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Mass spectrometry based studies of gas phase metal catalyzed reactions

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ABSTRACT

Over the past three decades gas-phase catalytic cycles involving metal ions, complexes or clusters as intermediates have been discovered using either multistage mass spectrometry based experiments in trapping instruments or via flow tube methods. These studies have their foundations in: (i) the development of ion cyclotron and quadrupole ion trap mass spectrometers and the flowing afterglow technique, which date back to the 1960s; (ii) the development of ionization methods that allow the formation of gas phase metal ions, including electrospray ionization. Selected examples are reviewed that highlight the range of reaction types that are catalyzed in these processes, including: (i) oxidation of inorganic and organic substrates; (ii) decomposition of acetic acid via either water loss or decarboxylation channels (protodecarboxylation); (iii) decarboxylative C—C bond coupling reactions; and (iv) the dehydrogenation and trimerisation of ethylene to form benzene.

1. Introduction

The IUPAC definition of a catalyst is "*A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst is both a reactant and product of the reaction*" [1]. Mass spectrometry based techniques can be used to examine gas-phase catalytic cycles that involve metal catalysts with a net charge. A range of experimental and theoretical methods have been developed over the past 50 years to provide fundamental structural, mechanistic and energetic information about intermediates and reactions associated with these catalytic cycles. These include the development of: (i) Ion Cyclotron Resonance (ICR) mass spectrometers [2]; (ii) quadrupole ion trap mass spectrometers [3]; (iii) the flowing afterglow (FA) technique [4]; (iv) ionization methods that allow the formation of gas phase metal ions [5], including electrospray ionization [6]; and (v) Density Functional Theory (DFT), which is now commonly used to probe the mechanisms of steps associated with experimentally determined gas phase catalytic cycles [7]; and the concept of two state reactivity [8].

Two key classes of experimental methods have proven their worth in examining complete catalytic cycles in the gas phase: (i) trapping instruments such as Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometers [9] and ion trap mass spectrometers [10] have proven particularly useful, since their multistage mass spectrometry (MS^n) capabilities often allow each of the ionic intermediates in a catalytic cycle to be isolated and their reactivity explored in detail. (ii) Flow tube methods in which ions are entrained in a flowing bath gas which thermalizes the ions to the temperature of the bath gas [11]. Since different reagents can be delivered though individual ports at different distances along the flow tube, multiple ion-molecule reactions can be examined.

This article is not meant to be a comprehensive review of all gas phase metal ion chemistry of relevance to catalysis [12], which date back to early electron ionization mass spectrometry experiments on inorganic or organometallic complexes [13]. While thermochemical measurements have provided key information on bond energies associated with key metal containing intermediates associated with catalysis, these are not reviewed here [14]. I also do not review studies where mass spectrometry is used as an analytical technique to intercept possible intermediates and products of solution phase catalytic cycles [15]. Instead a 1968 report [16] and two pivotal papers from the 1980s are discussed [17,18], followed by a review of selected examples from the literature in which complete catalytic cycles have been identified using trapping instruments or flow tubes. These examples have been chosen to highlight the range of catalytic reactions that have been studied.

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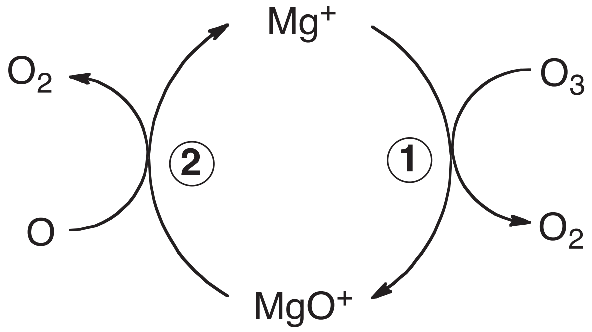
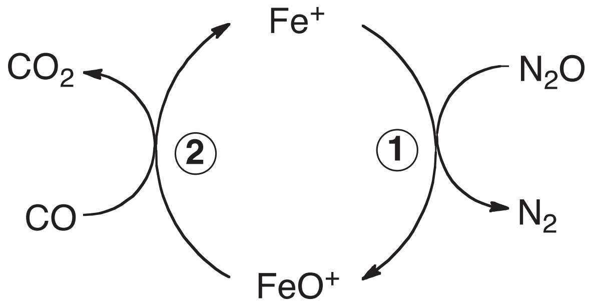


Scheme 1. Mg^+ catalyzed destruction of ozone by atomic oxygen [16]. Step **1** is oxygen atom abstraction from ozone; step **2** is oxygen atom transfer.



Scheme 2. Fe^+ catalyzed oxidation of CO by N_2O [17]. Step **1** is oxygen atom abstraction; step **2** is oxygen atom transfer.

