Decomposition of Halogenated Molybdenum Sulfide Dianions \([\text{Mo}_3\text{S}_7\text{X}_6]^{2-} (\text{X} = \text{Cl, Br, I})\)

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ABSTRACT: Molybdenum sulfides are considered a promising and inexpensive alternative to platinum as a catalyst for the hydrogen evolution reaction. In this study, we perform collision-induced dissociation experiments in the gas phase with the halogenated molybdenum sulfides \([\text{Mo}_3\text{S}_7\text{Cl}_6]^{2-}, [\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}\), and \([\text{Mo}_3\text{S}_7\text{I}_6]^{2-}\). We show that the first fragmentation step for all three dianions is charge separation via loss of a halide ion. As a second step, further halogen loss competes with the dissociation of a disulfur molecule, whereas the former becomes energetically more favorable and the latter becomes less favorable from chlorine via bromine to iodine. We show that the leaving S group is composed of sulfur atoms from two bridging groups. These decomposition pathways differ drastically from the pure \([\text{Mo}_3\text{S}_{13}]^{2-}\) clusters. The obtained insight into preferred dissociation pathways of molybdenum sulfides illustrate possible reaction pathways during the activation of these substances in a catalytic environment.

INTRODUCTION

The transition to renewable energies entails several problems. The geographical and temporal fluctuation of most renewable energy sources needs to be overcome via storage solutions for a successful transition from fossil fuels to sustainable energy. One possibility for this is to produce hydrogen, which is storable and transportable, by electrolysis of water. Hydrogen produced using renewables such as solar or wind power is called green hydrogen, which plays a prominent role in power-to-gas schemes. The electrolysis of water consists of two half-reactions, the oxygen evolution reaction (OER), and the hydrogen evolution reaction (HER). To produce economically viable amounts of hydrogen, both reactions need to be efficient and therefore catalysts are needed. The HER under acidic conditions is best catalyzed by platinum. However, the scarcity and high price of platinum makes it economically unviable for large scale hydrogen evolution catalysis. Therefore, a goal of recent studies is to find an inexpensive and abundant material with a comparable catalytic activity toward hydrogen evolution.

A promising alternative for platinum are molybdenum sulfides such as \(\text{MoS}_2\). In 2012, Karunadasa et al. reported the synthesis of a well-defined molybdenum disulfide. After electrochemical reduction, it was possible to catalyze the HER in acidic solution. However, to make molybdenum-based catalysts economically viable, the number of active sites, namely the number of edge sites, needs to be increased. Kibsgaard et al. investigated submonolayers of \([\text{Mo}_3\text{S}_{13}]^{2-}\) nanoclusters and reported excellent HER activity and stability in 2014. Furthermore, the synthesis of the studied \([\text{Mo}_3\text{S}_{13}]^{2-}\) clusters follows a scalable route. The high catalytic activity of amorphous molybdenum sulfides \(\text{MoS}_{2+x}, x < 1\), has been reported by several groups. In 2016, Tran et al. showed that amorphous \(\text{MoS}_{2+x}\) prepared as nanoparticles or thin films consists of discrete \([\text{Mo}_3\text{S}_{13}]^{2-}\) building blocks. Following these promising results, a series of different molecular molybdenum sulfide models have been synthesized by Wu and co-workers. Dave et al. for the first time reported high reactivity of \([\text{Mo}_3\text{S}_{13}]^{2-}\) in homogeneous, visible light-driven HER in 2018. They highlighted the importance of the terminal disulfides in the catalytic process and found a higher reactivity if the terminal disulfides were partially replaced by water. However, the nanoclusters showed reduced catalytic activity if the terminal disulfides were replaced by halogenides to form \([\text{Mo}_3\text{S}_7\text{Cl}_6]^{2-}\) and \([\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}\). An acid–base-resistant ligand-modified molybdenum sulfur cluster was recently reported by Zhang, Lin, and co-workers to exhibit enhanced photocatalytic HER activity.

