

Dinitrogen and Carbon Dioxide Fixation by Transition Metal Oxo Complexes

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Received August 27, 1996

While metal carbonyls have been, since their discovery, extensively studied, much less known is the chemistry of metal compounds with weaker bound ligands. Even though investigations of complexes with ligands such as dioxygen,¹ dinitrogen,² or carbon dioxide³ in condensed phase are making considerable progress, they still suffer from the lack of understanding of the subtle metal–ligand and ligand–ligand interactions involved. A number of recent theoretical and experimental gas phase studies have addressed this problem. Among the main group metals, magnesium^{4–7} has been the most extensively studied. As examples of first-row transition metals, complexes of vanadium,⁸ iron,⁹ cobalt,¹⁰ and nickel¹¹ with CO₂, and N₂^{12–16} have been investigated. Dinitrogen addition was also examined with ligated iron,¹⁷ and dioxygen compounds of iron¹⁸ have recently been identified using matrix isolation spectroscopy. There are, to the best of our knowledge, no similar studies on the second- or third-row transition metal ions.

In this paper, we investigate the ionic dioxygen, dinitrogen, and carbon dioxide complexes of rhenium. These are produced using a laser vaporization source, and their ligand exchange reactions are studied by FT-ICR (ion cyclotron resonance) mass spectrometry. The experiments were performed on a modified Spectrospin CMS47X mass spectrometer described in detail elsewhere.¹⁹ Rhenium cations ligated with oxygen, nitrogen, or carbon dioxide were produced in a disk type laser vaporization source. The target material was pure rhenium, the helium carrier gas at 10 bar was, for the different experiments, seeded with 0.2 mbar of O₂, 1.0 bar of N₂, or 0.4 bar of CO₂,

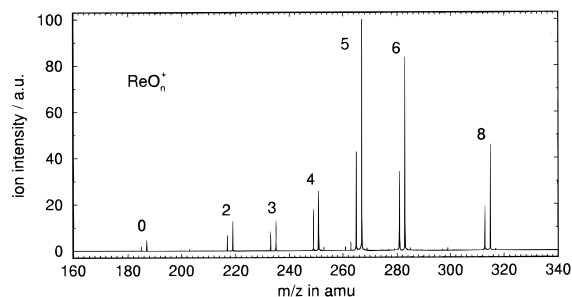


Figure 1. Typical mass spectrum of rhenium–oxygen compounds ReO_n^+ , $n = 0, 2–6, 8$, produced with a laser vaporization source by addition of a small amount of oxygen to the carrier gas.

respectively. The metal plasma was entrained in the carrier gas pulse, cooled by flowing through a confining channel and by subsequent supersonic expansion into high vacuum, resulting in formation of ligated rhenium cations. The ions were transferred through several stages of differential pumping into the high-field region of the superconducting magnet and stored inside the ICR cell at a pressure of $\sim 6 \times 10^{-10}$ mbar. To avoid kinetic excitation during the ion selection procedure, no broadband excitation was employed and ions within a mass range of 10 mass units around the desired ion were not ejected. Reactant gases were introduced to the ultrahigh vacuum region by two needle valves at pressures between 9.4×10^{-9} and 5.5×10^{-8} mbar, depending on the efficiency of the reactions. Rate constants were determined by fitting the observed intensity–time profiles of the reactions to pseudo-first-order reaction kinetics.

