Ion-cyclotron resonance study of elementary stages of the catalytic oxidation of CO by N_2O in the presence of VIA-group metal ions

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Gas phase reactions of Mo^+ and W^+ ions with the molecules of various oxidants (NO, O_2, N_2O, CH_2O, C_2H_4O) were studied using ion cyclotron resonance. In oxidation with N_2O the mono-, di- and trioxide metal cations are formed consecutively. The trioxide MO_3^+ ions of both metals react with CO to form CO_2 and MO_2^+ ions. In this way, catalytic reaction $N_2O + CO \rightarrow N_2 + CO_2$ occurs in the gas phase with MoO_3^+/MoO_2^+ and WO_3^+/WO_2^+ couples as catalysts. The rate constants have been measured for both stages of the catalytic cycle as well as for the stages of the catalyst preparation. Metal–oxygen bond energies were estimated for MoO_x^+ and WO_x^+ species with various x. The mechanism of CO oxidation with MoO_x^+ and WO_x^+ cations as catalysts in the gas phase is discussed in comparison with that for the oxidation over classical solid oxide catalysts.

Keywords: Ion-cyclotron resonance; gas phase catalytic oxidation; nitrogen monoxide; carbon monoxide; MO_x^+; rate constants; bond energies

1. Introduction

Oxidation reactions of carbon monoxide by dioxygen and other oxidants are classical reactions of both homogeneous catalysis in solutions and heterogeneous catalysis over solid surfaces. However, due to the complexity of both these types of catalytic systems the mechanism of these reactions is still revealed insufficiently. For this reason, their study with the ion cyclotron resonance (ICR) method in more simple gas phase systems is of a considerable interest. In such systems the mechanism of the catalytic oxidation can be elucidated indeed at the molecular level.

Using the ICR method Kappes and Staley [1] have shown that CO oxidation with N_2O is catalysed by such transition metal ions as Fe^+, Ti^+, Cr^+, Nb^+, Zr^+ and V^+. In these simple systems two principal mechanisms are realised:

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$$\text{mechanism A}\quad \begin{cases} M^+ + N_2O \rightarrow MO^+ + N_2 & (1)\\ MO^+ + CO \rightarrow M^+ + CO_2 & (2)\end{cases}$$

$$\text{mechanism B}\quad \begin{cases} MO^+ + N_2O \rightarrow MO_2^+ + N_2 & (3)\\ MO_2^+ + CO \rightarrow MO^+ + CO_2\,. & (4)\end{cases}$$

Here M^+ are metal ions, MO^+ and MO_2^+ mono- and dioxide ions. For mechanism A the catalyst alternates during the catalytic reactions between the M^+ and MO^+ states, while for mechanism B it alternates between the MO^+ and MO_2^+ states. For mechanism B the ion MO^+ is formed in the same reaction (1), as for mechanism A. But for mechanism B this reaction serves as the stage of catalyst preparation rather than participates in the catalytic cycle. As found in ref. [1], only the Fe^+ ion exhibits mechanism A, while all the other ions exhibit mechanism B.

Similar mechanisms have been proposed by Matsuda [2,3] in his study with the shock waves method of the catalytic oxidation of CO by O_2 in the presence of the chromium, iron, and nickel oxides formed from carbonyl vapor:

$$\text{mechanism C}\quad \begin{cases} MO_n + O_2 \rightarrow MO_{n+2} & (5)\\ MO_m + CO \rightarrow MO_{m-1} + CO_2 & (6)\end{cases}$$

where M are Cr, Fe or Ni; $n = 0, 1$; $m = 1, 2, 3$. According to refs. [2,3], reactions involving a set of species with various n and m can occur simultaneously.

In the present work we have investigated the mechanism of catalytic oxidation of CO by N_2O in the presence of VIA- group metal ions Mo^+ and W^+.

