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**Gas-Phase Reactions of the Rhenium Oxide Anions, [ReO<sub>x</sub>]<sup>-</sup> (x = 2 – 4) with the  
Neutral Organic Substrates Methane, Ethene, Methanol and Acetic Acid.**

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**ABSTRACT:**

The ion-molecule reactions of the rhenium oxide anions,  $[\text{ReO}_x]^-$  ( $x = 2 - 4$ ) with the organic substrates methane, ethene, methanol and acetic acid have been examined in a linear ion trap mass spectrometer. The only reactivity observed was between  $[\text{ReO}_2]^-$  and acetic acid. Isotope labeling experiments and high-resolution mass spectrometry measurements were used to assign the formulas of the ionic products. Collision-induced dissociation and ion-molecule reactions with acetic acid were used to probe the structures of the mass-selected primary product ions. DFT calculations (PBE0/LanL2DZ6-311+G(d)) were used to suggest possible structures. The three primary product channels observed are likely to arise from the formation of: the metallalactone  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277) and  $\text{H}_2$ ;  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  251) and  $\text{CO}$ ; and  $[\text{ReO}_3]^-$  ( $m/z$  235),  $\text{H}_2$  and  $\text{CH}_2\text{CO}$ .

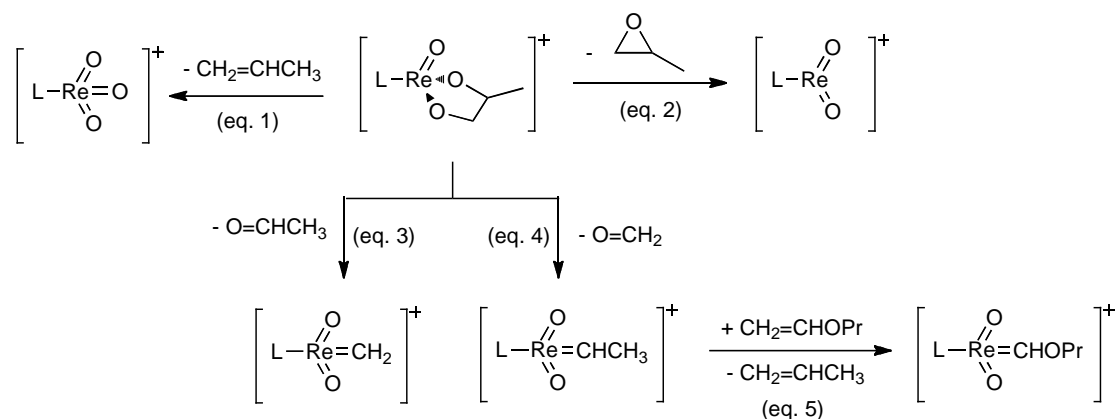
**KEYWORDS:** Mass spectrometry. Rhenium Oxide Anions. Ion-molecule reactions.

**Running Title:** Reactions of rhenium oxide anions.

## INTRODUCTION:

Transition metal oxide catalysts are widely used in the synthesis of bulk commodity and fine chemicals and there is continued interest in designing more selective and efficient catalysts [1-3]. Catalyst design can be potentially informed by gas-phase studies of the reactions of transition metal oxide ions with neutral substrates using mass spectrometry based techniques. Such studies have shed light on the role of the metal oxide (charge, spin state, oxidation state) on reactivity [4] towards a wide range of organic substrates including alkanes [5-7], alkenes [8-11], alcohols [12-23] and carboxylic acids [24-29]. Indeed, the intimate details of several complete catalytic cycles have been uncovered [30-32].

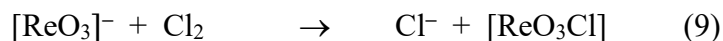
Although rhenium oxides have proven to be mild and versatile catalysts in organic chemistry [33-36], only a few studies have examined the gas-phase chemistry of rhenium oxide ions, including their reactions with organic substrates [37-43]. For example, Chen's group has examined the energy resolved collision-induced dissociation (CID) reactions of rhenaoxetane cations in the gas phase (Scheme 1) and have noted how the competition between the losses of an alkene (eq. 1), epoxide (eq. 2) and aldehydes (eqs. 3 and 4) is influenced by the coordination number of the starting complex [39]. In subsequent work, the metathesis reactions of the carbenes in ion-molecule reactions with vinyl ethers was studied, as illustrated for *n*-propyl vinyl ether in eq. 5 of Scheme 1 [40].



**Scheme 1:** Gas-phase fragmentation chemistry of rhenaoxetane cations and ion-molecule reaction of a rhenium carbene (eq. 5).

With regards to the gas-phase chemistry of rhenium oxide anions [44-48], the photoelectron spectroscopy of  $[\text{ReO}_x]^-$  ( $x = 2 - 4$ ) have been studied [44,45]. From these spectra the energy required to remove an electron (eq. 6), also defined as the electron affinity of the neutral,  $[\text{ReO}_x]$ , has been determined to be 2.5 eV for  $[\text{ReO}_2]^-$  [44], 3.53 eV for  $[\text{ReO}_3]^-$  [45], and 5.58 eV for  $[\text{ReO}_4]^-$  [45]. Calculations in support of matrix isolation studies on the same rhenium oxide anions suggest that the ground state of  $[\text{ReO}_2]^-$  is a triplet, in contrast to  $[\text{ReO}_3]^-$  and  $[\text{ReO}_4]^-$ , which are predicted to be singlets [46]. Sahureka et al have noted that the source conditions used for electrospray ionization of ammonium perrhenate,  $[\text{ReO}_4]^-[\text{NH}_4^+]$ , play a role on the types of anions formed [47]. Under gentle ionization conditions  $[\text{ReO}_4]^-$  is the sole anion observed, while under harsher conditions  $[\text{ReO}_3]^-$  and  $[\text{ReO}_2]^-$  are formed via collision-induced oxygen atom loss reactions (eq. 7). Finally, the only ion-molecule reactions of rhenium oxide studied to date are those between  $[\text{ReO}_3]^-$  and either  $\text{NO}_2$  or  $\text{Cl}_2$  [48]. These proceed via O (eq. 8) and Cl (eq. 9) atom abstraction reactions respectively.