Two beginnings: two pivotal papers from the 1980s

Although the first example of a metal catalyzed reaction appears to have been Ferguson and Fehsenfeld's 1968 report on the oxygen atom decomposition of ozone (Eq. (1)) catalyzed by the magnesium cation, although they did not identify the catalytic cycle shown in Scheme 1 [16]. The first papers to explicitly discuss gas phase catalysis by metal ions did not appear until the 1980s.

$$O_3 + O \rightarrow 2O_2 \tag{1}$$

1.1. ICR-MS study on oxidation of CO and catalyzed by Fe^+

In 1981, Kappes and Staley reported the first gas-phase catalytic cycles involving ionic transition metal catalysts [17]. They used a pulsed YAG laser to produce the atomic Fe^+ cation and studied its reactions in an ICR mass spectrometer. In the simplest of these cycles (Scheme 2), CO was oxidized to CO_2, with Fe^+ as the catalyst and N_2O as the oxidant (Eq. (2)). In the first step, Fe^+ reacted with N_2O by oxygen atom transfer to yield FeO^+, which in the second step transferred an oxygen atom to CO to yield neutral CO_2, thereby regenerating the Fe^+ catalyst. Although this oxidation reaction (Eq. (2)) is exothermic ($\Delta H^\circ = -107\ \mathrm{kcal\ mol^{-1}}$), it does not occur at room temperature in the absence of the Fe^+ catalyst.

$$N_2O + CO \rightarrow N_2 + CO_2 \tag{2}$$

In 2005 Bohme's group revisited this catalytic cycle using a selected ion flow tube (SIFT) and DFT calculations [19a]. Their DFT calculations on the uncatalyzed and catalyzed oxidation reaction are shown in Fig. 1, which highlights that Fe^+ acts as a catalysts by changing the reaction from a concerted one step reaction with a high activation energy (47.2 $\mathrm{kcal\ mol^{-1}}$) to the originally proposed two step oxygen transport reaction (Scheme 2), with both steps having modest barriers.

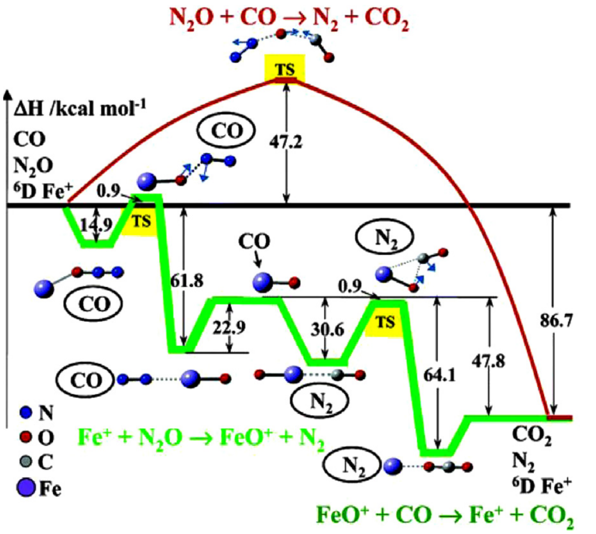


Fig. 1. DFT calculated (B3LYP/SDD/6-311+G*) energy diagram for the oxidation of CO by N_2O in the absence and presence of Fe^+ (^{6}D). The red profile corresponds to the neutral reaction of N_2O with CO. The green profile corresponds to the linked catalytic ion–molecule reactions of Fe^+ with N_2O and of FeO^+ with CO. The bold black line corresponds to the energy of the separated reactants. Spectator molecules are indicated in ovals. Transition state structures are labelled with TS; transition state vectors are sketched. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure reproduced from reference [19a].

There have been several other studies on metal catalyzed oxidation of CO using N_2O as the oxidant (Eq. (2)). Bohme's group have: (i) surveyed the reactions of 26 different atomic metal cations that lie within the thermodynamic window for O-atom transport catalysis and found only the following 10 behaved as catalysts – Ca^+, Fe^+, Ge^+, Sr^+, Ba^+, Os^+, Ir^+, Pt^+, Eu^+, and Yb^+ [19a]; (ii) established that other oxides of nitrogen can be used as oxidants for the oxidation of CO [19b]; and (iii) examined the role of benzene ligands in the oxidation of CO (cf. Scheme 1) [19c]. Metal clusters can act as catalysts, as demonstrated for platinum cluster anions [19d,e] and $[Y_2O_2]^{+\bullet}$ and $[YAlO_2]^{+\bullet}$ [19f].

The other catalytic cycle that Kappes and Staley reported in their pioneering study involved the oxidation of ethyne by N_2O catalyzed by Fe^+. Two reactions occur: O atom transfer (Eq. (3)) and the production of formaldehyde and CO (Eq. (4)) via the reaction with 2 equivalents of N_2O [17]. These reactions have recently been revisited using the variable temperature SIFT method [20].

$$N_2O + C_2H_2 \rightarrow N_2 + C_2H_2O \tag{3}$$

$$2N_2O + C_2H_2 \rightarrow 2N_2 + CH_2O + CO \tag{4}$$

It is worth noting that FeO^+ has been the subject of a large number of gas phase studies, many involving gas phase catalytic cycles, and these have been reviewed elsewhere [12a,d]. Of particular interest is C—H bond activation of typically inert substrates such as methane [21]. This work has been driven by the conceptual and electronic relationship between 'bare' FeO^+ and the ferryl group at the heart of cytochrome P-450, which is involved in the hydroxylation of alkanes [22].

1.2. FA study on neutral–neutral reactions catalyzed by metal ions

Early in 1982, the team of Rowe, Viggiano, Fehsenfeld, Fahey and Ferguson from the NOAA Environmental Research Laboratories in Boulder noted that the rate of the gas phase reactions of O_3 and N_2O_5 molecules with NO (Eqs. (5) and (7)) were enhanced when the O_3 and N_2O_5 molecules are clustered to alkali metal cations (e.g.