2. Experimental

All experiments were performed using a standard [4] Bruker-Spectrospin ion-cyclotron resonance spectrometer CMS-47 equipped with a 33 mm cubic trapping cell and an Oxford Instruments vertical type superconducting magnet with a field of 4.7 T. A warm hole of the magnet was 89 mm. The trapping plates voltage was +1.0 V, the side plates voltage was −0.1 V. The plates were kept at room temperature. Molybdenum and tungsten ions were produced with electron impact (EI) at the energy of 70 eV of the corresponding vaporised metal hexacarbonyls:

$$M(CO)_6 + e^- \begin{cases} \xrightarrow{D} M^+ + 2e^- + 6CO \\ \xrightarrow{E} M(CO)_n^+ + 2e^- + (6-n)CO\,. \end{cases} \qquad (7)$$

Carbonyl metal ions formed in channel E were ejected from the cell with the double resonance pulses, while trapped ions M^+ could react with molecules of the oxidants (NO, O_2, N_2O, CH_2O, C_2H_4O) and reductant CO. A vacuum system was evacuated by means of the ion pump (160 ℓ/s). The best pressure obtained was about 1×10^{-9} mbar. Sample pressures were $(0.5–5.0) \times 10^{-7}$ mbar. Bayard-Alpert's ionization gauge was used to monitor pressure. Molybdenum and tungsten hexacarbonyls of the pure "for analysis" grade (Souzchimreactiv) were used without further purification. The gas phase reagents were admitted into the vacuum system through the UHV gas dosing valves. An ICR spectrum was excited by the pulse sequence, which was repeated in each experiment for several dozen times to obtain a better signal/noise ratio. The absence of the electron excited states of M^+ ions was probed with the method suggested in ref. [5], i.e. by checking whether the M^+ ions decay due to their reaction with carbonyl molecules was exponential. According to such tests, the excited ions constituted less than 5% for both Mo^+ and W^+ ions.

3. Results and discussion

We found that reaction of Mo^+ and W^+ ions with NO or CH_2O yielded only tungsten monoxide ions MO^+. The reaction of Mo^+ and W^+ with oxygen yielded mono- and dioxide ions, while the reaction between Mo^+ and W^+ ions with N_2O leads to the deeper oxidation to trioxide cations via consecutive processes:

$$M^+ + N_2O \rightarrow MO^+ + N_2 \tag{8}$$

$$MO^+ + N_2O \rightarrow MO_2^+ + N_2 \tag{9}$$

$$MO_2^+ + N_2O \rightarrow MO_3^+ + N_2 . \tag{10}$$

Consecutive formation of MO^+, MO_2^+, and MO_3^+ cations was observed also for oxidation with ethylene oxide.

Using the known values of the bond energy in the O_2 molecule and the energy of the oxygen atom abstraction from N_2O molecule, and taking into account that for a MO_{x+1}^+ ion to be observed in our experiments, the reaction of its formation from the MO_x^+ ion and O_2 or N_2O molecules must be exothermic, we can estimate the top and bottom limits for the metal–oxygen bond energy D^0 in mono-, di- and trioxide ions of Mo and W. These estimates are presented in table 1 together with the similar experimental data of ref. [6] for Cr^+ and the D^0 values calculated using the thermochemical cycle $D^0(MO_x^+–O) = D^0(MO_x–O) + IP(MO_x) - IP(MO_{x+1})$, where $x = 0, 1$ or 2, and the needed values of bond energies $D^0(MO_x–O)$ and ionisation potentials IP were taken from ref. [7]. Note the good agreement between the experimental estimates based on ICR data and the thermochemical calculations. For comparison, in table 2 oxygen bond energies for gaseous molecules of VIA-group metal oxides are presented. In all cases these energies are considerably smaller for the cations than for the neutral molecules of the same composition. Energy diagrams for reactions of MO_x^+ ions with O_2 and N_2O (where $x = 0, 1$ or 2) are shown in fig. 1.

From the diagram of fig. 1 it follows that dissociation of O_2 into O atoms and

Table 1
Oxygen bond energy (kcal/mol) of VIA-group metal oxide cations

Metal		$D^0(M^+–O)$	$D^0(MO^+–O)$	$D^0(MO_2^+–O)$
Cr	exp.	81 [a]	77–84 [a]	–
	calc. [b]	70 ± 10	74 ± 19	84 ± 23
Mo	exp.	$D^0 < 151$	$118 < D^0 < 151$	$85 < D^0 < 118$
	calc.	99 ± 15	125 ± 15	82 ± 14
W	exp.	$175 < D^0$	$118 < D^0 < 151$	$85 < D^0 < 118$
	calc.	136 ± 24	125 ± 15	107 ± 15

[a] According to ref. [6].