As part of a series of studies on the gas-phase reactions of transition metal oxide anions with organic substrates [18-23;27-29], here we use electrospray ionization in conjunction with multistage mass spectrometry ( $\text{MS}^n$ ) experiments in a linear ion trap mass spectrometer [49,50] to examine the reactions of rhenium oxide anions  $[\text{ReO}_x]^-$  ( $x = 2 - 4$ ) with the organic substrates methane, ethene, methanol and acetic acid.

## Experimental

### *Reagents:*

The following reagents were used as received: tetrabutylammonium perrhenate,  $[\text{ReO}_4^-][\text{NBu}_4^+]$  (98%, Sigma-Aldrich); methanol (99.8%, Sigma-Aldrich); acetic acid ( $\geq 99.5\%$ , Sigma-Aldrich), D4-acetic acid (99.5%, Cambridge Isotope Laboratories, Inc.); Rhenium(V) chloride,  $\text{Re(V)Cl}_5$  (99.9%-Re, STREM Chemicals). The gaseous samples methane and ethene were purchased from Coregas as mixtures in helium (1.04% and 0.02% respectively).  $\text{H}_2^{18}\text{O}$  was a gift from Professor Jonathon M. White.

### *Mass Spectrometry:*

All experiments were carried out on a Finnigan LTQ-FTMS instrument equipped with electrospray ionization (ESI) [51], which has been modified to allow the study of ion-molecule reactions [52,53] under near thermal conditions [54].

Briefly, a 0.5 mM solution of tetrabutylammonium perrhenate in MeCN was introduced into the mass spectrometer at 5.0  $\mu\text{Lmin}^{-1}$  via electrospray ionization. Typical ESI conditions used were: spray voltage, 3.0-5.0kV, capillary temperature, 250 - 270°C, nitrogen sheath pressure, 15-20 (arbitrary units), and capillary voltage/tube lens offset, were tuned to maximize the desired peak. The injection time was set using the AGC (automatic gain control) function. All ions mass selected for ion-molecule reactions and CID consisted of the most abundant rhenium isotope,  $^{187}\text{Re}$ , and mass selection was achieved using a 1 – 2 Th window. To generate  $[\text{Re}^{[18]}\text{O}_2]^-$ , 5 mg of Rhenium(V) chloride was dissolved in 500  $\mu\text{L}$  of  $\text{H}_2^{[18]}\text{O}$ , then diluted in acetonitrile and injected into the ESI source.

The ion-molecule-reactions conditions were: activation energy 0%; Q of 0.25, and the reaction time was varied between 10 ms and 10000 ms prior to ejection from the ion-trap for detection. A syringe pump operating at between 4.0 and 8.0  $\mu\text{Lh}^{-1}$  was used to inject liquid neutral substrates (methanol or acetic acid) into a flow of Helium between 3.5 to 4.0  $\text{Lmin}^{-1}$  and the injection chamber was heated to maintain a temperature higher than the boiling point of substrate. The helium pressure regulator that controls the flow of gas into the ion trap under normal operating conditions is bypassed, and instead, the helium pressure is controlled manually by matching the pressure in the vacuum chamber surrounding the ion trap, measured using the ion gauge, to that under normal operating conditions (*ca*  $7 - 8 \times 10^{-6}$  Torr). This will then indicate a pressure of *ca.*  $2 \times 10^{-3}$  Torr inside the linear ion trap. Since the flow of helium is controlled, the composition of the liquid substrate/helium mixture can be calculated using the known molar flow rates of helium and neutral substrate, thereby

allowing the concentration of the neutral substrate to be calculated. Under pseudo-first order conditions, the ion-molecule reactions of  $[\text{ReO}_2]^-$  with excess acetic acid (concentration of *ca.*  $4 \times 10^{-9}$  molecules  $\text{cm}^{-3}$ ) were monitored. A total of 17 data sets for product ion intensity vs. various reaction times (30 - 2000ms) were recorded. The experimental rates were calculated by fitting a kinetic model to the temporal evolution of product ions using the DynaFit program [55].

CID was carried out by and subjecting the mass selected anions to the following typical conditions: activation energy between 20% and 35%; activation (Q), 0.25, and activation time 30 ms prior to ejection from the ion-trap and detection.

High-resolution mass spectra were acquired in the FTICR to confirm the identity of the precursor and product ions observed, as described previously [51].

### ***DFT calculations***

Density functional theory (DFT) calculations were used to examine the structure and the stability of rhenium containing anions and to estimate the energetics of their reactions using the Gaussian 09 package.[56] Based upon a number of previous benchmarking studies [57-60], full geometry optimizations were carried out using the PBE0 functional [61] together with a mixed basis set consisting of the LanL2DZ effective core potential [62] for rhenium combined with the 6-311+G(d) basis set for all other atoms (C,O,H) [63-65], which we designate hereafter as PBE0/LanL2DZ6-311+G(d). Vibrational frequency analysis was carried out at the same level of theory in order to confirm that the structures are local minima. All energies were corrected for zero-point vibrational energies ( $E_{\text{reported}} = E_{\text{electronic}} + E_{\text{zpv}}$ ). All calculated structures are available in the supplementary material.