Eqs. (6) and (8)) [18]. While this work did not involve a complete catalytic cycle, it is important for two reasons: (1) the rate enhancement of over 9 orders of magnitude for the reaction of $Li^+(N_2O_5)$ with NO (Eq. (8)) compared to the reaction of N_2O_5 with NO (Eq. (7)) highlights the role of a metal ion in lowering the activation energy for a neutral reaction (recall Fig. 1); (2) it has inspired a range of researchers to consider the role of metal ions in catalyzing neutral–neutral reactions in the atmosphere and the interstellar medium [23].

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad k(3) = 2.3 \times 10^{-12}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \tag{5}$$

$$Na^+(O_3) + NO \rightarrow NO_2 + O_2 + Na^+ \quad k(4) = 6.5 \times 10^{-11}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \tag{6}$$

$$N_2O_5 + NO \rightarrow N_2O_4 + NO_2 \qquad k(5) < 10^{-20}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \tag{7}$$

$$Li^+(N_2O_5) + NO \rightarrow Li^+(N_2O_4) + NO_2 \quad k(6) = 1.2 \times 10^{-11}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \tag{8}$$

2. Oxidation of other inorganic and organic substrates

There have been a large number of gas phase ion chemistry studies on the oxidation of inorganic (e.g. H_2 [24a]) and organic substrates (e.g. ethene [24b], CH_3OH [25] and benzene [26]), and many of these have been reviewed previously [11]. A range of oxidants has been used, including N_2O [24], CH_3NO_2 [25b] and O_2 [25a,c]. Catalytic cycles have been reported for the oxidation of H_2 by N_2O (Eq. (9)) [24a] catalyzed by atomic metal cations and oxidation of ethene by N_2O (Eq. (10)) [24b] catalyzed by atomic alkaline earth cations. In the latter reaction, other competing reaction channels were observed [24b]. DFT calculations of the reaction of $CaO^{+\bullet}$ with ethene were employed to determine the barriers associated with forming various isomers with the molecular formula "C_2H_4O". It was found that the formation of acetaldehyde is favoured both thermodynamically as well as kinetically.

$$N_2O + H_2 \rightarrow N_2 + H_2O \tag{9}$$

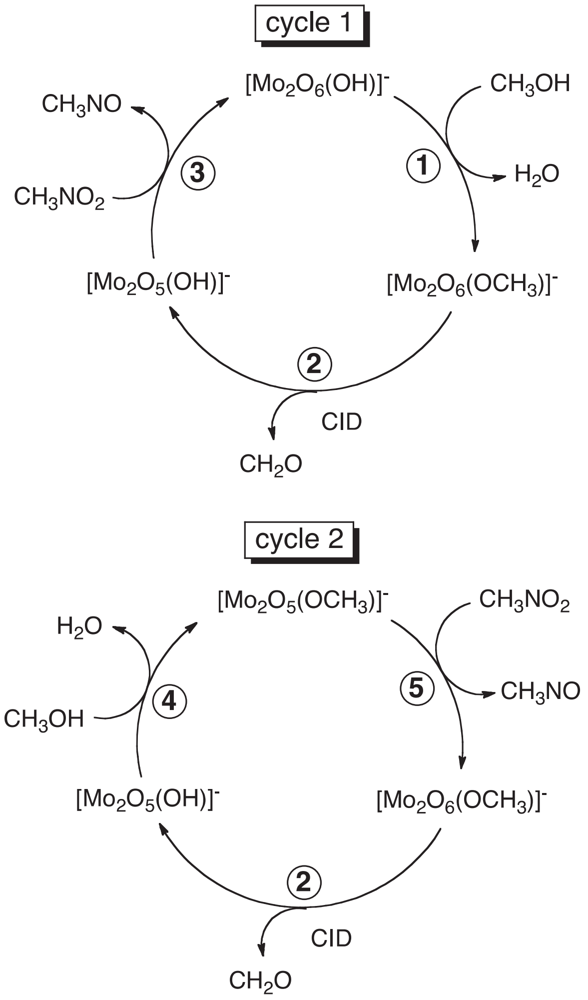
$$N_2O + C_2H_4 \rightarrow N_2 + C_2H_4O \tag{10}$$

With the advent of electrospray ionization, it is possible to transfer metal oxides ions from solution into the gas phase. Thus the gas phase reactivity of species that are directly relevant to homogeneous or heterogenous metal oxide catalysts can be interrogated. Two studies highlight that the nature of the metal oxide species can dictate the type of mechanism associated with the catalytic oxidation of methanol to formaldehyde with either nitromethane (Eq. (11), Scheme 3) or oxygen (Eq. (12), Scheme 4) as the oxidant.

$$CH_3OH + CH_3NO_2 \rightarrow CH_2O + CH_3NO + H_2O \tag{11}$$

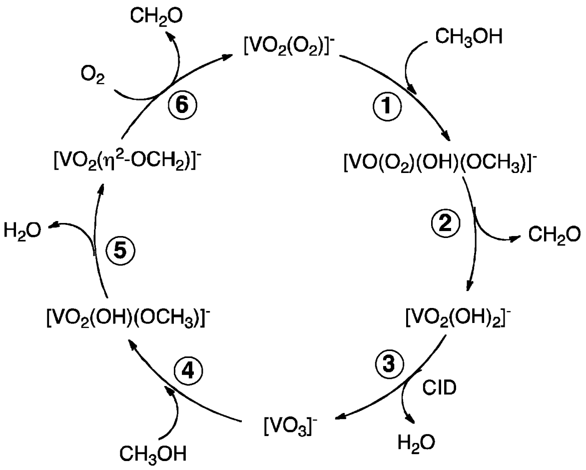
$$2\,CH_3OH + O_2 \rightarrow 2\,CH_2O + 2\,H_2O \tag{12}$$