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Gas-phase studies offer the advantage of dealing with well-defined and controllable systems. Such investigations give conceptual insight into the structure and behavior of individual molecules or small clusters as a model system for heterogeneous catalysis.  Lang, Zhou, and Schwarz managed to obtain FeS₅⁺ (x = 1–3) clusters and reacted them with small alkanes, which provided insight into the oxidative power of these species. Earlier, molybdenum chalcogenide cations were investigated in the Schwarz group. Intrinsic properties of molybdenum sulfide and oxide clusters were investigated by Jarrold, Raghavachari, and co-workers, including reactions with H₂ and H₂O. A reactivity experiment of small cationic molybdenum clusters with dimethyl disulfide in our group illustrated the high sulfur affinity of molybdenum.

We recently used a bottom-up approach and studied the [Mo₃S₁₃]²⁻ nanocluster and its protonated forms [HMo₃S₁₃]⁻ and [H₂Mo₃S₁₃]⁺ in the gas phase. Collision-induced dissociation (CID) experiments showed a variety of H₂S₆ elimination channels, and together with quantum chemical calculations it was shown that the Mo₃ core stays intact. Furthermore, it was concluded that the studied clusters are structurally very flexible. The calculations suggested that the protonation primarily happens on the terminal disulfides, supporting a sulfur-centered HER mechanism. Infrared multiple photon dissociation spectroscopy of the [HMo₃S₁₃]⁺ cluster confirmed that the terminal disulfide is the protonation site. Protonation in the gas phase followed by Coulomb explosion was probed in the reactions of [Mo₃O₆S₆]²⁻ and [Mo₃O₂S₄]⁻ with organic acids. Further insight was gained by the comparison with the fragmentation pathways of molybdenum oxide and oxysulfide clusters. The halogenated molybdenum sulfides [Mo₃SₓClₓ]²⁻, [Mo₃SₓBrₓ]²⁻, and [Mo₃SₓIₓ]²⁻ result from replacing each terminal disulfide unit of [Mo₃S₁₃]²⁻ by two halide ions. These species are particularly useful for mechanistic studies, because only bridging disulfide units or apical sulfur atoms are available. Scheme 1 illustrates the structure for the molybdenum sulfides [Mo₃SₓClₓ]²⁻, [Mo₃SₓBrₓ]²⁻, and [Mo₃SₓIₓ]²⁻. The study of these structures is interesting not only because of their changed HER activity but also because it could help to understand the decomposition and rearrangements of [Mo₃S₁₃]²⁻ during catalyst activation, building on our earlier CID study of [Mo₃S₁₃]²⁻.

### EXPERIMENTAL AND COMPUTATIONAL DETAILS

#### Sample Preparation

Our sustained off-resonance irradiation CID (SORI-CID) experiments were performed with isotopically enriched [²⁹Mo₃SₓClₓ]²⁻ and [⁷⁹Mo₃SₓBrₓ]²⁻, as well as nonisotopically enriched [⁷⁷Mo₃-Iₓ]²⁻. For the preparation of the halogenated clusters, a synthesis route described by Fedin et al. was followed. (NH₄)₂[²⁹Mo₃S₁₃] was produced as described previously.

To obtain [(CH₃)₄N][²⁹Mo₃SₓClₓ], 150 mg of (NH₄)₂[²⁹Mo₃S₁₃] was mixed with 15 mL of concentrated hydrochloric acid HCl (37%), heated for 20 min, and then filtered. The filtrate was mixed with 150 mg of tetramethylammonium chloride (CH₃)₄NCl and left in the refrigerator to crystallize. The product was then washed with water (2 × 8 mL), ethanol (6 mL), and diethyl ether (8 mL) and left to dry overnight under air. The obtained [(CH₃)₄N][²⁹Mo₃SₓClₓ] is a red powder. [(CH₃)₄N][²⁹Mo₃SₓBrₓ] was synthesized in a very similar manner. 20.15 mg of (NH₄)₂[⁷⁹Mo₃S₁₃] was mixed with 2 mL of concentrated hydrobromic acid HBr (48%), heated for 20 min, and filtered. The filtrate was mixed with 56 mg of tetrathiomalmonium bromide (CH₃)₂NBr and left in the refrigerator to crystallize. The product was washed in the same way and with the same amounts of water, ethanol, and diethyl ether as for the chlorinated compound described above. The product was obtained as an orange powder.