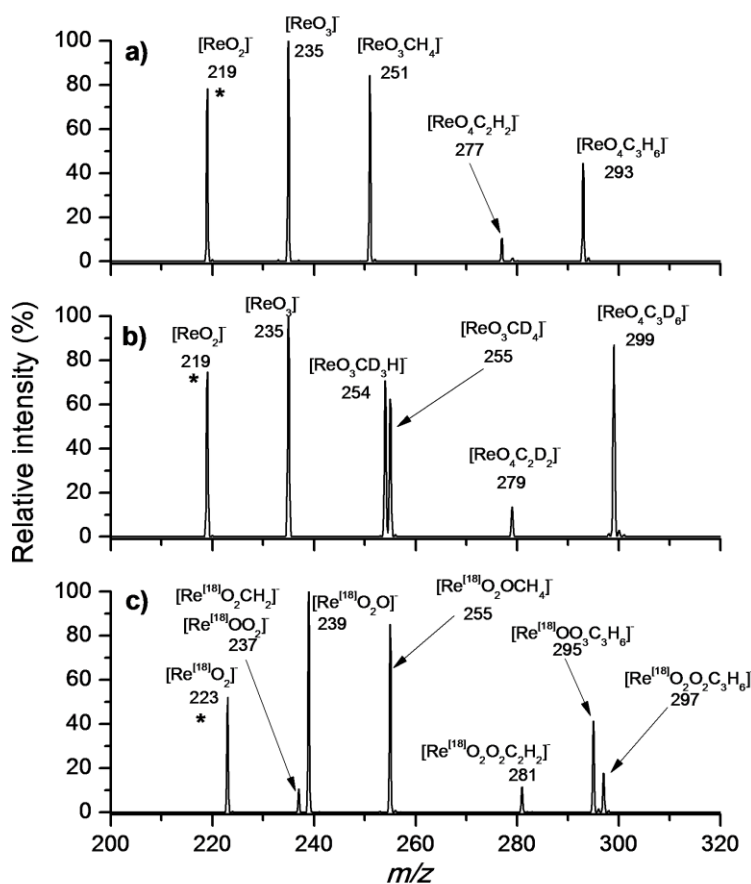
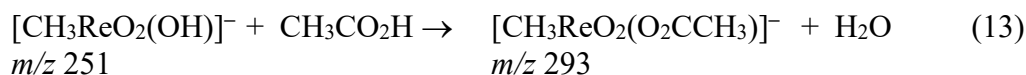
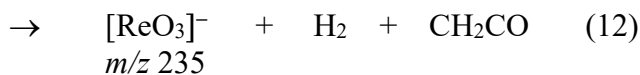
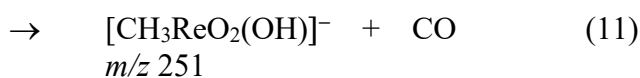
## Results and Discussion

We have used the method of Sahureka et al [47] to generate the rhenium oxide anions,  $[\text{ReO}_x]^-$  ( $x = 2 - 4$ ) via ESI of tetrabutylammonium perrhenate,  $[\text{ReO}_4]^-$   $[\text{NBu}_4^+]$ , under different source conditions:  $[\text{ReO}_4]^-$  (gentle ionization conditions) and  $[\text{ReO}_2]^-$  and  $[\text{ReO}_3]^-$  (harsh ESI conditions) – data not shown. The ion-molecule reactions of all three mass selected rhenium oxide anions with the substrates methane, ethene, methanol and acetic acid were examined. Even at the longest reaction times studied (10 seconds),  $[\text{ReO}_2]^-$ , **1**, is unreactive towards methane, ethene and methanol while  $[\text{ReO}_3]^-$ , **2**, and  $[\text{ReO}_4]^-$ , **3**, are unreactive towards methane, ethene, methanol and acetic acid (data not shown). Based on the estimates of the number density in the ion trap, this puts an upper limit of a reaction efficiency of less than 1 out of every  $10^5$  collisions with these neutral reagents. The lack of reactivity of  $[\text{ReO}_4]^-$  towards ethene is consistent with a recent DFT study which suggests that there are significant barriers for the formation of products arising from a  $3 + 2$  cycloaddition reaction [66].

In contrast,  $[\text{ReO}_2]^-$  reacts with acetic acid to produce three primary products (Figure 1a). Based on reactivity studies and DFT calculations discussed in later sections, we assign these products as:  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277, eq. 10), **4**;  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  251, eq. 11), **5**; and  $[\text{ReO}_3]^-$  ( $m/z$  235, eq. 12), **2**. The product ion at  $m/z$  293 arises from a secondary reaction, which is discussed further below.



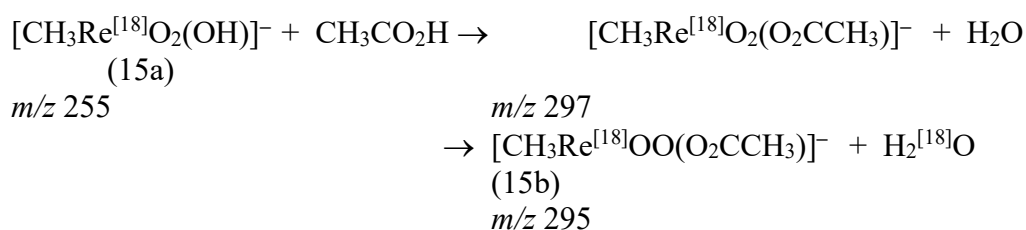
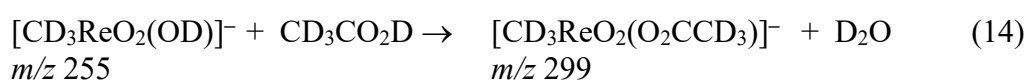


$m/z$  219 $m/z$  277

**Figure 1:** Ion-molecule reactions of  $[\text{}^{187}\text{ReO}_2]^-$  with acetic acid (concentration of *ca.*  $4 \times 10^9$  molecules  $\text{cm}^{-3}$ ) in gas phase: (a)  $[\text{}^{187}\text{ReO}_2]^-$  with  $\text{CH}_3\text{CO}_2\text{H}$  500 ms; (b)  $[\text{}^{187}\text{ReO}_2]^-$  with  $\text{CD}_3\text{CO}_2\text{D}$  500 ms; (c)  $[\text{}^{187}\text{Re}^{18}\text{O}_2]^-$  with  $\text{CH}_3\text{CO}_2\text{H}$  500 ms. The mass selected precursor ion is designated by a \*.

