

Reactions of 29 Transition Metal Cations, in the Same Oxidation State and under the Same Gas-Phase Conditions, with Sulfur

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A total of 29 transition metals (all except Tc), all as ions M^+ , have been reacted with gaseous S_8 . The reactivities and reaction products provide a unique set of comparative data on a fundamental reaction of the elements. The results underlie the interpretation of many other processes and compounds in condensed phases. Series of product ions $[MS_y]^+$ are formed, with y generally starting at 4, and increasing with time through 8 up to 10, 12, 16, or 21 (for La^+). A general mechanism is proposed, in which the first $\{MS_8\}^+$ encounter complex is reactive and undergoes S–S bond scission and rearrangement around the metal, such that $[MS_8]^+$ is not an early product. The early transition metals react faster than later members of the series, and third row metals react about twice as fast as first row metals. The metals which are more chalcophilic in condensed-phase chemistry are apparently less so as M^+ ; Hg^+ does not form observable $[HgS_y]^+$ (except for a very low yield of $[HgS_3]^+$) and is remarkably less reactive with sulfur than most of the other metal ions. Simple electron transfer between M^+ and S_8 does not occur except possibly for Ir^+ , but S_8^+ is sometimes observed and is believed to be formed by electron transfer from S_8 to some $[MS_y]^+$ complexes. Interpretation of the rates of reaction of the ions of groups 3, 4, and 5 with S_8 is complicated because they react with adventitious water in the cell forming oxo-species. The results are discussed in the context of condensed-phase metal polysulfide chemistry.

Introduction

In comparative inorganic chemistry, an investigation of the reactivities and reactions of all of the metallic elements, in the same oxidation state, with the same elemental reactant, and under the same conditions, provides the basis for fundamental understanding. Such investigation is possible in the gas phase, using bare M^+ ions generated by laser ablation and trapped in an ion cyclotron resonance (ICR) mass spectrometer.^{1–5} In this paper we survey the reactions and reactivities of the transition metal ions $M^+(g)$ with elemental sulfur, $S_8(g)$.

For most transition metals under conventional conditions the M^+ state is not normal, and in solution the solvation energies usually lead to other stable oxidation states. However in the gas phase $M^+(g)$ is common, and reactions of $M^+(g)$ with various reagents, mainly organic, have been investigated and reviewed.^{2–6} There have been no prior *systematic* investigations of $M^+(g)$ with S_8 , although $[MS_y]^+$ gaseous ions have been generated by other methods,^{7,8} and there is mention of $Fe^+(g) + S_8(g)$.^{7c} There have been systematic studies of $M^+(g)$ with O_2 . Kappes and Staley⁹ reacted first row transition metal M^+

ions (in an ICR cell) with O_2 , and with O_3 : Ti^+ and V^+ but not Cr^+ , Mn^+ , Fe^+ , Co^+ , and Cu^+ reacted with O_2 to give the MO^+ ion, while all of the M^+ ions investigated reacted with O_3 to give MO^+ . An extensive study has been carried out by Fisher et al.,¹⁰ who reacted the first row transition metal ions Ca^+ to Zn^+ with O_2 for the determination of $M^+–O$ bond dissociation energies: this study used ions produced by surface ionization and then an ion beam apparatus with an octopole ion guide, allowing the study of ions with a desired kinetic energy. The reactions of Nb^+ ¹¹ and U^+ ¹² with O_2 have been described. Schwarz et al.¹³ have probed reactions of transition metal monocations with O_2 , in the presence of oxidisable substrates and have described different geometries and energies for $[MO_2]^+$.

We have previously reported briefly the reactions of the first row transition metal monocationic ions M^+ with elemental sulfur,¹⁴ and in this paper we extend the report to the behavior of all of the transition metals, except Tc. This is a comparative overview of reactions and reactivity: details for individual metals and consideration of the relevant thermochemistry will follow in separate publications.