For the synthesis of [(CH₃)₄N][⁷⁷Mo₃-Iₓ], about 10 times more starting material was required because of low yields. Because iodine is monoisotopic, experiments without isotopic enrichment were still manageable. Nonisotopically enriched (NH₄)₂[⁷⁷Mo₃S₁₃] was prepared as described above for the isotopically enriched version. Then 256 mg of (NH₄)₂[⁷⁷Mo₃S₁₃] was mixed with 25 mg of concentrated, nonstabilized hydroiodic acid HI (57%), heated for 20 min, and filtered. The filtrate was mixed with 250 mg of tetrathiomalmonium chloride (CH₃)₂NClI and left in the refrigerator to crystallize. The product was washed with 30 mL of water, 20 mL of ethanol, and 20 mL of diethyl ether. [(CH₃)₄N][⁷⁷Mo₃-Iₓ] was obtained as a dark red powder.

#### Experimental Setup and Measurements

CID experiments were performed on a Bruker Apex Q E FT-ICR mass spectrometer with Nanobase Console, equipped with a 9.4 T superconducting magnet. The ions are produced in a Dual Source II, a combined electrospray ionization/matrix-assisted desorption/ionization (ESI/MALDI) source. Typically, solutions of the samples at a concentration of about 0.3 mM in acetonitrile were used. After the ions are produced by ESI, they are transferred through multiple stages of radiofrequency and electrostatic ion guides into the ICR cell, where they were mass selected via sweep and shot isolation. Argon was used as a collision gas at a pressure regime of around 10⁻⁶ mbar. SORI-CID was performed by acquiring multiple mass spectra after off-resonance irradiation of the mass-selected ions with a fixed frequency offset of 500 Hz and a pulse length of 1 s, with increasing SORI power. Plotting the normalized intensities of reactant and fragment ions as a function of SORI power yields the fragmentation curve.

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**Scheme 1. Three Types of Sulfur Atoms in [Mo₃SₓXₖ]²⁻:**

Equatorial (Sₑ), Axial (Sₐ), and Apical (Sₚₐ)
With the samples of the chlorinated molybdenum sulfide, we performed SORI-CID on $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^2\text{−}]$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^2\text{−}]$. The brominated sample, we only studied $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^2\text{−}]$ because this experiment already provided the relevant information. For the iodinated species, no isotopically enriched version was available. $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^2\text{−}]$ has a broad natural isotope distribution (see Figure S1). We isolated the full peak group and performed a relatively crude SORI-CID experiment to identify the primary fragmentation pathway by SORI at $m/z$ 636.847 with a SORI power of 1.5%. This allowed us to identify the preferred dissociation to $I^−$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ (Figures S2 and S3). This dissociation pathway is very efficient, which leads to overall low signal levels of $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^2\text{−}]$ due to dissociation events in the ion source region.

However, $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ was obtained from the ESI source in high yields, and the SORI CID breakdown diagram of this species was obtained with decent signal-to-noise level. In this case, the peak at $m/z$ 1148 was isolated. A simulation of an ultrahigh resolution mass spectrum with the different combinations of stable molybdenum and sulfur isotopes yields 91 isotopologues of $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$, with their exact mass ranging from $m/z$ 1148.0253 to 1148.0466. This complexity is largely due to the isotopes of molybdenum. Fortuitously, fragmentation of $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ does not involve loss of molybdenum atoms, while loss channels involving multiple iodine atoms or molecules dominate, and iodine is monoisotopic. For the observed disulfide loss, only the contribution of $^{32}\text{S}_2$ with $m/z$ 63.944 was considered, disregarding the minor contributions of, for example, $^{32}\text{S}^{34}\text{S}$ and $^{32}\text{S}^{30}\text{S}$.