When deuterium labelled acetic acid,  $\text{CD}_3\text{CO}_2\text{D}$ , is used, the related product ions  $[\text{ReO}_2(\text{CD}_2\text{CO}_2)]^-$  ( $m/z$  279);  $[\text{CD}_3\text{ReO}_2(\text{OD})]^-$  ( $m/z$  255); and  $[\text{ReO}_3]^-$  ( $m/z$  235) are observed (Figure 1b). Mass selection of  $[\text{CD}_3\text{ReO}_2(\text{OD})]^-$  ( $m/z$  255) does not give

rise to  $[\text{CD}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  254) via H/D exchange with background water (data not shown). Thus the latter ion is likely to be directly formed via reaction of  $[\text{ReO}_2]^-$  with  $\text{CD}_3\text{CO}_2\text{H}$ . Reacting the  $^{18}\text{O}$  labelled precursor ion  $[\text{Re}^{18}\text{O}_2]^-$  with  $\text{CH}_3\text{CO}_2\text{H}$  gives rise to the following primary product ions:  $[\text{Re}^{18}\text{O}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  281);  $[\text{CH}_3\text{Re}^{18}\text{O}_2(\text{OH})]^-$  ( $m/z$  255); and  $[\text{Re}^{18}\text{O}_2(^{16}\text{O})]^-$  ( $m/z$  239) (Figure 1c). A minor amount of  $[\text{Re}^{16}\text{O}_2(^{18}\text{O})]^-$  ( $m/z$  237) is observed. We are not certain how the latter ion arises, but based upon the lack of reactivity of  $[\text{ReO}_3]^-$  towards a range of substrates, we suggest that this maybe a primary product ion in which the oxygen atoms are partially scrambled between  $[\text{Re}^{18}\text{O}_2]^-$  and acetic acid in an intermediate along the reaction coordinate. These results suggest that reaction of  $[\text{ReO}_2]^-$  with  $\text{CH}_3\text{CO}_2\text{H}$  proceeds via addition with loss of  $\text{H}_2$  (eq. 10); addition with loss of  $\text{CO}$  (eq. 11); addition with loss of  $\text{H}_2$  and  $\text{CH}_2\text{CO}$  (eq. 12). Ions at  $m/z$  293 (reaction with  $\text{CH}_3\text{CO}_2\text{H}$ ); 299 (reaction with  $\text{CD}_3\text{CO}_2\text{D}$ ); 295 and 297 (reaction of  $[\text{Re}^{18}\text{O}_2]^-$  with  $\text{CH}_3\text{CO}_2\text{H}$ ) are due to secondary ion-molecule reactions of  $m/z$  251 (eq. 13), 255 (eq. 14) and 255 (eq. 15) respectively.

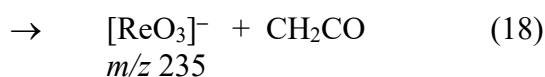
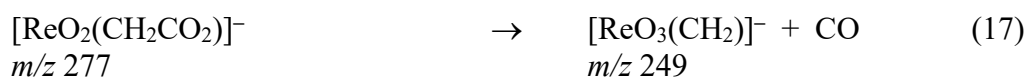


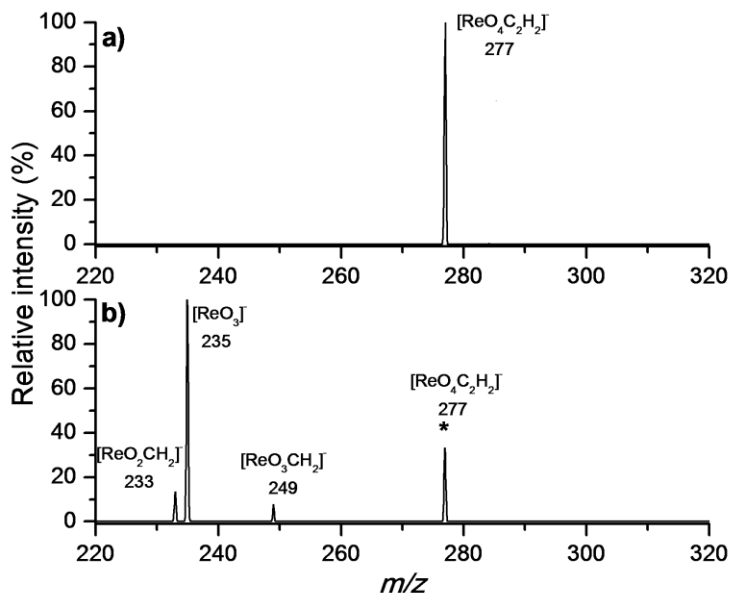
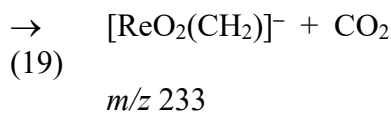
In the next sections we describe: (i) the gas-phase reactivity of these primary product ions under ion-molecule reaction conditions with acetic acid and under collision-induced dissociation conditions aimed at supporting the assignments of these

ions; (ii) a kinetic model developed to account for the formation of all primary and secondary product ions; (iii) the results of DFT calculations on potential structures of product ions and the energetics for their formation.