There is a large literature on the syntheses, structures, and reactions of metal polychalcogenide complexes in condensed phases,¹⁵ including syntheses by elemental combination.¹⁶ Solvent is a crucial and influential experimental variable, as is the identity of cations used to crystallise anionic complexes.¹⁷ Further, there is general recognition that transition metals have variable chalcophilicity in their condensed phase chemistry. The

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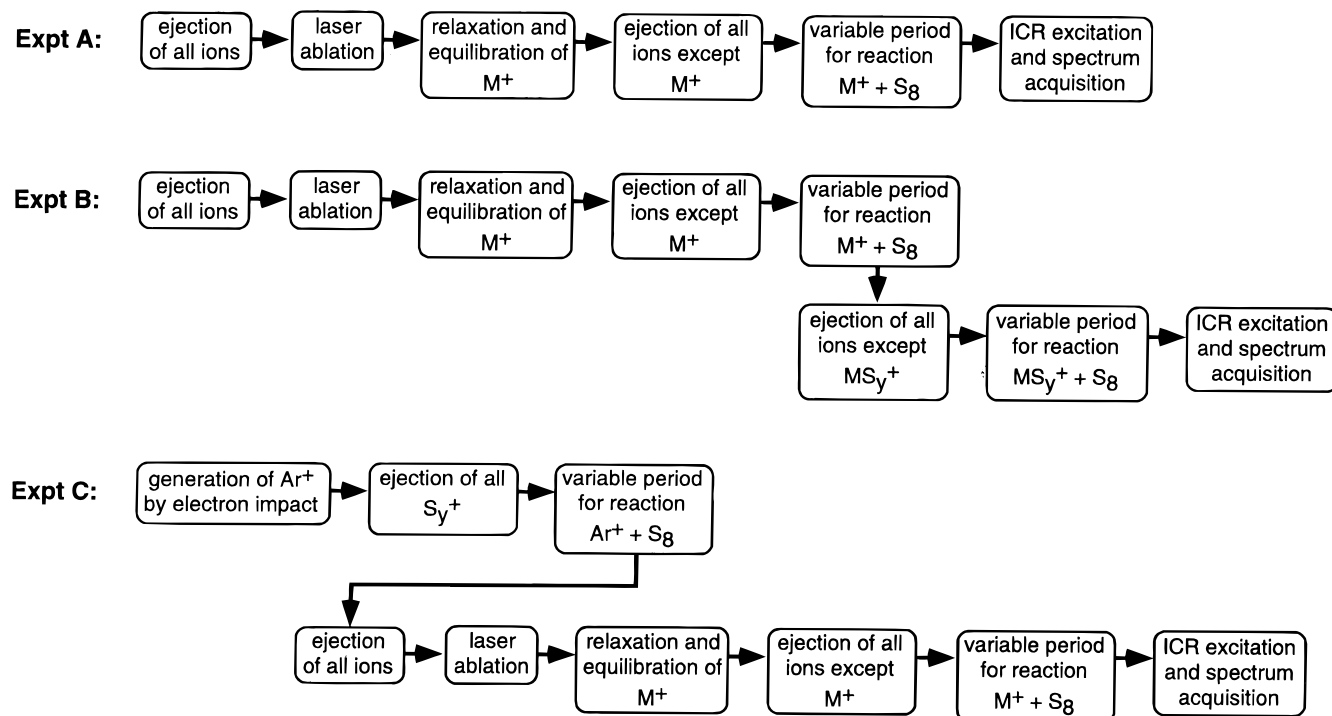


Figure 1. Sequences of events in the three types of FT-ICR-MS experiments on the reactions of M^+ with S_8 . The basic experiment is A; experiment B loops through two additional stages in which product ions $[MS_y]^+$ are isolated and reacted further; experiment C includes a comparative investigation of $Ar^+ + S_8$ under the same conditions prior to experiment A. Throughout experiment C the filament of the electron gun is kept on (but shielded except during generation of Ar^+) in order to maintain constant temperature in the cell.

fundamental and pristine $M^+ + S_8$ systems provide reference data for assessment of the influences of environment in condensed-phase metal polychalcogenide systems.

The chemistry of metals with sulfur, of metal sulfides, of metal polysulfides, and of the homologous chalcogenides, is also relevant to materials and surfaces with photoelectronic and catalytic properties, and investigation of the gas phase chemistry provides data which is applicable to technologies such chemical vapor deposition of semiconductor materials.

Experimental Section

Experiments were carried out using a Spectrospin CMS-47 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with a 4.7 T superconducting magnet. The ICR cell was cylindrical (radius 30 mm, length 60 mm) with titanium plates for trapping, excitation, and detection of ions. A turbomolecular pump was used to keep the base pressure at $\sim 1 \times 10^{-9}$ mbar and 10 h overnight pumpouts at 200 °C were used to remove water. The sample to be ablated was secured to a satellite probe tip which was placed at the end of the cell, in contact and flush with one of the trapping plates. The probe tip was designed to hold a capillary tube, containing sulfur, adjacent to the metal precursor. Gaseous sulfur was generated by continuous vaporisation of the solid in the capillary, allowing maintenance of an uncorrected ion gauge pressure of $\sim 1 \times 10^{-8}$ mbar S_8 at a nominal

temperature of 25 °C. Some experiments were carried out with the cell at 55 °C using the filament of the electron gun as heater, resulting in gauge pressures of $\sim 5 \times 10^{-8}$ mbar.