**Computational Details**. To interpret the experimental results, quantum chemical calculations were performed at the B3LYP/def2TZVP level of theory using the D3 dispersion as suggested by Grimme et al. The obtained energetics are benchmarked against the oB97XD/def2TZVP method in the Supporting Information (see Table S1). For the most relevant ions observed in the experiment, the structure with the lowest (zero-point corrected) energy was searched by optimizing different arrangements of molybdenum clusters in the lowest spin multiplicity. Minima are verified via frequency calculations while the stability of the wave function was tested prior to each optimization. Transition states (TS) are verified via intrinsic reaction coordinate (IRC) calculations or by applying a minor offset along the normal vector of the corresponding imaginary frequency in the TS followed by optimization. All calculations are zero-point energy (ZPE) corrected and were performed employing the Gaussian 16 package.

**RESULTS AND DISCUSSION**

We investigated the decomposition pathways of the three halogenated molybdenum sulfides $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^2\text{−}]$, $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^2\text{−}]$, and $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^2\text{−}]$. For better readability, we omit the isotope label of $^{95}$Mo. An overview of all observed reactions is provided in Table 1.

**CID of $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^2\text{−}]$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$**. The fragmentation curve of the chlorinated molybdenum sulfide dianion $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$ shows a large onset (~20%) of $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ which corresponds to a Cl$^−$ loss, shown in Figure 1. This suggests that it is energetically feasible to remove a chloride ion from the precursor. However, the $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ in the fragmentation curve only rises to a SORI power of around 0.5%, after which it declines. Thus, the next fragment is $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$, most likely originating from $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$ via loss of $S_2$. Four more fragments appear with increasing SORI power, $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ and $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$. It is interesting to note that these four fragments involve loss of molybdenum atoms, i.e., the Mo$_2$ subunit is destroyed. To verify that none of these products is a direct fragment of $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$, we also performed a SORI-CID experiment using $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ as a precursor.

Interestingly, Cl$^−$ does not appear in the mass spectrum of the $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$ fragmentation, although the corresponding $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ is prominent. This can be explained by the kinetic energy release during Coulomb explosion: in dissociation of $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$ into $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ and Cl$^−$, the two negatively charged ions undergo Coulomb explosion. Due to conservation of momentum, the lighter partner, in this case Cl$^−$, carries the major fraction of the Coulomb energy as kinetic energy and can escape from the

![Figure 1. Fragmentation curve obtained from the SORI-CID experiment of $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$.](image-url)

**Table 1. Overview of Fragmentation Channels for $[^{35}\text{Mo(S}_2\text{S}_4\text{X}_6\text{)}^{2−}]$, X = Cl, Br, I, along with Suggested Neutral Counterparts**

| X | reactants | products | abundance |
|---|----------|----------|-----------|
| Cl | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^{2−}]$ | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ + Cl | high |
| Cl | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ + S | high |
| Cl | | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ + MoSCl | low |
| Cl | | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ + MoSCl | low |
| Cl | | $[^{35}\text{Mo(S}_2\text{S}_4\text{Cl}_6\text{)}^−]$ | low |
| Br | $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^−]$ | $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^−]$ + Br | low |
| Br | | $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^−]$ + Br | low |
| Br | | $[^{35}\text{Mo(S}_2\text{S}_4\text{Br}_6\text{)}^−]$ + Br | low |
| I | $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ | $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ + I | high |
| I | | $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ + I | low |
| I | | $[^{35}\text{Mo(S}_2\text{S}_4\text{I}_6\text{)}^−]$ + I | low |

*Neutral fragments Mo$_3$S$_X$ are given as stoichiometric sum and may have fragmented further.*
trapping potential. The alternative pathway, electron detachment followed by loss of a neutral Cl atom, is not plausible at low SORI power because the electron affinity of Cl is 3.61 eV.\textsuperscript{51}