An examination of Scheme 3 reveals two competing catalytic cycles for the oxidation of methanol to formaldehyde by nitromethane (Eq. (11)). In cycle 1, $[Mo_2O_6(OH)]^-$ reacts with methanol to yield $[Mo_2O_6(OCH_3)]^-$ (step **1**), which then undergoes loss of formaldehyde under conditions of collision-induced dissociation (CID) (step **2**). In step **3**, nitromethane reoxidizes $[Mo_2O_5(OH)]^-$ to regenerate the catalyst. Cycle 2 shares the same step **2** of cycle 1, but differs in the order of reaction with methanol (step **4**) and oxidation by nitromethane (step **5**).

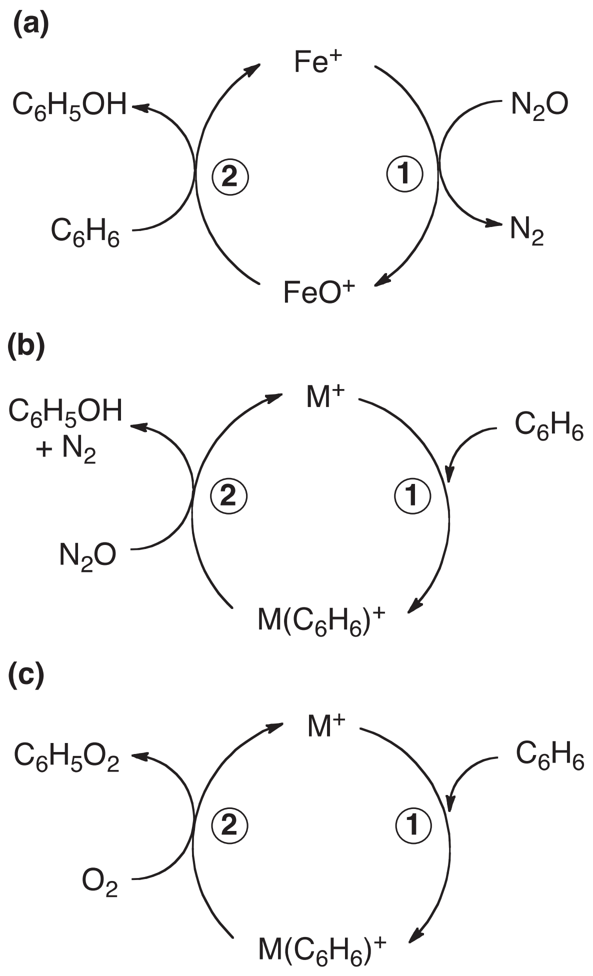


Scheme 3. Competing gas phase catalytic cycles for the oxidation of methanol to formaldehyde (Eq. (11)). Reaction (2) links $[Mo_2O_6(OCH_3)]^-$ and $[Mo_2O_5(OH)]^-$ and appears in both cycles. Cycles 1 and 2 differ in the sequence of reaction with CH_3NO_2 and CH_3OH [25b].

The catalytic cycle shown in Scheme 4 utilizes the mononuclear dioxo-peroxo anion $[VO_2(O_2)]^-$ as a catalyst and dioxygen as terminal oxidant [25c]. The 2e⁻ oxidation of methanol is linked to the 4e⁻ reduction of dioxygen. In step **1**, condensation of methanol



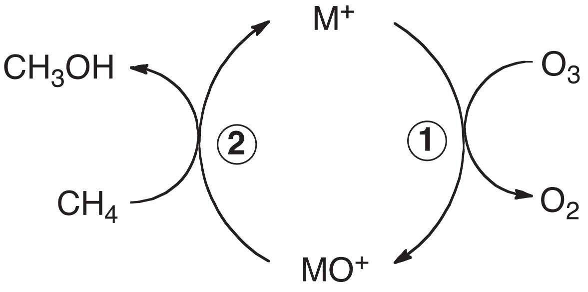
Scheme 4. Gas-phase catalytic cycle for the oxidation of methanol catalyzed by the dioxo-peroxo anion $[VO_2(O_2)]^-$ [25c].



Scheme 5. Gas-phase transition metal cation catalyzed oxidation of benzene [26].

occurs, which is followed by loss of the first molecule of formaldehyde (step **2**). CID of the resultant vanadate anion, $[VO_2(OH)_2]^-$, yields the metavanadate anion $[VO_3]^-$ (step **3**), which reacts with a second molecule of methanol via condensation (step **4**) and then elimination of water to form $[VO_2(\eta^2\text{-}OCH_2)]^-$ (step **5**). The final step involves switching a OCH_2 ligand for O_2, to regenerate the catalysts. The $[\eta^2\text{-}O,C\text{-}OCH_2]^{2-}$ ligand can formally be regarded as doubly deprotonated methanol or as $2e^-$ reduced formaldehyde, and is isoelectronic with the peroxo ligand $O_2{}^{2-}$, thereby providing a crucial linking to the $2e^-$ oxidation of two equivalents of methanol to the $4e^-$ reduction of dioxygen.