The composition of the sulfur vapor was investigated using low energy electron impact, which showed S_5^+ to be the only positive ion. This agrees with previous mass spectrometric investigation of sulfur vapor¹⁸ and with X-ray photoelectron spectroscopy,¹⁹ which reveals the presence of $S_8(g)$. We observe that after isolation of S_5^+ in the ICR cell it underwent reaction with S_8 to generate S_5^+ in less than 1 s.

The M^+ ions were generated by laser ablation of the metal powder or sheet, or of the metal oxide (for Sc, Y, Rh) or the metal sulfide (Fe, La, Hg). In a few cases mixed metal powders were used so that comparative rates could be measured under the same conditions. Ablation was effected with a Q-switched pulse from a Nd-YAG laser at 1064 nm, using pulse powers of 150 or 340 MW cm^{-2} . After ablation in the presence of S_8 (and in some experiments with additional argon to 1×10^{-7} mbar; see below) all of the ions trapped in the cell were allowed a period of at least 100 ms (and up to 1 s) for collisional cooling and electronic relaxation. Then all ions other than M^+ were ejected from the cell, and after a period for reaction of M^+ with S_8 the mass spectrum was acquired. This sequence of events is outlined as experiment type A in Figure 1. The temporal evolution of the intensities of M^+ and positively charged reaction products was measured from a series of experimental sequences with variable reaction periods. The maximum reaction times varied with the metal, but in most experiments at ambient temperature sufficient ions could be detected for reaction times up to 100 s.

In other experiments designed to study the properties of intermediates $[MS_y]^+$, these ions were isolated after an initial reaction time and then allowed to react further with S_8 , in experiment type B of Figure 1.

In order to characterize and calibrate our experimental conditions, we also measured the reactions of Ar^+ with $S_8(g)$ by experiment type C (Figure 1). These experiments used an electron gun which was energized continuously in order to keep the system thermally equilibrated at about 55 °C. Argon was introduced into the cell in addition to the $S_8(g)$ at $\sim 5 \times 10^{-8}$ mbar to increase the total pressure to $1 \times$

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10^{-7} mbar, and Ar^+ was generated by electron impact. All S_5^+ ions also generated by electron impact and by immediate reaction with Ar^+ were ejected, and then a clean reaction of Ar^+ with S_8 was monitored by recording spectra after different time intervals. Then, under the same conditions (but with the electron gun shielded such that the cell was free of Ar^+), M^+ was generated by laser ablation and the reaction $\text{M}^+ + \text{S}_8$ monitored as described above.

Results

The Characteristics of the Experiment. Our experiments involve the production of positive ions M^+ by laser ablation of solid precursors (elemental metal, metal oxide, or metal sulfide). These ions are trapped in the ion cyclotron resonance cell of the mass spectrometer, in the presence of $\text{S}_8(\text{g})$ continually introduced from a capillary of $\text{S}_8(\text{s})$ which is arranged such that the pressure of $\text{S}_8(\text{g})$ is $\sim 1 \times 10^{-8}$ mbar (at $\sim 25^\circ\text{C}$) and almost constant. The sulfur vapor was shown to consist solely of S_8 molecules (see Experimental Section). Cations only are trapped and monitored in these FTICR experiments: neutral species as well as S_8 are continually removed from the cell by dynamic pumping.

The $\text{M}^+(\text{g})$ ions are first allowed to reach thermal equilibrium and undergo electronic relaxation through collisions with the $\text{S}_8(\text{g})$ (and in many cases with the $\text{Ar}(\text{g})$ also present). Then all ions other than the thermalized ground state $\text{M}^+(\text{g})$ are ejected from the cell using a radiofrequency chirp pulse, which defines time zero. Thereafter the equilibrated $\text{M}^+(\text{g})$ trapped in the cell collide and react with $\text{S}_8(\text{g})$, and after a defined time period all positive ions in the cell are monitored by the FTICR technique. By variation of the reaction time periods a temporal profile of the reaction products is developed. The sequences of events in these experiments are portrayed in Figure 1.