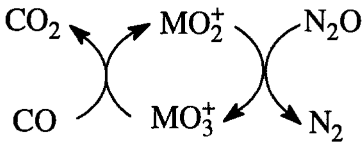
[b] Values calculated using the thermochemical cycle $D^0(MO_x^+–O) = D^0(MO_x–O) + IP(MO_x) - IP(MO_{x+1})$, $x = 0, 1$ and 2, according to ref. [7].

reactions between MO_x^+ and O_2 to produce MO_{x+1}^+ ion and O atom are spin-correlated processes, while dissociation of N_2O into N_2 molecule and O atom is not. This allows to suggest that no activation barrier should exist for the exothermic reactions between MO_x^+ and O_2, while such a barrier E_a may exist even for the exothermic reactions of MO_x^+ oxidation with N_2O (see the diagram in the right-hand side of fig. 1b). The barrier height is tentatively expected to decrease with the increase of the exothermicity of the reaction $MO_x^+ + N_2O \rightarrow MO_{x+1}^+ + N_2$, i.e. with the decrease of the bond energy $D^0(MO_x^+–O)$.

The addition of carbon monoxide to the reaction medium was accompanied by the shift of equilibrium in the $MO_x^+ + N_2O + CO$ reaction mixture to the formation of dioxide ions. Apparently, this is due to the reaction

$$MO_3^+ + CO \rightarrow MO_2^+ + CO_2 . \qquad (11)$$

Therefore, in our system the catalytic cycle presented in scheme 1 is carried out.



Scheme 1.

Table 2
Oxygen bond energy (kcal/mol) of VIA-group metal oxides [a]

Metal	$D^0(M–O)$	$D^0(MO–O)$	$D^0(MO_2–O)$
Cr	108 ± 7	118 ± 15	114 ± 20
Mo	120 ± 10	156 ± 11	142.3 ± 7
W	161 ± 7	143 ± 10	148 ± 10

[a] According to ref. [7].

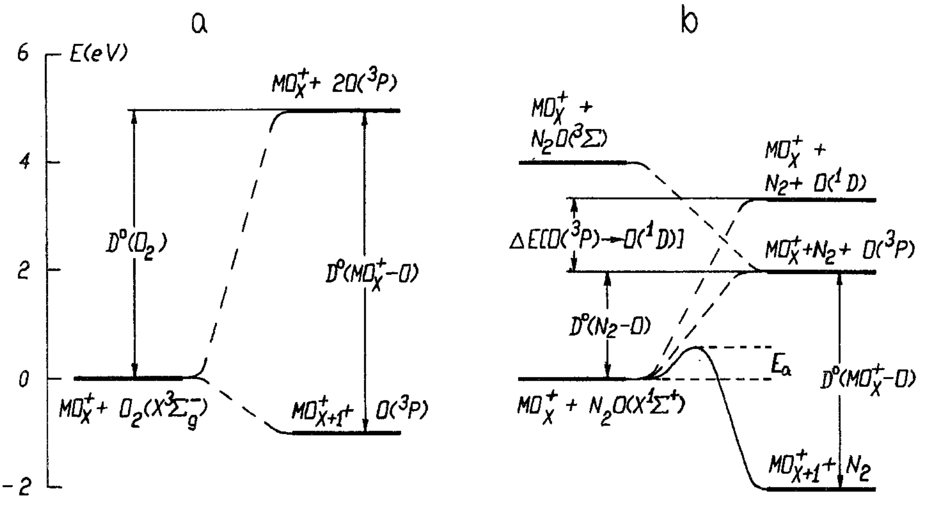


Fig. 1. Energy diagrams of the oxidation of MO_x^+ ions ($x = 0, 1$, and 2) with O_2 (a) and N_2O (b).

