecules coordinated to Fe.

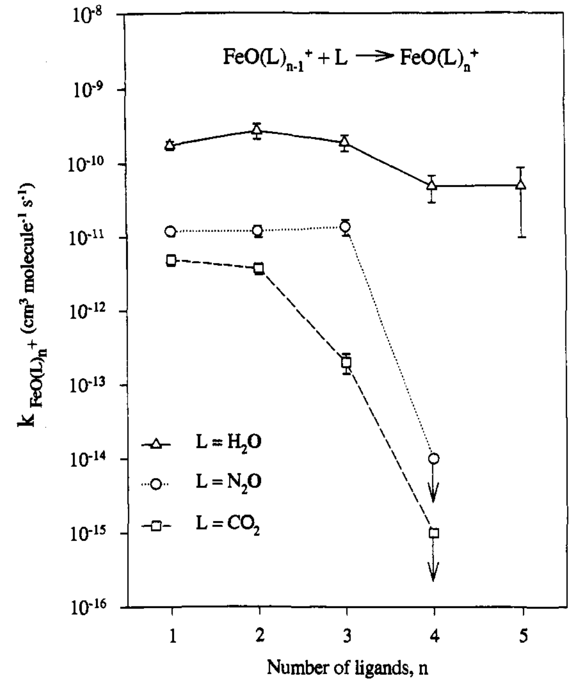


Figure 8. A semilogarithmic correlation of the rate coefficient for the sequential ligation of FeO^+ with H_2O, N_2O, and CO_2 with the number of ligands added in the gas phase at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr.

The results for the reactions of the ligated $FeO(N_2O)_n^+$ species with CO have extended the catalytic role of FeO^+ in the oxidation of CO to CO_2 to ligated FeO^+. They also provide the first kinetic results for the dependence of reactivity on the degree of ligation of FeO^+.

Taken together, the results reported in this study also establish that the SIFT technique is highly suited for experimental studies of sequential ligation reactions, and the study of the influence of ligation on the chemistry of ligated ions in the gas phase.

Acknowledgment. D.K.B. is grateful to the Natural Sciences and Engineering Research Council of Canada for the financial support of this research. Also, the authors thank Peter Armentrout, Detlef Schröder, and Robert Squires for valuable discussions, the two reviewers for valuable comments, and Helmut Schwarz for making available a manuscript prior to publication.

JA9506059