**(a) Gas-phase reactivity of  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277), **4**.**

The primary product  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277), **4**, was mass selected and allowed to undergo ion-molecule reactions with acetic acid (Figure 2a) or CID with the helium bath gas (Figure 2b). No reaction was observed between  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  and acetic acid (Figure 2a, eq. 16). Three fragment ions are observed upon CID of  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  (Figure 2b):  $[\text{ReO}_3(\text{CH}_2)]^-$  ( $m/z$  249, eq. 17), **6**;  $[\text{ReO}_3]^-$  ( $m/z$  235, eq. 18), **2**; and  $[\text{ReO}_2(\text{CH}_2)]^-$  ( $m/z$  233, eq. 19), **7**. These product assignments were also confirmed via CID of the isotope labelled ions  $[\text{ReO}_2(\text{CD}_2\text{CO}_2)]^-$  ( $m/z$  279) and  $[\text{Re}^{18}\text{O}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  281) (Supplementary Figure S1). This fragmentation chemistry is related to the extrusion of alkenes or aldehydes from rhenaoxetane cations (Scheme 1) [39-41], suggesting a metallalactone structure [68] that can undergo ring-opening reactions with extrusion of either ketene (eq. 18) or  $\text{CO}_2$  (eq. 19).





**Figure 2:** Gas-phase reactivity of mass-selected of  $[\text{}^{187}\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$ : (a) with acetic acid (concentration of *ca.*  $4 \times 10^9$  molecules. $\text{cm}^{-3}$ ) for 10,000 ms; (b) CID for 50 ms with a normalized collision energy (NCE) of 20. The mass selected precursor ion is designated by a \*.

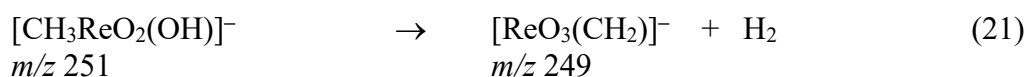
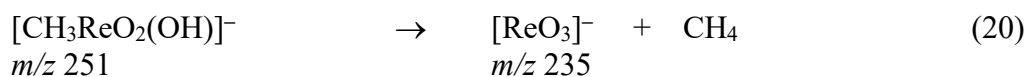
**(b) Gas-phase reactivity of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (*m/z* 251), **5**.**

The primary product  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (*m/z* 251), **5**, was mass selected and allowed to undergo ion-molecule reactions with acetic acid (Figure 3a) or CID with the helium bath gas (Figure 3b).  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  reacts with acetic acid (Figure 3a) to give an ion at *m/z* 293, which is formulated as the mixed anhydride  $[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^-$ , **8**, and arises from addition of acetic acid followed by loss of water (eq. 13). This assignment is confirmed by the reaction of  $[\text{CH}_3\text{Re}^{181}\text{O}_2(\text{OH})]^-$  with acetic acid (Supplementary Figure S2).

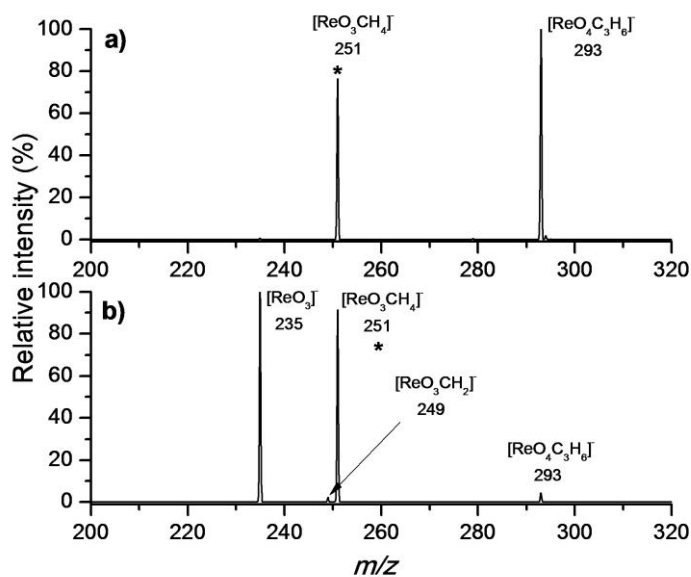
CID of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (Figure 3b) gives rise to  $[\text{ReO}_3]^-$  ( $m/z$  235, eq. 20), **2**, as the major product and  $[\text{ReO}_3(\text{CH}_2)]^-$  ( $m/z$  249, eq. 21), **6**, as a minor product.

These products were also confirmed via CID on the isotopically labelled ions

$[\text{CD}_3\text{ReO}_2(\text{OD})]^-$  and  $[\text{CH}_3\text{Re}^{[18]\text{O}}_2(\text{OH})]^-$  (Supplementary Figure S3).



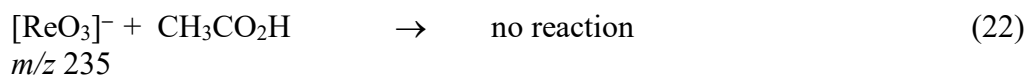
Based on the CID reactions observed (eqs 20 and 21), there are at least two potential structures for the primary product formed at  $m/z$  251: a Re(V) organometallic ion containing a hydroxide,  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$ , **5**, or a Re(VII) organometallic ion containing a hydride,  $[\text{CH}_3\text{ReO}_3(\text{H})]^-$ , **9**. The bimolecular reactivity observed for  $m/z$  251 is, however, more consistent with the known gas-phase reactivity of transition metal complexes containing hydroxide ligands rather than those containing hydride ligands. The former are protonated at the hydroxide ligand to liberate water (cf eq. 13) [19,27], while the latter are protonated at the hydride ligand to liberate  $\text{H}_2$  [68], a reaction that we do not observe.



**Figure 3:** Gas-phase reactivity of mass-selected of  $[\text{CH}_3^{187}\text{ReO}_2(\text{OH})]^-$ : (a) with acetic acid (concentration of *ca.*  $4 \times 10^9$  molecules. $\text{cm}^{-3}$ ) for 500 ms; (b) CID for 30 ms with a normalized collision energy (NCE) of 20. The mass selected precursor ion is designated by a \*.