The time scale of these gas phase reactions of M^+ is of the order of seconds (1–100 s). These times become meaningful when expressed in terms of the collision rate, that is in terms of the proportion of collisions which are productive. Theoretical methodology for calculation of the collision frequency of ions undergoing nonrandom ion–cyclotron motion with large polarizable molecules such as S_8 is inadequate, and so an empirical method was used to assess the collision frequency under our experimental collisions. The ionization energy of Ar (15.8 eV) is very much greater than that of S_8 (9.04 eV), and because the reaction of Ar^+ with S_8 will be very exothermic, it can be assumed to occur at the collision frequency. Following generation of Ar^+ by electron impact and then ejection of all other ions (experiment type C, Figure 1), it is observed that after 20 ms more than half of the Ar^+ has reacted, with generation of S_5^+ , S_2^+ , S_8^+ , S_4^+ , S_3^+ , and S_6^+ in order of decreasing intensity. This range of products confirms the violence of the reaction and the assumption that it occurs at close to collision frequency, which is therefore $\geq 100 \text{ s}^{-1}$ at 55°C . We also measured the rate of resonant charge transfer of S_8 with C_6H_6^+ , which is similar to the rate of reaction of Ar^+ with S_8 and again indicates that this represents the collision frequency.

Because the M^+ ion is generated under very high energy conditions it is important to establish that prior to monitoring its reactions sufficient time has been allowed for thermal equilibration and electronic relaxation, through collision with the $\text{S}_8(\text{g})$ which is always present. The consequences of this collisional relaxation can be detected as multiple $[\text{MS}_n]^+$ ions immediately after laser ablation. In general the relaxation and equilibration period in experiments of type A and B (Figure 1) was at least 100 ms and generally 1 s (i.e., ca. 10 – 100 collisions). The sufficiency of this period was checked by confirming that the product development during the subsequent $\text{M}^+ + \text{S}_8$ reactions was independent of the length of this initial

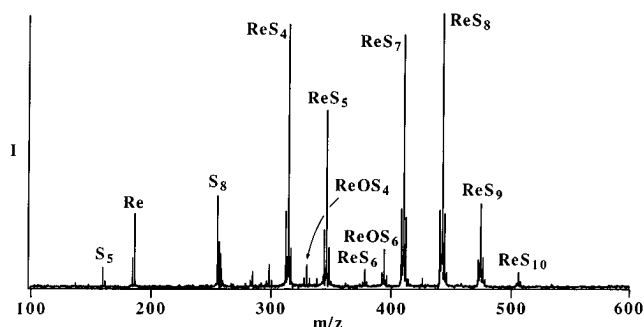


Figure 2. Mass spectrum of the positive ion products of the reaction between $\text{Re}^+(\text{g})$ and $\text{S}_8(\text{g})$, after 50 s at $\sim 25^\circ\text{C}$.

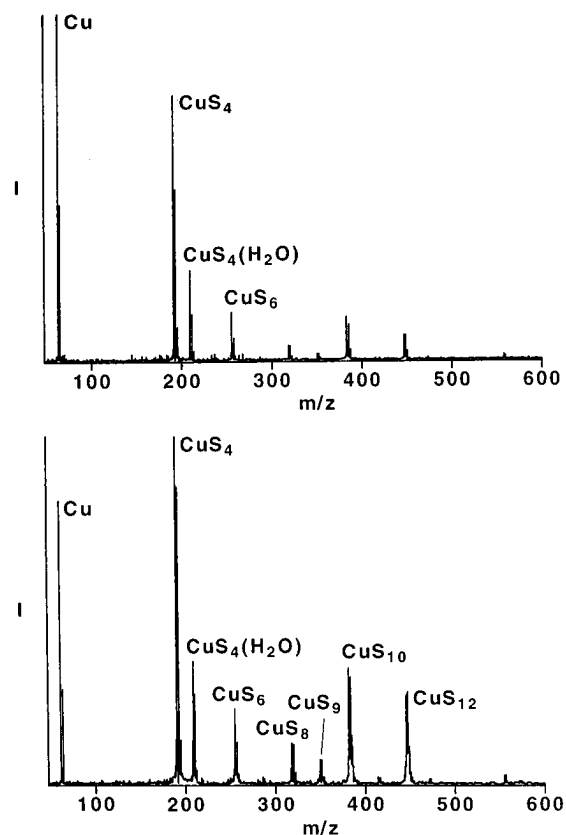


Figure 3. Mass spectrum of the positive ion products of the reaction between $\text{Cu}^+(\text{g})$ and $\text{S}_8(\text{g})$, after reaction times of (a) 10 s and (b) 20 s at $\sim 25^\circ\text{C}$.

delay. Further, these $\text{M}^+ + \text{S}_8$ reactions showed pseudo-first-order kinetics, consistent with (but not confirming) M^+ reacting in one (ground) state.