This cycle consists of reactions (10) and (11), while reactions (8) and (9) are the stages of the catalyst preparation. Reaction rate constants of stages (8)–(10) were calculated from the experimental curves of formation and decay of M^+ and MO_x^+ ions in the presence and absence of CO using the computer program [8] for solving the inverse kinetic problems. As typical examples, in figs. 2a and 2b the kinetic

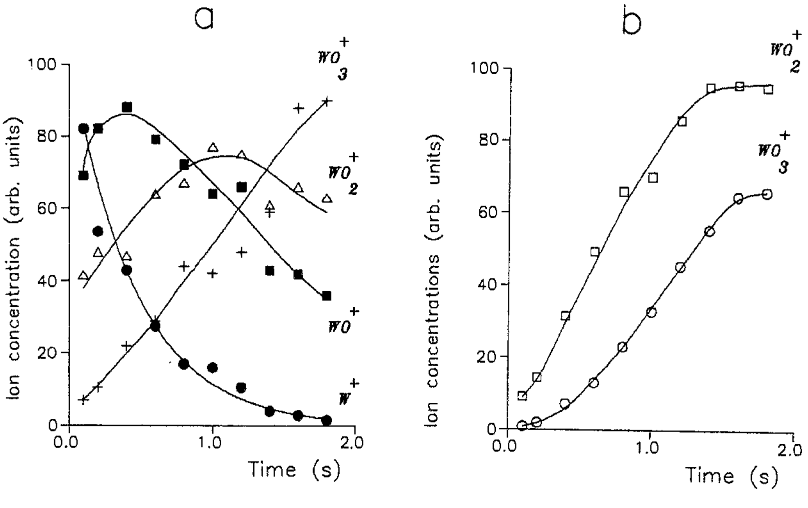


Fig. 2. Kinetic curves for the oxidation of W^+ ions (generated by electron impact of $W(CO)_6$) with N_2O to mono-, di-, and trioxide tungsten cations. $P_{W(CO)_6} = 5 \times 10^{-8}$ mbar, $P_{N_2O} = 5 \times 10^{-7}$ mbar; $P_{CO} = 0$ (a) and 3×10^{-7} mbar (b). Note the difference in the kinetic curves for WO_2^+ and WO_3^+ in (a) and (b). The kinetic curves for W^+ and WO^+ in (b) are omitted since they are the same as in (a).

curves for W^+ and WO_x^+ ions are presented, that have been obtained in the presence of solely N_2O and $N_2O + CO$ mixture, respectively. Rate constants for various steps of reactions between Mo^+ or W^+ and O_2 or N_2O oxidants that have been calculated from such curves, are presented in table 3. Note that the rate constants for oxidation with O_2 are very close to the values that have been calculated using the Langevin–Gioumousis–Stevenson model (LGS). However, for oxidation with N_2O the experimental rate constants are significantly smaller than the values calculated using the LGS model, except the constant k_9 for molybdenum. It means that the stages of oxidation with N_2O have a potential barrier. As expected, the smaller this barrier E_a is (i.e., the corresponding rate constant is the bigger, see table 3), the stronger is the bond energy $D^0(MO_x^+\text{–}O)$ in the species that is formed in the reaction (see table 1).

The rate constant k_{11} for reaction (11) can be calculated from the steady state concentrations $[\overline{MO_x^+}]$ of MO_2^+ and MO_3^+ cations that are achieved with the time (see fig. 2b) for a given ratio of the N_2O and CO pressures,

$$\frac{[\overline{MO_2^+}]}{[\overline{MO_3^+}]}\frac{P_{N_2O}}{P_{CO}} = \frac{k_{11}}{k_{10}}\,. \tag{12}$$

We have measured the constants k_{11} at various partial pressures of all reagents. As expected, identical values have been obtained in all cases. The rate constants were found to be $k_{11} = (0.28 \pm 0.06) \times 10^{-10}$ cm^3 s^{-1} for WO_3^+ and $k_{11} = (0.60 \pm 0.03) \times 10^{-10}$ cm^3 s^{-1} for MoO_3^+. These values are notably smaller than those calculated using the LGS model. Thus, reaction (11) is an activated one for both MoO_3^+ and WO_3^+.

Thus, for the gas phase reaction $N_2O + CO \rightarrow N_2 + CO_2$ catalyzed by Mo^+ and W^+ ions in oxygen environments, we have elucidated with the ICR method the detailed reaction mechanism and measured the rate constants for both reactions (10) and (11) that constitute the catalytic cycle and for reactions (8) and (9) that are the steps of the catalyst preparation. We have also estimated the binding energy of the oxygen atom to the metal cation in various MO_x^+ species and found them to agree well with the thermochemical data.