**(c) Gas-phase reactivity of  $[\text{ReO}_3]^-$  ( $m/z$  235), **2**.**

The primary product  $[\text{ReO}_3]^-$  ( $m/z$  235), **2**, was mass selected and allowed to undergo ion-molecule reactions with acetic acid or CID with the helium bath gas. No reaction was observed between  $[\text{ReO}_3]^-$  and acetic acid (eq. 22, data not shown), consistent with the lack of reactivity of  $[\text{ReO}_3]^-$  generated via ESI/MS. The only fragment ion observed upon CID of  $[\text{ReO}_3]^-$  is  $[\text{ReO}_2]^-$  (eq 1 where  $n = 3$ , data not shown), **1**.



**(d) Kinetic model for reaction of  $[\text{ReO}_2]^-$  with acetic acid.**

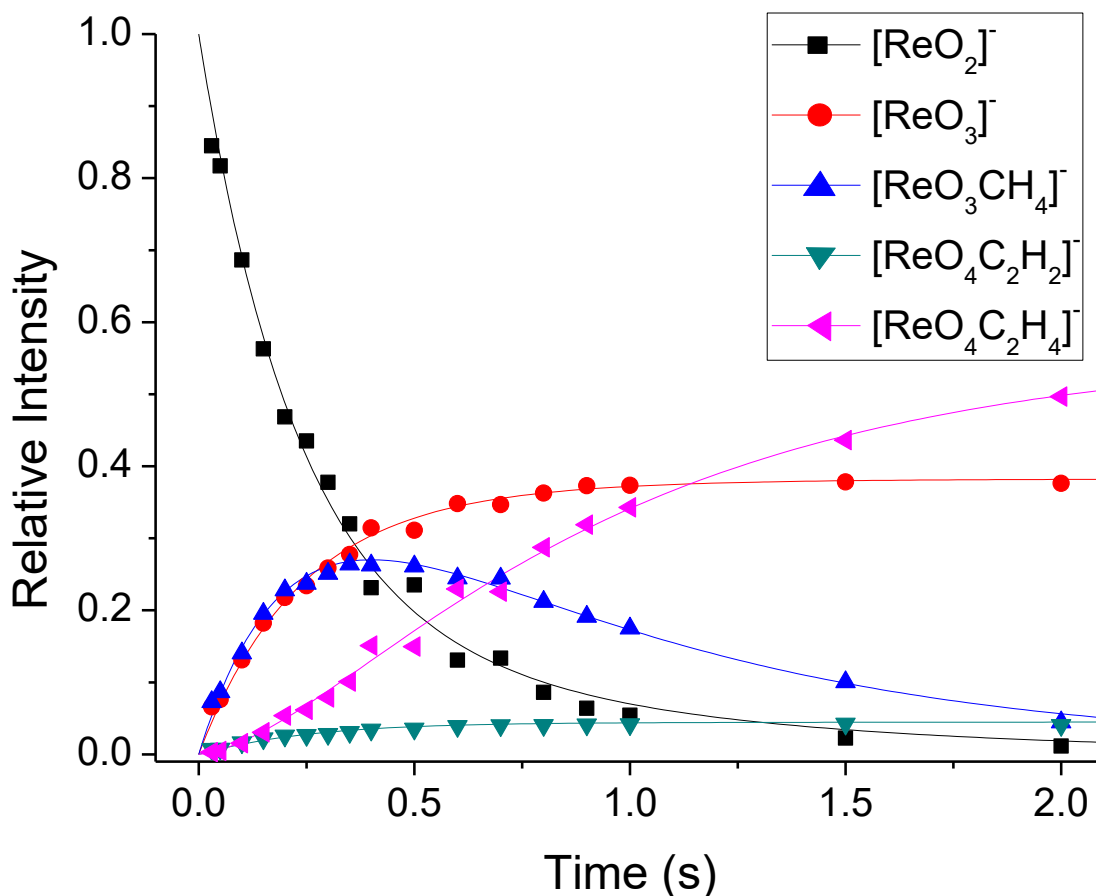
The DynaFit program [55] was used to determine the experimental rate constant for the formation of primary products in the ion-molecule reactions of  $[\text{ReO}_2]^-$  ( $m/z$  219) with acetic acid (eq. 10-12) and the secondary product (eq. 13) Table 1.

**Table 1:** Rate data for product formation derived from fitting experimental temporal evolution of  $[\text{ReO}_2]^-$  ( $m/z$  219),  $[\text{ReO}_3]^-$  ( $m/z$  235),  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  251),  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277), and  $[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^-$  ( $m/z$  293) to a kinetic model using the DynaFit program [55].

Reactant	Product	$k_{\text{expt}}^{\text{a,b}}$	Reaction Efficiency
$[\text{ReO}_2]^-$	$[\text{ReO}_3]^-$ , $m/z$ 235, eq. 12	$4.2 \times 10^{-10}$	34
$[\text{ReO}_2]^-$	$[\text{CH}_3\text{ReO}_2(\text{OH})]^-$ , $m/z$ 251, eq. 11	$5.2 \times 10^{-10}$	42
$[\text{ReO}_2]^-$	$[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$ , $m/z$ 277, eq. 10	$4.4 \times 10^{-11}$	3.6
$[\text{CH}_3\text{ReO}_2(\text{OH})]^-$	$[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^-$ , $m/z$ 293, eq. 13	$4.2 \times 10^{-11}$	1.5

<sup>a</sup> In units of  $\text{cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ . <sup>b</sup> Rates for the reaction with  $[\text{ReO}_2]^-$  with acetic acid. Rates were determined by monitoring the ion evolution with time. <sup>c</sup> Reaction efficiency =  $(k_{\text{expt}}/k_{\text{ADO}}) \times 100$ . The  $k_{\text{ADO}}$  is the theoretical ion-molecule collision rate constant obtained from the average-dipole orientation (ADO) theory,<sup>[69]</sup> which was calculated using the Colrate program.<sup>[70]</sup>

A plot of relative ion intensity (y-axis) over time (x-axis) is shown in Figure 5 where the solid symbols indicate experimentally recorded data points. The solid lines refer to the predicted model produced as a result of nonlinear least-squares regression analysis, which are in good agreement with the experimental data sets. The decay of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  251, blue line), **5**, and concomitant increase in  $[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^-$   $m/z$  293, **8**, is consistent with a secondary reaction (Figure 3a and eq. 13).