The CID experiment of \([\text{Mo}_3\text{S}_7\text{Cl}_3]^-\) is shown in Figure 2. The first fragment that arises is \([\text{Mo}_3\text{S}_7\text{Cl}_4]^-\), confirming sequential fragmentation. Overall, the results of this experiment illustrate a few challenging aspects: The intensity of multiple structures is initially in the % or ‰ range and stagnates up until a SORI power of around 0.5%, pointing toward residual kinetic excitation of a small fraction of ions during mass selection. Above 0.5%, many different fragments arise. Near the end of the fragmentation curve, there is a jump in the intensity of most fragments, hinting toward problems in maintaining a constant pressure during the measurements. Nevertheless, \([\text{Mo}_3\text{S}_7\text{Cl}_4]^-\), \([\text{Mo}_3\text{S}_7\text{Cl}_5]^-\), \([\text{Mo}_3\text{S}_7\text{Cl}_6]^-\), and \([\text{Mo}_3\text{S}_7\text{Cl}_7]^-\) fragments appear in the same order as in the previous experiment, suggesting that direct fragmentation of \([\text{Mo}_3\text{S}_7\text{Cl}_6]^-\) into one of those fragments did not take place. However, an additional fragment, \([\text{Mo}_3\text{S}_7\text{Cl}_5]^-\), is observed that was missing previously. On the other hand, the intensity of the \([\text{Mo}_3\text{S}_7\text{Cl}_5]^-\) ion, which could be seen very well in the experiment with \([\text{Mo}_3\text{S}_7\text{Cl}_6]^-\), is barely above the noise level in the present experiment and lies well below other fragments, which have not been seen before. These two observations suggest that a small fraction of the dissociation events take different routes in the two experiments.

**CID of \([\text{Mo}_3\text{S}_7\text{Br}_3]^-\):** The fragmentation curve of the brominated molybdenum sulfide \([\text{Mo}_3\text{S}_7\text{Br}_3]^-\), Figure 3, shows a very similar pattern as the chlorinated species. The first and most prominent fragmentation is the loss of Br\textsuperscript{−}, leading to \([\text{Mo}_3\text{S}_7\text{Br}_2]^-\), which is the dominant fragment at all energies. Subsequent \(S_2\) loss leads to the next fragment, \([\text{Mo}_3\text{S}_7\text{Br}_1]^-\). In contrast to \([\text{Mo}_3\text{S}_7\text{Cl}_7]^-\), the brominated structure shows fragmentation paths where the number of molybdenum atoms is mostly preserved. For example, the next most prominent fragment is \([\text{Mo}_3\text{S}_7\text{Br}_1]^-\), corresponding to a sequential Br\textsuperscript{−} loss. At SORI powers beyond 0.5%, a number of other fragments arise. Interestingly, the bromide ion is now seen in the mass spectrum, with its intensity rising with increasing SORI power. The ion is not shown in the figure, as its intensity is still compromised by the high kinetic energy release during Coulomb explosion, which explains why Br\textsuperscript{−} appears consistently with an intensity lower than that of the corresponding fragment \([\text{Mo}_3\text{S}_7\text{Br}_2]^-\). A fraction of the bromide ions probably still escapes from the trapping potential.

**CID of \([\text{Mo}_5\text{S}_8\text{I}_3]^-\):** The SORI-CID experiment of \([\text{Mo}_5\text{S}_8\text{I}_3]^-\) was much more difficult, as no isotopically enriched sample was available. The seven natural isotopes of molybdenum lead to a complex isotope pattern. In addition, \(\Gamma\) loss is very facile, making ESI of the intact compound challenging. An example of the \([\text{Mo}_5\text{S}_8\text{I}_3]^-\) peak group in the mass spectrum can be seen in Figure S1. More than 20 different peaks can be identified in this case, and each of these peaks is composed of numerous isotopologues, with more than 1000 isotopologues for the peak group in total. In contrast to bromine or chlorine, however, iodine is monoisotopic, which makes the experiment still feasible.