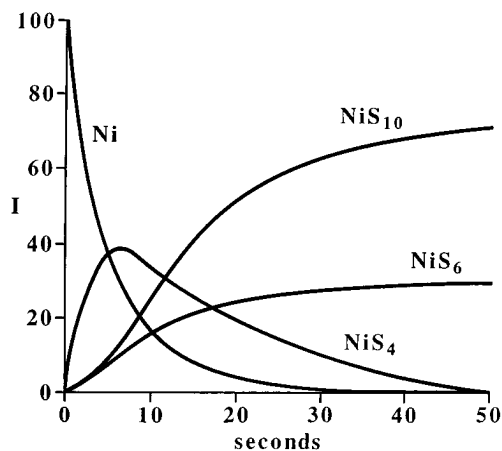
Product Distributions. There is no evidence of multiply-charged ions (identifiable by high resolution isotopomer patterns) in our experiments. Figure 2 shows a spectrum from the reaction of Re^+ with S_8 after a period of 50 s. At this stage there remains some unreacted Re^+ , and in addition to the developing major product ions $[\text{ReS}_4]^+$, $[\text{ReS}_5]^+$, $[\text{ReS}_7]^+$, and $[\text{ReS}_8]^+$, there are minor amounts of $[\text{ReS}_6]^+$, $[\text{ReS}_9]^+$, and $[\text{ReS}_{10}]^+$, trace amounts of two oxo ions $[\text{ReOS}_4]^+$ and $[\text{ReOS}_6]^+$, and some S_8^+ and S_5^+ . This spectrum demonstrates almost all of the types of product ions observed in this study. Note that 50 s is very long on the normal mass spectrometry time scale, and that these ions have undergone ca. 10^3 collisions.

Figure 3 shows the spectrum of the positive ions produced in the reaction of Cu^+ with S_8 , after 10 and 20 s. At the shorter reaction time Cu^+ is still the most intense ion, while $[\text{CuS}_4]^+$ is the most abundant product. Also present as significant ions in the spectra after 10 s are $[\text{CuS}_4\text{H}_2\text{O}]^+$, $[\text{CuS}_6]^+$, $[\text{CuS}_8]^+$,