The transition metal cation catalyzed oxidation of benzene by N_2O (Eq. (13)) [26a] and O_2 (Eq. (14)) has been reported [26b]. Two different catalytic cycles were identified for the oxidation by N_2O [26a], which vary in the order of reaction. In the first cycle (Scheme 5a) Fe^+ abstracts an O atom to yield FeO^+, which then undergoes O atom transfer to benzene to regenerate Fe^+. The alternative cycle (Scheme 5b) involves condensation of benzene to form $M(C_6H_6)^+$, followed by oxidation by N_2O, which liberates phenol and N_2 and regenerates M^+. This reaction occurs when M = Co. Caraiman and Bohme have carried out a detailed study of the reactions of metal cation benzene clusters, $M(C_6H_6)_n{}^+$ (where M = a first-, second-, or third-row transition metal, and $n = 1$ and 2) with molecular oxygen [26b]. A wide range of product channels are observed, including a catalytic cycle for the oxidation of benzene (Scheme 5c, Eq. (14)), which only occurs for Fe^+, Cr^+, and Co^+. Since the neutral product(s) are not detected, based on



Scheme 6. Oxidation of methane by ozone catalyzed by M^+ (M = Ni, Pd, Pt) to yield methanol (Eq. (15)) [27a].

thermochemical considerations, they postulated that catechol is formed.

$$C_6H_6 + N_2O \rightarrow C_6H_6O + N_2 \tag{13}$$

$$C_6H_6 + O_2 \rightarrow C_6H_6O_2 \tag{14}$$

3. Oxidation of methane to methanol, ethene or formaldehyde

There has been considerable interest in developing metal catalysts that can selectively transform methane into other valuable chemical feedstocks without over-oxidation [12i,j]. Here three gas-phase catalytic cycles that yield either methanol, ethene or formaldehyde are discussed. The room temperature catalytic oxidation of methane to methanol by ozone (Eq. (15)) catalyzed by Group 10 atomic cations (Scheme 6) has been studied in a SIFT [27a]. Ni^+ was found to be the most efficient catalyst. It reacts cleanly with ozone to solely produce NiO^+, with a reaction efficiency of 41%. NiO^+ also cleanly reacts with methane to only regenerate Ni^+ with a reaction efficiency of 16%. In contrast, PdO^+ reacted with methane to give Pd^+, $PdOCH_2{}^+$ and $PdO(CH_4)^+$, while PtO^+ only gave $PtCH_2{}^+$ and $PtH_2{}^+$. To rationalize the difference in behaviour of Ni^+ and Pd^+, DFT calculations were performed to establish the potential energy diagram shown in Fig. 2.

$$CH_4 + O_3 \rightarrow CH_3OH + O_2 \tag{15}$$

An examination of Fig. 2 reveals that even though the uncatalyzed reaction is predicted to be exothermic, it does not occur at room temperature due to barriers associated with the two-step reaction. In contrast, the atomic metal cations help catalyze the oxidation of methane. A noteworthy aspect is that the reaction proceeds via spin inversion or "two state reactivity" a concept pioneered by Schwarz for gas phase transition metal reactions [8]. The small difference in energy between the entrance channel and **TS3-4** in the case of PtO^+ helps explain its slower rate of reaction with methane, since dissociation back to reactants can occur readily. The difference in product branching ratios can also be explained by an examination of the later parts of the energy diagram shown in Fig. 2. In particular, the barrier for **TS6-7** is closer to the energy of the entrance channel in the case of NiO^+, which is why over oxidation to produce formaldehyde is not observed.

A variable temperature ion trap has been used to discover two ways of oxidizing methane that result in either the formation of ethene via dehydrocoupling (Eq. (16)) or formaldehyde (Eq. (17)) [27b–d]. Both reactions are catalyzed by the gold dimer cation (Scheme 7).

$$2\,CH_4 \rightarrow C_2H_4 + 2\,H_2 \tag{16}$$

$$2\,CH_4 + 2\,O_2 \rightarrow 2\,CH_2O + 2\,H_2O \tag{17}$$

Reversible absorption of methane onto $Au_2{}^+$ (step **1** of Scheme 7) provides the shared entry point into catalytic cycles 1 and 2, which