Because of the isotopic distribution and the overall low intensities of \([\text{Mo}_5\text{S}_8\text{I}_3]^-\), we were only able to perform a crude SORI-CID experiment by acquiring 200 mass spectra with a SORI power of 0% and 1.5%, irradiating at \(m/z\) 636.847. We managed to identify \([\text{Mo}_5\text{S}_8\text{I}_3]^-\) together with \(\Gamma^-\) as the dominant fragments of \([\text{Mo}_5\text{S}_8\text{I}_3]^-\). Again, we see the loss of a halogenide ion as the first fragmentation step. Already at 0% SORI power, the iodide ion can be seen in the mass spectrum (see Figure S2) whereas \([\text{Mo}_5\text{S}_8\text{I}_4]^-\) is missing. At a SORI power of 1.5% (Figure S3), the \(\Gamma^-\) peak is higher than the peaks of \([\text{Mo}_5\text{S}_8\text{I}_4]^-\). Because \(\Gamma^-\) is monoisotopic, all the intensity adds up in one peak while the \([\text{Mo}_5\text{S}_8\text{I}_4]^-\) fragment intensity is distributed over several peaks, explaining this difference. Again, iodine is heavier than bromine and chlorine and does not as easily escape from the trapping potential after Coulomb explosion.

Having confirmed the first fragmentation step as \(\Gamma^-\) loss, we used \([\text{Mo}_5\text{S}_8\text{I}_3]^-\) as the precursor for a scanned SORI-CID experiment. Because of the many isotopes and the resulting low intensity, we chose very soft isolation parameters. For the analysis, we added up the intensities of all the isotopologues of a specific ion. For disulfur loss, only loss of \(S_2\) is considered, which accounts for 90% of \(S_2\) loss products. The fragmentation curve obtained can be seen in Figure 4. Unlike with the other halogenated molybdenum sulfides, loss of \(S_2\) to form \([\text{Mo}_5\text{S}_8\text{I}_2]^-\) was not observed. In addition, all observed fragments up to a SORI power of 1.5% retained all three molybdenum atoms. Interestingly, the fragments come in three intensity ranges. The loss of an iodine atom leading to

![Figure 2. Fragmentation curve obtained from the SORI-CID experiment of \([\text{Mo}_3\text{S}_7\text{Cl}_6]^-\).](image-url)

![Figure 3. Fragmentation curve obtained from the SORI-CID experiment of \([\text{Mo}_3\text{S}_7\text{Br}_3]^-\).](image-url)
[MoS₄I₄]⁻ is the most prominent fragmentation path. The fragments in the medium intensity range, consisting of [MoS₅I₃]⁻, [MoS₅I⁺]⁺, and [MoS₅]⁰, cover loss of multiple I or I₂ units, up to the elimination of all iodine atoms from the cluster. The [MoS₅]⁰ fragment is particularly interesting, because five electrons have been transferred from the I⁻ ligand upon leaving as I atoms or I₂ molecules, underlining the high redox capacity of the Mo₅S₅ core structure. In the low-intensity range, there are structures involving loss of disulfur units. The three ions observed at low intensities are [MoS₃I₁]⁻, [MoS₃I₂]⁻, and [MoS₃I₃]⁻.

**Computational Results.** To obtain insight into the cluster chemistry, we performed quantum chemical calculations of prominent dissociation pathways as summarized in Figures 5 and 6, which are potentially representative of the rearrangements taking place in a catalytic environment. The onset of the first fragment, [MoS₅Cl₃]⁺, can easily be explained (see Figure 5). The dissociation of the chloride ion is slightly endothermic and only stabilized by a Coulomb barrier of 1.37 eV. The endothermicity is expected to be sensitive to the basis set size, as was the case for the molybdenum oxy sulfides.⁴⁰ For the brominated molybdenum sulfide [MoS₅Br₂]²⁻, the dissociation of the halogenide ion is exothermic with −0.05 eV along with a Coulomb barrier of 1.16 eV, again explaining the large initial intensity in the experiment. This trend continues and the halogenide ion loss for [MoS₅I₂]²⁻ is even more exothermic at −0.18 eV, with a lower Coulomb barrier of 0.99 V. This, in addition to the scattering of the peak in the mass spectrum due to the isotopes, explains the very low intensity of [MoS₅I₃]²⁻ in the mass spectrum. It is quite intriguing that the kinetic energy release KER = Eₜₛ − ΔE is almost identical for the three species, ranging from 1.17 to 1.22 eV.