A series of rhenium–oxygen cations has been observed (Figure 1) and identified by collision-induced dissociation (CID) experiments²⁰ as $\text{Re}(\text{O}_2)^+$, $\text{Re}(\text{O}_2)_2^+$, $\text{Re}(\text{O}_2)_3^+$, $\text{Re}(\text{O}_2)_4^+$, ReO_3^+ , and $\text{ReO}_3(\text{O}_2)^+$. The present report concentrates on the $\text{ReO}_3(\text{O}_2)^+$ cation, consisting of the ReO_3^+ entity with one dioxygen ligand according to the CID experiment. In a series of experiments, we found that a number of ligands, including CO, CO₂, and N₂, can be attached to ReO_3^+ in highly efficient ligand exchange reactions of $\text{ReO}_3(\text{O}_2)^+$ which proceed at near collision rate. Similar reactions with $\text{Re}(\text{O}_2)_3^+$ are 2 orders of magnitude slower, and no reactions are observed in our experiments with $\text{Re}(\text{O}_2)_4^+$. This observation is actually quite surprising, as CID²⁰ suggests that the energies required for the abstraction of a dioxygen ligand from $\text{Re}(\text{O}_2)_3^+$ and $\text{Re}(\text{O}_2)_4^+$ are even lower than in $\text{ReO}_3(\text{O}_2)^+$, the values being $D(\text{Re}(\text{O}_2)_3^+ - \text{O}_2) = 71 \pm 14$ kJ/mol, $D(\text{Re}(\text{O}_2)_2^+ - \text{O}_2) = 88 \pm 14$ kJ/mol, and $D(\text{ReO}_3^+ - \text{O}_2) = 97 \pm 20$ kJ/mol, respectively.

By introducing both N₂ and CO₂ to the ultrahigh vacuum region, we could establish that the N₂ ligand in the ReO_3N_2^+ complex formed from $\text{ReO}_3(\text{O}_2)^+$ could be completely replaced by CO₂ (Figure 2). In a similar experiment, we found that CO₂ can be replaced by CO. Finally, all the ligands mentioned so far are efficiently exchanged against H₂O present in traces in the ultrahigh vacuum region. These findings are summarized in Scheme 1. The easy and quantitative replacement of N₂ by CO₂ indicates that the latter ligand is more strongly bound to ReO_3^+ . This observation is interesting, since for iron,¹³ cobalt,¹⁵ and nickel,^{11,16} the situation is reversed, with the bare Fe⁺, Co⁺, and Ni⁺ ions binding N₂ more strongly than CO₂. The observed behavior suggests a considerable influence of either the metal center or of its ligation (or both) upon the bonding of additional weak ligands like dioxygen, dinitrogen, and carbon dioxide.

To address the question of whether the specific nature of the metal or the three oxygen ligands cause this difference, we have generated the ReCO_2^+ and ReN_2^+ complexes and examined their

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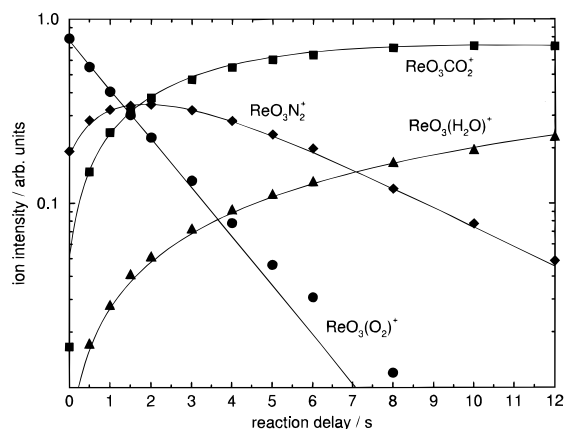
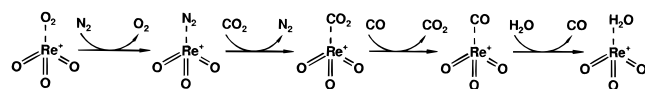


Figure 2. Intensity-time profile of the reaction of $\text{ReO}_3(\text{O}_2)^+$ with a 1:1 mixture of N_2 and CO_2 . In the first step, $\text{ReO}_3(\text{O}_2)^+$ (●) reacts with N_2 to ReO_3N_2^+ (◆) and with CO_2 to $\text{ReO}_3\text{CO}_2^+$ (■). The N_2 ligand in ReO_3N_2^+ is further replaced by CO_2 . All three ligands are efficiently exchanged against H_2O , which is present in traces in the ultrahigh vacuum region, thus finally forming $\text{ReO}_3(\text{H}_2\text{O})^+$ (▲).