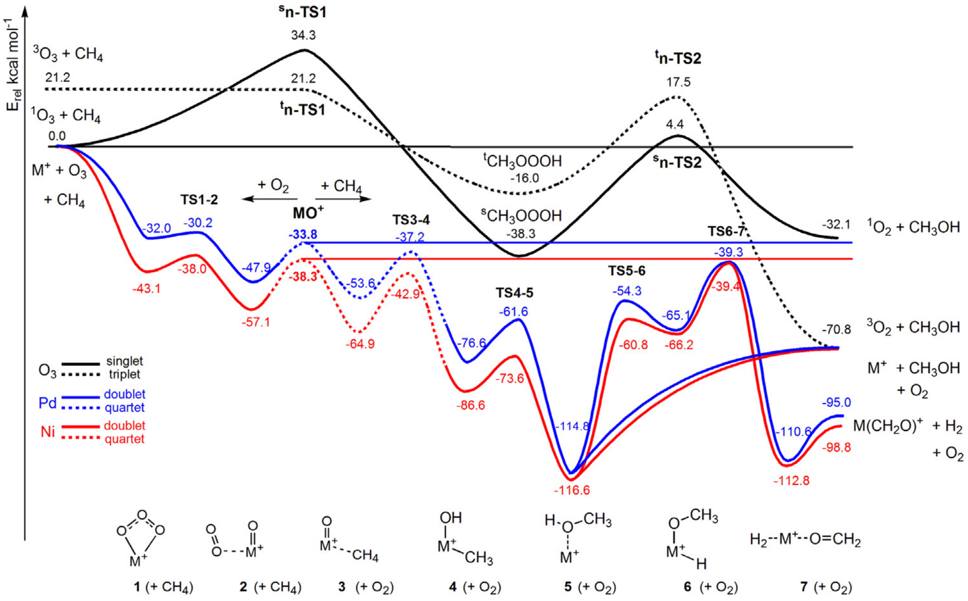
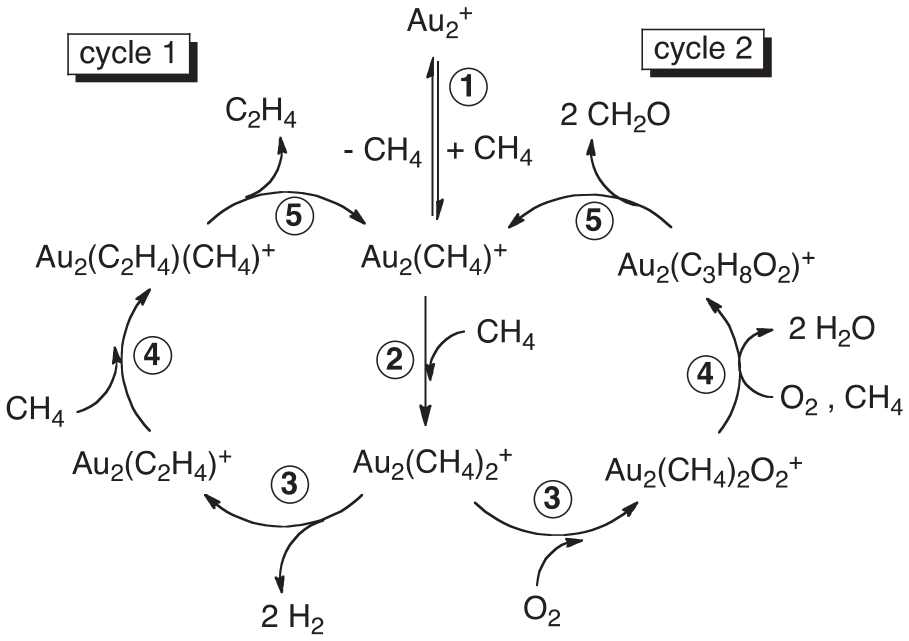


Fig. 2. Potential-energy surfaces computed for the oxidation of CH_4 with O_3 in the absence (black lines) and presence of Ni^+ (red line) or Pd^+ (blue line) calculated at B3LYP/def2-TZVP. The dashed lines represent the pathways for the species in their higher electronic states. For clarity, only the electronic states in the lowest energy are shown for metal-mediated reactions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

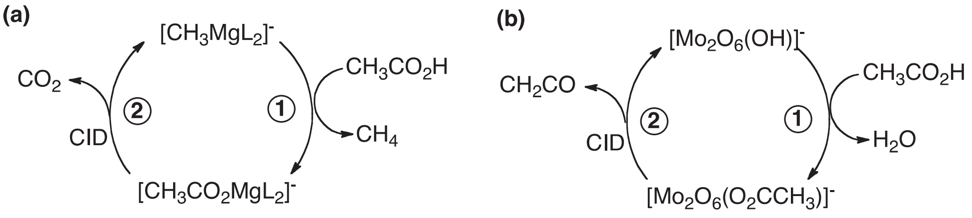
Figure reproduced from [27a].

also share the same next step, **2**, involving reaction with a second molecule of methane. The subsequent reactions of $Au_2(CH_4)_2^+$ represent the branch points for the competing cycles. Cycle 1 proceeds via elimination of H_2 (step **3**). Desorption of ethene from $Au_2(C_2H_4)^+$ does not occur spontaneously, but rather is triggered by reaction with a third molecule of methane. This cycle corresponds to the dehydrocoupling of two molecules of methane to form ethene (Eq. (16)). DFT calculations reveal that the mechanistic sequence for dehydrogenation of $Au_2(CH_4)_2^+$ involves stepwise losses of H_2 via 11 intermediates and 9 transition states. More recently, Au_2^+ has been shown to be a superior catalysts compared to Pd_2^+ in the dehydrocoupling of methane [27d].

Cycle 2, which corresponds to the oxidation of methane to formaldehyde (Eq. (17)) involves the cooperative action of multiple substrate and oxidant molecules [27c]. Only $Au_2(CH_4)_2^+$ can react with a molecule of O_2 to form $Au_2(CH_4)_2O_2^+$ (step **3**), which reacts with a third molecule of methane and a second molecule of O_2 to form $Au_2(C_3H_8O_2)^+$ and two equivalents of water (step **4**). The final step involves loss of two molecules of formaldehyde from $Au_2(C_3H_8O_2)^+$ to regenerate the catalyst $Au_2(CH_4)^+$. A



Scheme 7. Competing catalytic cycles for oxidation of methane catalyzed by Au_2^+: cycle 1 involves dehydrocoupling of methane to yield ethene (Eq. (16)) [27b–d]; cycle 2 involves oxidation of methane to formaldehyde (Eq. (17)) [27c].



Scheme 8. Decomposition of acetic acid via: (a) decarboxylation (Eq. (18)) catalyzed by organomagnesates [28a]; or (b) dehydration (Eq. (19)) catalyzed by the oxometallates [28b].

multistep process for oxidation of both adsorbed methane molecules to formaldehyde was predicted via DFT calculations.