After initial halogenide ion dissociates, there are multiple channels available, with the loss of S₂ and the loss of a halogen atom being the most relevant (see Figure 5). Loss of another halogenide ion is unfavorable, and retaining the negative charge at the [MoS₅X₄] moiety is favored by 0.15−0.40 eV. For the S₂ loss, two different pathways are plausible. The first is the direct loss of a bridging S₂ unit, which is replaced by a bridging halogen atom at a cost of about 2.6 eV. However, a second pathway toward S₂ loss, which requires prior transfer of one sulfur atom between two separate bridging units, is more plausible from both thermochemical and kinetic perspectives, with a barrier lying at 0.5−0.6 eV below the dissociation limit for the direct S₂ loss channel.

The detailed reaction pathway of S₂ loss from [MoS₅X₄]⁻ is shown in Figure 6. In the first step, the S=S bond of a bridging disulfide unit is weakened, leading to a short Mo−S bond from the equatorial sulfur atom to the molybdenum atom that has a vacant coordination site due to the previous loss of a halide ion. In the next step, the S=S bond breaks, and the S atom starts interacting with the neighboring bridging disulfide unit. A deep local minimum is reached with a bridging S₂ unit that distorts the cluster structure. The rate-limiting transition state, lying at 1.97–2.12 eV, prepares for the elimination of a S₂ unit, with the initially transferred S atom taking a stable bridging position. In the local minimum reached after this TS, the S₂ unit is only weakly bound, and its final elimination requires the
passage of several low-lying transition states. Note that the original bridging S$_2$ group leaves and the transferred S atom fills the gap, avoiding undercoordinated molybdenum centers. However, it is quite probable that pathways exist which allow for scrambling of the sulfur atoms before the final S$_2$ loss.

Due to the structural flexibility of molybdenum sulfide, which leads to a large number of possible rearrangements, we calculated the full reaction path only for X = Cl. For X = Br, I, the most relevant stationary points were located, including the rate-limiting transition state and the local minima it connects. The energy required for S$_2$ loss increases with decreasing halogen electron affinity from chlorine to iodine, while the loss of a halogen atom becomes less endothermic. At the same time, direct dissociation of a halogen atom is entropically favorable over the S$_2$ dissociation pathway shown in Figure 6, which involves a series of tight transition states; dissociation of an iodine atom from [Mo$_3$S$_7$I$_2$]$^-$ with 2.04 eV lies below the barrier for S$_2$ dissociation at 2.12 eV. While this small difference lies within the computational uncertainties, both entropy and calculated energetics are in line with the experimental observation of exclusive iodine loss.

**Discussion.** The experiments also yield further insight into the stability of the Mo$_3$ core unit. After the loss of S$_2$ as the second step, the required energy for halogen atom loss remains relatively unchanged (see Figure 5). The pathways listed in Table 1 show that further fragmentation of the X = Cl species involves disintegration of the Mo$_3$S$_7$ core and loss of [Mo$_5$S$_7$Cl$_3$] species, consistent with the high binding energy of chlorine. In contrast, the much weaker bound iodine atoms are readily lost as I or I$_2$ units, while S$_2$ elimination is observed in overall low abundance and most likely only after additional iodine loss. The strength of the Mo–X bond decreases from Mo–Cl through Mo–Br to Mo–I, and consistently, loss of [Mo$_5$S$_7$Br$_3$] as well as Br$_2$ and even SBr is observed.