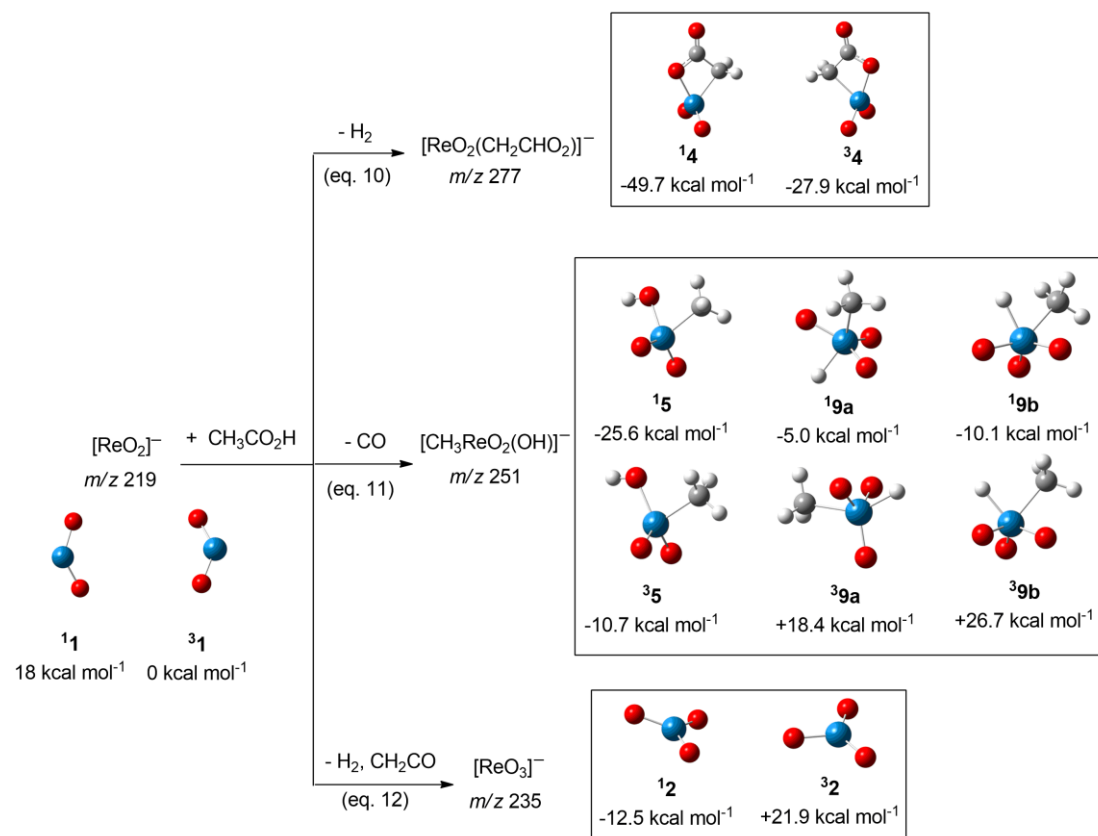
**Figure 4:** Plot of the temporal evolution of  $[\text{ReO}_2]^-$  ( $m/z$  219, black), **1**,  $[\text{ReO}_3]^-$  ( $m/z$  235, red), **2**,  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  ( $m/z$  277, green), **4**,  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  ( $m/z$  251, blue), **5**, and  $[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^-$  ( $m/z$  293, purple), **8**, based on a kinetic model as determined by DynaFit [55].

*(e) DFT calculations on primary products formed in the reaction of  $[\text{ReO}_2]^-$  with acetic acid.*

Although a detailed theoretical study on the reactions of  $[\text{ReO}_2]^-$  with acetic acid is beyond the scope of this work, we have carried out DFT calculations to gain insights into possible structures of the product ions and the results are given in Figure 5, while the DFT estimated energetics associated with the primary and secondary ion-molecule reactions and CID reactions examined are given Table 2. Structures,



Cartesian coordinates and electronic energies (in Hartrees) of all species calculated are given in Supplementary Figures S4 and S5.



**Figure 5:** PBE0/LanL2DZ6-311+G(d) calculated reactant and primary products for the reaction of  $[\text{ReO}_2]^-$  with acetic acid.

We have considered reactions of acetic acid with  $[\text{ReO}_2]^-$  starting from either the triplet or singlet state of the anion.  $[\text{}^3\text{ReO}_2]^-$  was calculated to be 18 kcal mol $^{-1}$  more stable than the  $[\text{}^1\text{ReO}_2]^-$ , consistent with previous studies [46]. Since ions at  $m/z$  277 and 251 with formulas  $[\text{Re,C}_2\text{H}_2\text{O}_4]^-$  and  $[\text{Re,C,H}_4\text{O}_3]^-$  appear to be previously unreported in the literature, our strategy for examining potential structures was to use their observed bimolecular and unimolecular reactivity in conjunction with chemical intuition to prepare input guesses for several isomers, which were then subjected to full geometry optimizations.