4. Selectivity in the metal catalyzed decomposition of acetic acid

In the absence of a metal catalyst, the thermal decomposition of acetic acid produces two competing sets of products: (i) methane and carbon dioxide (Eq. (18)); (ii) ketene and water (Eq. (19)). The latter products are formed about twice as much as the former. Multistage mass spectrometry experiments in a quadrupole ion trap mass spectrometer have uncovered two different types of metal catalysts that allow the selective decomposition of acetic acid via: (i) decarboxylation (Eq. (18), Scheme 8a) [28a]; or dehydration (Eq. (19), Scheme 8b) [28b].

$$CH_3CO_2H \rightarrow CH_4 + CO_2 \quad (18)$$

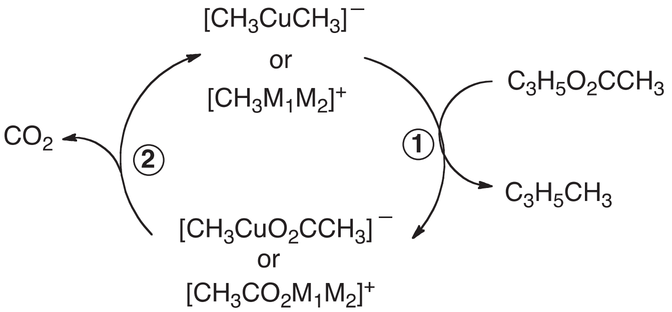
$$CH_3CO_2H \rightarrow CH_2CO + H_2O \quad (19)$$

The decarboxylation of acetic acid (Eq. (18)) is catalyzed by the organomagnesate anions $[CH_3MgL_2]^-$, (where L = Cl or CH_3CO_2) (Scheme 8a) [27a]. The first step is an acid–base metathesis reaction, in which the CH_3 ligand is switched for a carboxylato ligand (step **1** in Scheme 8a). The second step is the rate determining step (step **2** in Scheme 8a) since it requires CID to induce decarboxylation of the magnesium acetate anion $[CH_3CO_2MgL_2]^-$, to reform the organometallic catalyst $[CH_3MgL_2]^-$. A related catalytic cycle has been observed for the decarboxylation of formic acid catalyzed by the magnesium hydrides $[HMgL_2]^-$ [29]. These decarboxylation reactions are related to widely used condensed phase protodecarboxylation reactions of other carboxylic acids, RCO_2H (where R is typically an aryl group) catalyzed by other metal salts [30].

The dehydration of acetic acid (Eq. (19)) is catalyzed by oxo-anions of group VI, including mononuclear $[Mo_3(OH)]^-$ and binuclear $[Metal_2O_6(OH)]^-$ (Metal = Mo, W) [28b]. The first step is a metathesis reaction where the OH ligand is swapped for a carboxylato ligand (step **1** in Scheme 8b). Once again, the second step is rate determining (step **2** in Scheme 8b) since it requires CID conditions to induce dehydration to reform the oxo-anion catalyst. There are similarities to this gas phase catalytic process and previous reports on the preparation of ketenes via catalytic dehydration of carboxylic acids over silica, metal or metal–oxide surfaces, a reaction of industrial importance for the production of acetic anhydride using ketene as a feedstock [31]. These catalytic processes have also been proposed to occur via two steps: (i) interaction of the carboxylic acid with a surface hydroxyl site to form a surface carboxylate with elimination of water; (ii) decomposition at high temperature to induce ketene loss with regeneration of the surface hydroxyl site.

5. Decarboxylative C—C bond coupling reactions

There has been considerable interest in developing metal catalyzed decarboxylation reaction of allyl esters as a way of installing carbon—carbon bonds for use in organic synthesis [32]. We have discovered two related catalytic cycles (Scheme 9) that promote the decarboxylative C—C bond coupling of allylacetate (Eq. (20)) involving the organocuprate anion $[CH_3CuCH_3]^-$ [33a] and the coinage metal organometallic cluster cations, $[CH_3M_1M_2]^+$ [33b].



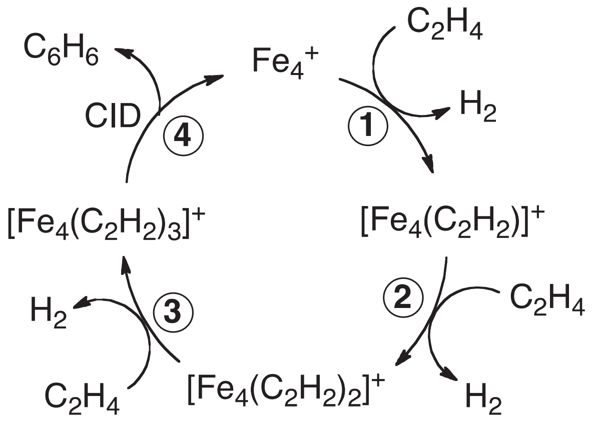
Scheme 9. Decarboxylative C—C bond coupling of allylacetate (Eq. (20)) catalyzed by the cuprate anion, $[CH_3CuCH_3]^-$ [33a], or by coinage metal organometallic cluster cations, $[CH_3M_1M_2]^+$ [33b].