Scheme 1. Successive Ligand Exchange Reactions of $\text{Re}(\text{O}_3)\text{L}^+$



reactions. While ReN_2^+ undergoes a rapid ligand exchange with CO_2 , ReCO_2^+ reacts only extremely slowly with N_2 , establishing that also to the bare rhenium cation CO_2 is more strongly bound than N_2 by 8 ± 2 kJ/mol, derived from the rate constants in Table 1. With CoCO_2^+ and CoN_2^+ , we found the opposite behavior as described in the literature, thus excluding an influence of the mode of ion generation. Change of the metal alone, without invoking effects of the other ligands causes the difference of the relative binding strength of the N_2 and CO_2 ligands.

Another question which we tried to address by experiment was whether the ligand exchange of dioxygen against N_2 or CO_2 is special for $\text{ReO}_3(\text{O}_2)^+$ or a common feature of transition metal dioxygen complexes. In several quick preliminary experiments, we have succeeded in producing various oxygen rich manganese and tungsten cations. In each case, we have observed a behavior similar to the oxo complexes of rhenium, easy exchange of the O_2 ligand against N_2 and CO_2 . Table 1 summarizes the observed reactions, together with absolute rate constants k_{abs} and reaction efficiencies Φ derived from ADO²¹ theory.

An interesting observation which requires comment involves reactions of $\text{Re}(\text{O}_2)_3^+$ and $\text{Re}(\text{O}_2)_4^+$ which, in spite of the weaker binding, exchange the O_2 ligands against N_2 and CO_2 and even CO much less efficiently than $\text{ReO}_3(\text{O}_2)^+$. One possibility is to explain this as a steric effect. In $\text{ReO}_3(\text{O}_2)^+$ the reactant may still have a direct access to the metal center. The energy released by the adsorption would then cause the dissociation of the peroxo ligand bond. In $\text{Re}(\text{O}_2)_3^+$ the metal seems to be less accessible, which results in a much smaller rate constant of the ligand exchange, and in the presumably fully saturated $\text{Re}(\text{O}_2)_4^+$, there is no possibility for the reactant gas to attack the metal.

Table 1. Ligand Exchange Reactions, Measured Rate Constants k_{abs} and Reaction Efficiencies (Φ)