In our earlier study on the decomposition of [Mo$_3$S$_7$I$_2$]$^{2-}$ in the gas phase, we have shown that the initial step is S$_2$ loss. From the thermochemical perspective, it was shown that in the most feasible dissociation reaction, S$_2$ is formed from sulfur atoms from two bridging groups. Through introduction of halogen anions in the present study, we were able to pin down the mechanism for S$_2$ elimination in [Mo$_5$S$_7$X$_6$]$^{2-}$, X = Cl, Br, and show that bridging S$_2$ units are able to transfer a S atom to the adjacent Mo center. This makes it plausible that two adjacent bridging S$_2$ groups transfer a S atom to the Mo center. The following scenarios for S$_2$ loss from [Mo$_5$S$_7$I$_2$]$^{2-}$ are conceivable: (1) the initial terminal S$_2$ is lost, followed by its reconstruction from two bridging S$_2$ units; (2) two bridging S$_2$ units transfer a S atom each to an adjacent Mo center, leading to two end-on bound S$_2$ ligands; one S$_2$ ligand is lost, while the other resides the original side-on coordination of a terminal S$_2$ ligand; (3) a S atom is transferred from a bridging S$_2$ unit to Mo, transforming a terminal S$_2$ unit to S$_7$; S$_2$ is eliminated from the S$_7$ unit; a second S atom transfer from bridging S$_2$ allows for the reconstruction of a terminal S$_2$.

The S$_2$ elimination from [Mo$_3$S$_7$X$_2$]$^{2-}$ bears some parallels to the reaction of [Mo$_5$S$_7$X$_6$]$^{2-}$ with phosphines. Both are only observed for X = Cl, Br, and both involve the loss of equatorial sulfur atoms in the initial reaction step. This suggests that the rearrangements observed upon CID in the gas phase reflect the inherent reactivity of these species.

Because our experiments do not involve any hydrogen atoms, the relevance of this work to electrochemical hydrogen evolution catalyzed by molybdenum sulfide is only indirect. The mechanism for disulfide loss in Figure 6 illustrates the mobility of sulfur atoms between bridging and terminal disulfide units. Similar rearrangements were observed in our earlier studies on Mo$_3$S$_7$I$_2$ and Mo$_3$O$_2$S$_6$. These pathways seem quite robust, which suggests that they also may be involved in the reconstruction of molybdenum sulfide surface species during catalyst activation preceding HER.

**CONCLUSION**

We studied halogenated molybdenum sulfides, specifically [Mo$_5$S$_7$Cl$_6$]$^{2-}$, [Mo$_5$S$_7$Br$_6$]$^{2-}$, and [Mo$_5$S$_7$I$_2$]$^{2-}$. We observed the dissociation of a halogen anion as a first fragmentation step in each case. This fragmentation channel goes from slightly endothermic via thermoneutral to slightly exothermic from Cl$^-$ through Br$^-$ to I$^-$, respectively, according to our calculations. In addition to the overall reaction energy, however, the dianion is stabilized by a Coulomb barrier against dissociation into two negatively charged fragments, which makes [Mo$_5$S$_5$Br$_3$]$^{2-}$ and [Mo$_5$S$_7$I$_2$]$^{2-}$ metastable species. The second fragmentation step is loss of S$_2$ for X = Cl, Br, while an I atom is lost from [Mo$_5$S$_7$I$_2$]$^{2-}$, in line with the calculated barrier heights along the two competing pathways. The S$_2$ loss mechanism involves a complex reconstruction of the cluster, involving S atom transfer from a bridging S$_2$ unit. Similar rearrangements occur, for example, in the reaction of [Mo$_5$S$_7$Cl$_6$]$^{2-}$ and [Mo$_5$S$_7$Br$_6$]$^{2-}$ with phosphines and most likely are involved in the fragmentation of [Mo$_3$S$_7$]$^{2-}$ in the gas phase. The ability to bridge any two Mo atoms in the Mo$_3$ core by either one or two sulfur atoms is an intriguing chemical property, which may play an important role during catalyst activation.

**Figure 6.** Reaction pathway for elimination of S$_2$ from [Mo$_3$S$_7$X$_2$]$^{2-}$, X = Cl. Calculated at the B3LYP+D3/def2TZVP level of theory, all energies are given in eV. For X = Br, I, the most important points are shown. Atom color code: Mo, blue; S, yellow; X, green.
Further experimental data, benchmark of quantum chemical methods, and Cartesian coordinates and electronic energies of all isomers (PDF)

Author Contributions

M.P. and T.F.P. contributed equally.

Notes

The authors declare no competing financial interest.

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