With regards to the ion at  $m/z$  277, all isomeric structures converged to the metallalactones, which are predicted to be formed in an exothermic reaction for both **14** and **34** (Figure 5, Table 2), although formation of **14** is considerably more exothermic. While the experimental data (Figure 3) support  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  for the ion at  $m/z$  251, we have considered several different isomeric structures, which converge to three isomeric structures in both the singlet and triplet states:  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (**15** and **35**);  $[\text{CH}_3\text{ReO}_3(\text{H})]^-$  in which the  $\text{CH}_3$  and  $\text{H}$  ligands are either both in the apical positions (**19a** and **39a**), or in the equatorial positions (**19b** and **39b**). Formation of **15** is considerably more exothermic than **35** or the other isomers (Figure 5, Table 2). Finally the reaction to produce  $[\text{ReO}_3]^-$  is only exothermic if it is produced in the singlet state. This suggests that the reaction of  $[\text{ReO}_2]^-$  with acetic acid proceeds via two state reactivity, with curve crossing occurring at some point along the reaction coordinate [71,72].

**Table 2:** PBE0/LanL2DZ6-311+G(d) calculated energetics associated with the ion-molecule reactions (eqs 10-13) and CID reactions (eqs 7, 17-21) of rhenium anions.

Reactant(s)	Products <sup>(a), (b)</sup>	Eq.	$\Delta E$ Reaction (kcal mol <sup>-1</sup> ), singlet	$\Delta E$ Reaction (kcal mol <sup>-1</sup> ), triplet
$[\text{ReO}_2]^- + \text{CH}_3\text{CO}_2\text{H}$	$[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^- + \text{H}_2$	10	-49.7	-27.9
$[\text{ReO}_2]^- + \text{CH}_3\text{CO}_2\text{H}$	$[\text{CH}_3\text{ReO}_2(\text{OH})]^- + \text{CO}$	11	-25.6	-10.7
$[\text{ReO}_2]^- + \text{CH}_3\text{CO}_2\text{H}$	$[\text{ReO}_3]^- + \text{H}_2 + \text{CH}_2\text{CO}$	12	-12.5	+21.9
$[\text{CH}_3\text{ReO}_2(\text{OH})]^- + \text{CH}_3\text{CO}_2\text{H}$	$[\text{CH}_3\text{ReO}_2(\text{O}_2\text{CCH}_3)]^- + \text{H}_2\text{O}$	13	-5.6	(c)
$[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$	$[\text{ReO}_3(\text{CH}_2)]^- + \text{CO}$	17	+46.6	(c)
$[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$	$[\text{ReO}_3]^- + \text{CH}_2\text{CO}$	18	+37.2	(c)
$[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$	$[\text{ReO}_2(\text{CH}_2)]^- + \text{CO}_2$	19	+28.6	(c)
$[\text{CH}_3\text{ReO}_2(\text{OH})]^-$	$[\text{ReO}_3]^- + \text{CH}_4$	29	-13.8	(c)
$[\text{CH}_3\text{ReO}_2(\text{OH})]^-$	$[\text{ReO}_3(\text{CH}_2)]^- + \text{H}_2$	21	+22.4	(c)
$[\text{ReO}_3]^-$	$[\text{ReO}_2]^- + \text{O}$	7	+176.0	+158.1

<sup>a</sup> Structures, Cartesian coordinates and electronic energies (in Hartrees) of species involved in primary reactions are given in Supplementary Figure S4. <sup>a</sup> Structures, Cartesian coordinates and electronic energies (in Hartrees) of species associated with CID of  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$ , ion-molecule reactions and CID of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  are

given in Supplementary Figure S5. <sup>c</sup> The thermochemistry associated with the triplet manifold was not calculated as the primary products formed in eqs 10-12 were assumed to be formed in the singlet state.

Based on the likelihood of the primary anionic products of the reaction of  $[\text{ReO}_2]^-$  with acetic acid being formed in the singlet state, we have calculated the energetics of all remaining reactions listed in Table 2 in their singlet states. The reaction of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$ , **15**, with acetic acid (eq. 13) is predicted to be exothermic by  $-5.6 \text{ kcal mol}^{-1}$ . The CID reactions of  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$ , **14**, and  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$ , **15**, and  $[\text{ReO}_3]^-$ , **12**, are all predicted to be endothermic except for loss of methane from  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$ , **15**. This suggests there must be a barrier for methane loss, otherwise the ion at  $m/z$  251 would not be observed.

## Conclusions

The rhenium oxide anions of  $[\text{ReO}_2]^-$ ,  $[\text{ReO}_3]^-$  and  $[\text{ReO}_4]^-$  are considerably less reactive towards organic substrates than the group 5 and 6 metal oxide anions that we have previously investigated. Thus unlike  $[\text{VO}_3]^-$  and  $[\text{VO}_4]^-$  [21], each of the rhenium oxide anions is unreactive with methanol. The reactivity of  $[\text{ReO}_2]^-$  towards acetic acid is likely to be driven by its triplet spin state, which may facilitate the activation of the O-H, C-H, C-C and C-O bonds in acetic acid. The activation of both the C-C and C-O bonds with extrusion of CO to form  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  has precedence in the reactions of  $\text{Fe}^+$  with acetic acid [26]. The loss of  $\text{H}_2$  to form the metallalactone  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  appears to be unprecedented in the gas-phase ion-molecule reactions of transition metal ions with acetic acid. Although this reaction

involves activation of both the O-H and C-H bonds, we do not know whether this is a concerted reaction or a stepwise reactions, and if the latter, whether C-H activation precedes O-H activation or vice versa. Likewise, the formal oxygen atom abstraction of acetic acid to give of  $[\text{ReO}_3]^-$  appears to be unprecedented in the literature. This has prompted us to embark on an examination of the oxygen atom abstraction reactions of  $[\text{ReO}_3]^-$  with simple triatomic neutral substrates, and the results of these studies will be presented in due course.

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### **Supplementary material:**

Mass spectra for isotope labelling experiments in support of: CID of  $[\text{ReO}_2(\text{CH}_2\text{CO}_2)]^-$  (Figure S1), for ion-molecule reactions of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (Figure S2), CID of  $[\text{CH}_3\text{ReO}_2(\text{OH})]^-$  (Figure S3). Cartesian coordinates and electronic energies for all structures calculated (Figures S4 and S5).

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