reaction	k_{abs} ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	Φ (%)
$\text{ReO}_3(\text{O}_2)^+ + \text{N}_2 \rightarrow \text{ReO}_3\text{N}_2^+ + \text{O}_2$	3.57	58
$\text{ReO}_3(\text{O}_2)^+ + \text{CO}_2 \rightarrow \text{ReO}_3\text{CO}_2^+ + \text{O}_2$	7.37	98
$\text{ReO}_3(\text{O}_2)^+ + \text{CO} \rightarrow \text{ReO}_3\text{CO}^+ + \text{O}_2$	4.33	66
$\text{Re}(\text{O}_2)_3^+ + \text{N}_2 \rightarrow \text{Re}(\text{O}_2)_2\text{N}_2^+ + \text{O}_2$	0.01 - 0.06	0.2-1.0
$\text{Re}(\text{O}_2)_3^+ + \text{CO}_2 \rightarrow \text{Re}(\text{O}_2)_2\text{CO}_2^+ + \text{O}_2$	0.03 - 0.08	0.5-1.0
$\text{Re}(\text{O}_2)_3^+ + \text{CO} \rightarrow \text{Re}(\text{O}_2)_2\text{CO}^+ + \text{O}_2$	0.04	0.6
$\text{Re}(\text{O}_2)_4^+ + \text{N}_2 \rightarrow$	< 0.001	< 0.02
$\text{Re}(\text{O}_2)_4^+ + \text{CO}_2 \rightarrow$	< 0.002	< 0.03
$\text{Re}(\text{O}_2)_4^+ + \text{CO} \rightarrow$	< 0.003	< 0.04
$\text{ReO}_3\text{N}_2^+ + \text{CO}_2 \rightarrow \text{ReO}_3\text{CO}_2^+ + \text{N}_2$	4.94	65
$\text{ReO}_3\text{CO}_2^+ + \text{CO} \rightarrow \text{ReO}_3\text{CO}^+ + \text{CO}_2$	2.37	36
$\text{ReN}_2^+ + \text{CO}_2 \rightarrow \text{ReCO}_2^+ + \text{N}_2$	0.36	5
$\text{ReCO}_2^+ + \text{N}_2 \rightarrow \text{ReN}_2^+ + \text{CO}_2$	0.013	0.2
$\text{Mn}_2\text{O}_6^+ + \text{N}_2 \rightarrow \text{Mn}_2\text{O}_4\text{N}_2^+ + \text{O}_2$	2.38	38
$\text{Mn}_2\text{O}_6^+ + \text{CO}_2 \rightarrow \text{Mn}_2\text{O}_4\text{CO}_2^+ + \text{O}_2$	6.69	87
$\text{Mn}_2\text{O}_4\text{N}_2^+ + \text{CO}_2 \rightarrow \text{Mn}_2\text{O}_4\text{CO}_2^+ + \text{N}_2$	5.49	72
$\text{WO}_3^+ + \text{N}_2 \rightarrow \text{WO}_3\text{N}_2^+ + \text{O}_2$	4.29	69
$\text{WO}_6^+ + \text{N}_2 \rightarrow \text{WO}_4\text{N}_2^+ + \text{O}_2$	1.79	29
$\text{WO}_7^+ + \text{N}_2 \rightarrow \text{WO}_5\text{N}_2^+ + \text{O}_2$	2.62	43
$\text{WO}_3^+ + \text{CO}_2 \rightarrow \text{WO}_3\text{CO}_2^+ + \text{O}_2$	8.23	100
$\text{WO}_6^+ + \text{CO}_2 \rightarrow \text{WO}_4\text{CO}_2^+ + \text{O}_2$	2.57	34
$\text{WO}_7^+ + \text{CO}_2 \rightarrow \text{WO}_5\text{CO}_2^+ + \text{O}_2$	1.03	13
$\text{WO}_7^+ + \text{CO}_2 \rightarrow \text{WO}_3\text{CO}_2^+ + 2\text{O}_2$	5.32	71
$\text{WO}_3\text{CO}_2^+ + \text{CO}_2 \rightarrow \text{WO}_3(\text{CO}_2)_2^+ + \text{O}_2$	2.06	27

An alternative explanation would invoke two different types of peroxo ligands. In $\text{Re}(\text{O}_2)_3^+$ and $\text{Re}(\text{O}_2)_4^+$ could the peroxo ligands, in analogy to the known $\text{Cr}(\text{O}_2)_4^{3-}$ compound,¹ be coordinated side-on, with the coordination in $\text{ReO}_3(\text{O}_2)^+$ being of the end-on type? This could account for a different trend in binding energies of O_2 , N_2 , and CO_2 if the end-on ligated O_2 would be bound more weakly and the side-on one more strongly than N_2 and CO_2 to the ion in question. The lack of reactivity of $\text{Re}(\text{O}_2)_4^+$ with CO , however, is difficult to explain in that way.

In summary, we show that a variety of weakly bound complexes can be produced using laser vaporization technique. Examination of ligand exchange reactions of oxygen rich complexes of rhenium shows that this metal binds CO_2 more strongly than the dinitrogen ligand, in contrast with previous studies on several first-row transition metals, iron, cobalt or nickel. Evidence is presented that the type and degree of ligation, rather than differences in binding energies, determine the rate constants of gas phase ligand exchange reactions.

Acknowledgment. Financial support by the European Commission, program Environment, by the Deutsche Forschungsgemeinschaft, and by the Fond der Chemischen Industrie is gratefully acknowledged. The authors thank Wolfgang A. Herrmann for cooperation and for the rhenium sample.

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