$$CH_3CO_2C_3H_5 \rightarrow C_4H_8 + CO_2 \quad (20)$$

For the cuprate anion, $[CH_3CuCH_3]^-$ step **1** involves a cross-coupling reaction with allyl acetate to yield $[CH_3CuO_2CCH_3]^-$ as the major product ion. Step **2** involves subjecting the resultant acetate complex to collision-induced decarboxylation to reform $[CH_3CuCH_3]^-$, thereby closing the catalytic cycle [33c]. The reactivity of organometallic coinage metal clusters in the related two-step catalytic cycle can be "tuned" by varying the composition of the metal core (cycle 3) [33b]. In step **1** the organometallic cluster cations $[CH_3Cu_2]^+$, $[CH_3AgCu]^+$ or $[CH_3Ag_2]^+$ react with allyl acetate at the collision rate; however, the types of products formed and their yields vary considerably. For example, only $[CH_3Cu_2]^+$ and $[CH_3AgCu]^+$ undergo the desired C—C bond-coupling reaction to yield 1-butene, in yields of 52.7% and 1.2% respectively. In step **2**, the metal acetate cluster cation $[CH_3CO_2Cu_2]^+$, $[CH_3CO_2AgCu]^+$ or $[CH_3CO_2Ag_2]^+$ are subjected to CID to reform the organometallic cluster cations, thereby closing the catalytic cycle. All three metal acetates undergo decarboxylation although when competing reactions are taken into account, the yield of $[CH_3Cu_2]^+$ is highest (83.3%). Overall, the dicopper clusters are the superior decarboxylative coupling catalysts since they give the highest yields of the desired products for both steps **1** and **2** [33b].

6. Dehydrogenation and cyclotrimerisation of ethylene to form benzene

Dehydrogenation and cyclotrimerisation of ethylene to form benzene (Eq. (21)) has been shown to be catalyzed by the cluster Fe_4^+ (Scheme 10) [34]. Sequential dehydrogenation of three molecules of ethylene yields an ion of formula $[Fe_4(C_6,H_6)]^+$. CID is required to liberate neutral 'C_6H_6' (assigned as benzene) and regenerate Fe_4^+, thereby closing a catalytic cycle for the dehydrogenation and assembly of three molecules of ethylene to benzene. Based on incomplete ligand exchange reactions with C_6D_6 and differences



Scheme 10. Dehydrogenation and cyclotrimerisation of ethylene to form benzene (Eq. (21)) catalyzed by the iron cluster cation, Fe_4^+ [34].

in the fragmentation of $[Fe_4(C_6,H_6)]^+$ and 'authentic' $[Fe_4(C_6H_6)]^+$ prepared from reaction of Fe_4^+ with C_6H_6, $[Fe_4(C_6,H_6)]^+$ formed in the catalytic cycles is in fact a mixture of $[Fe_4(C_6H_6)]^+$ and a second isomer that did not contain an intact benzene ligand.

$$3\,C_2H_4 \rightarrow C_6H_6 + 3\,H_2 \tag{21}$$

Similar dehydrogenation and cyclotrimerisation of ethylene have been observed at bare metal ions [35]. For example, $U(C_6,H_6)^+$ is formed when U^+ consecutively dehydrogenates 3 molecules of ethylene [35c]. The third molecule of ethylene reacts significantly faster than the second, consistent with the formation of a stable benzene ligand in $U(C_6,H_6)^+$. Ligand switching reactions of $U(C_6,H_6)^+$ with C_6D_6 produced $U(C_6D_6)^+$, consistent with the presence of an intact benzene ligand. The benzene ligand could be removed upon CID, thereby regenerating U^+ and closing a catalytic cycle (cf. Scheme 10) [35c].

Finally there have been a number of other studies of metal catalyzed condensation reactions that result in C—C bond formation of cyclic systems. Earlier studies have been reviewed [12d], while there has been a recent report on a Diels–Alder reaction between phenylacetylene and isoprene catalyzed by the cobalt (I) complex, $[Co(I)(dppe)]^+$ (where dppe = 1,2-bis(diphenylphosphino)ethane) [36].

7. Conclusions

This article has attempted to illustrate how a combination of innovations in mass spectrometry instrumentation (developments of flow tubes and trapping mass spectrometers and ionization methods such as electrospray ionization) and the breakthrough papers of Kappes and Staley [17] and Rowe et al. [18] have helped drive studies of metal catalyzed reactions in the gas phase. The focus has been on mass spectrometry based experiments involving: (i) flow tubes, whereby thermal catalytic reactions can be examined and (ii) trapping instruments, which often allow each of the ionic intermediates in these cycles to be isolated and explored in detail. Gas phase cycles that mirror common condensed phase catalytic processes have been highlighted (e.g. Schemes 3, 4 and 8). A number of gas phase cycles that do not have precedence in the condensed phase have been discovered (e.g. Schemes 5, 6, 7 and 9). Although some of these are catalyzed by "exotic species" (e.g. bare transition atomic metal cations), conceptually, they may inspire the search for new condensed phase catalytic processes.

With the wide availability of commercial ion trap mass spectrometers, and the ease of their modification to allow the examination of ion-molecule reactions, it is anticipated that the study of gas phase catalytic cycles will continue in the coming years. Newer gas phase techniques such as IR and UV spectroscopy and ion mobility should provide additional structural information of potential intermediates. It will be exciting to see bridges being built between gas phase and solution phase catalytic studies. ESI will likely play a key role here since intermediates in condensed phase catalytic cycles might be intercepted for gas phase studies [37], while results from gas phase studies on less "exotic species" should appeal to chemists who mainly work on developing condensed phase catalytic reactions.

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