Table 3
Oxidation rate constants ($\times 10^{-10}$ cm^3/s): $M^+ \xrightarrow{k_8} MO^+ \xrightarrow{k_9} MO_2^+ \xrightarrow{k_{10}} MO_3^+$

Oxidants		Mo^+			W^+		
		k_8	k_9	k_{10}	k_8	k_9	k_{10}
O_2	theory[a]	7.92	7.74	7.61	7.31	7.26	7.22
	exp.	3.45 ± 0.40	2.78 ± 0.26	–	6.74	5.28	–
N_2O	theory[a]	9.50	9.29	9.13	8.77	8.70	8.64
	exp.	0.50 ± 0.02	7.20 ± 0.80	0.98 ± 0.04	2.28 ± 0.45	0.62 ± 0.12	0.46 ± 0.07

[a] Calculated using the LGS model: $k_{LGS} = 2\pi e(\alpha/\mu)^{0.5}$, where α is the polarizability of the molecule, μ reduced mass, e electron charge.

Catalytic oxidation in the systems studied in this work can be considered as a model of the stepwise mechanism of CO oxidation over oxide catalysts [9]:

$$CO + [O] \rightarrow CO_2 + [\,] \qquad (13)$$

$$\tfrac{1}{2}O_2 + [\,] \rightarrow [O]\,, \qquad (14)$$

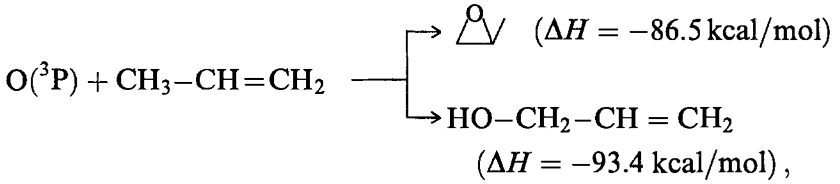
where [ ] is an oxygen vacancy, and [O] most probably is a species of the O^{2-} type, though other possible states of oxygen cannot be completely excluded as well [9]. From the data of this work it follows that in the gas phase almost every collision of the O_2 molecule with the Mo^+, W^+ and MoO^+, WO^+ ions leads to their consecutive oxidation to MO^+ and MO_2^+ states, respectively. For N_2O from three to ten collisions are needed for the oxidation step to occur. To compare these gas phase data with those for classical solid oxide catalytic systems, we used the data of ref. [10], where the surface of MoO_3 that had been preliminary reduced upto MoO_2, was reoxidized with oxygen. In this system the reaction proceeds in a kinetical rather than diffusional mode [10]. Using the data of ref. [10] for the reaction rate, surface concentration of the MoO_2 centers and pressure of the O_2, we have calculated: (1) the number of the reacting O_2 molecules per one MoO_2 center per second and (2) the number of O_2 molecules that collide with one MoO_2 center per second. The last value exceeded the first one by three orders of magnitude which corresponds to the activation energy of the reaction $E_a = 12$ kcal/mol. It means that the reaction of molybdenum sites with O_2 at about room temperature in the gas phase system occurs about two orders of magnitude more efficiently than in the heterogeneous system, at 853 K.

According to table 1, the energy of $O(^3P)$ atom abstraction from MoO_3^+ and WO_3^+ ions is between 85 and 118 kcal/mol. The comparison of these values with the enthalpy of the reaction,

$$O(^3P) + CO \rightarrow CO_2 \quad (\Delta H = -126\ \text{kcal/mol})\,, \qquad (15)$$

shows that reaction (11) is certainly exothermic. Therefore, it is not surprising that CO reacts with MoO_3^+ and WO_3^+ rather smoothly, though not at every collision. Moreover, according to the available thermochemical data [11], many reactions of hydrocarbon oxidation with $O(^3P)$ atom, e.g.

$$O(^3P) + CH_3{-}CH_2{-}CH_3 \rightarrow (CH_3)_2COH \quad (\Delta H = -99.3\ \text{kcal/mol}) \qquad (16)$$



$$O(^3P) + CH_3{-}CH{=}CH_2 \rightarrow \begin{cases} (\Delta H = -86.5\ \text{kcal/mol}) \\ HO{-}CH_2{-}CH = CH_2 \quad (\Delta H = -93.4\ \text{kcal/mol})\,, \end{cases} \qquad (17)$$

have enthalpies that also do not preclude the possibility of their stepwise catalytic oxidation with N_2O in the gas phase with MoO_3^+ and MoO_2^+ as catalytic intermediates. We plan to check whether this is true in the near future.

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