Table 1. Products of Reactions of Transition Metal Ions M^+ with S_8

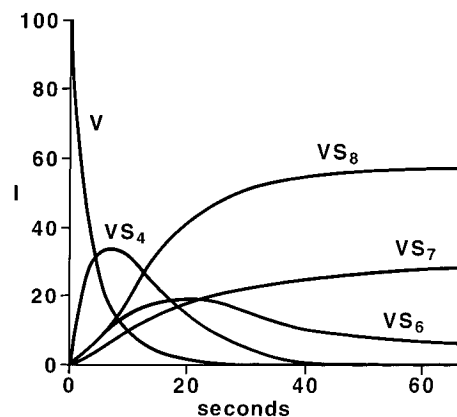
M^+	[MS_y] $^+$ ions listed as y values		[S_y] $^+$ ions ^b	other positive ions
	strong ^a	weak		
Sc ⁺	4, 10, 12	6, 8, 9, 11, 13, 14	S_8	ScO
Y ⁺	10, 14	2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13		YO (major ^c), YS_4O , $YS_6(H_2O)$
La ⁺	12, 14	2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 15, 16, 17, 18, 19, 20, 21		LaO (major ^c), $LaS_4(OH)$, $LaS_{11}(OH)$, $LaS_{14}(H_2O)$
Ti ⁺	4, 8	1, 2, 3, 5, 6, 7, 9, 10, 11, 12		TiO, TiO_2H_2
Zr ⁺	6, 10	1, 2, 3, 4, 5, 7, 8, 9, 11, 12	S_8, S_5	ZrO, ZrO_2H , ZrS_2O , ZrS_4OH
Hf ⁺	3, 4, 6, 8	5, 7, 9, 10, 11, 12	S_8	HfO, HfO_2H , HfS_yOH ($y = 3, 4, 6, 7, 8, 9, 10$), HfS_5O
V ⁺	4, 8	2, 3, 5, 6, 7, 9, 10	S_8, S_5	
Nb ⁺	2, 4	3, 5, 6, 7, 8, 9, 10		NbO, NbSO, NbO_2
Ta ⁺	6, 8	4, 5, 7, 9, 10	S_8	TaO, TaO_2 (major ^c), TaS_4O , TaS_5O , TaO_4H_4
Cr ⁺	4, 8	6, 10, 11, ^d 2, ^d 3, ^d 5, ^d 7, ^d 9 ^d		
Mo ⁺	4, 6, 8	2, 3, 5, 7, 9, 10, 11, 12		$MoS_4(H_2O)$, MoS_5O
W ⁺	6	1, 2, 3, 4, 5, 7, 8	S_8 (major ^c), S_5	WO, WS_yO ($y = 1, 2, 3, 4, 5, 6, 7$)
Mn ⁺	4, 6, 10	5, 7, 8, 9, 11, 12		
Re ⁺	4, 8	5, 6, 7, 9, 10	S_8	ReS_3O , ReS_4O , ReS_6O
Fe ⁺	4, 10	2, 3, 5, 6, 7, 8, 9		
Ru ⁺	4, 8	2, 3, 5, 6, 7, 9, 10, 11, 12	S_8	
Os ⁺	4, 8	1, 2, 3, 5, 6, 7, 9, 10, 11, 12	S_8 (major ^c)	
Co ⁺	4, 6, 10	2, 3, 5, 7, 8, 9		
Rh ⁺	4, 8	1, 2, 3, 5, 6, 7, 9, 10, 11, 12		RhO
Ir ⁺	4, 7	1, 2, 3, 5, 6, 8, 9	S_8 (major ^c), S_4, S_5, S_6	
Ni ⁺	4, 10	2, 3, 5, 6, 8, 9, 10		
Pd ⁺	4, 6, 10	2, 5, 8		
Pt ⁺	4, 6, 10	3, 5, 7, 8, 9	S_8 (major ^c), S_5, S_7 ^d	
Cu ⁺	4, 12	5, 7, 8, 9, 10, 11, 13, 14, 15, 16	S_8	$CuS_4(H_2O)$
Ag ⁺	4, 8, 16	5, 6, 11, 13, 15		$AgS_4(H_2O)$
Au ⁺	4, 10	3, 5, 6, 12, 16	S_8 (major ^c), S_5	
Zn ⁺	4	10, 12	S_8 (major ^c)	$ZnS_4(H_2O)$
Cd ⁺	6, 12	8, 10, 11	S_8 (major ^c), S_5, S_6	
Hg ⁺	none	3 ^d	S_8 (major ^c), S_3, S_4, S_5, S_6, S_7	

^a The product distribution and relative abundances change during the course of each reaction: [MS_y] $^+$ ions listed as strong develop major relative intensity at some stage during the reaction. ^b Minor intensity, except where indicated. ^c Most intense ion in the spectrum. ^d Trace.

**Figure 4.** Temporal development of the product ions formed during the reaction of $Ni^+(g)$ with $S_8(g)$ at ~ 25 °C.

[CuS_{10}] $^+$, and [CuS_{12}] $^+$. As the reaction progresses Cu^+ diminishes as [CuS_4] $^+$ increases in intensity, and then [CuS_4] $^+$ decreases in intensity as [CuS_{12}] $^+$ becomes the major ion at long reaction times. In general the smaller ions reach a maximum intensity at shorter reaction times to be replaced at longer times by larger ions. The highest mass ion is [CuS_{16}] $^+$, which has only minor intensity at a reaction time of 100 s.

Figure 4 shows the time course for the more intense product ions in the reaction of Ni^+ with S_8 . The Ni^+ decays as the major product ion, [NiS_4] $^+$, grows to a maximum and then decreases in intensity as [NiS_{10}] $^+$ becomes the major product ion. [NiS_6] $^+$ also grows in intensity as [NiS_4] $^+$ decays. All the other ions [NiS_y] $^+$ listed in Table 1 generally have intensities less than 10% of the total ion intensity. Figure 5 shows the time course of the reaction of V^+ with S_8 . Both [VS_4] $^+$, the

**Figure 5.** Temporal development of the product ions formed during the reaction of $V^+(g)$ with $S_8(g)$ at ~ 25 °C.

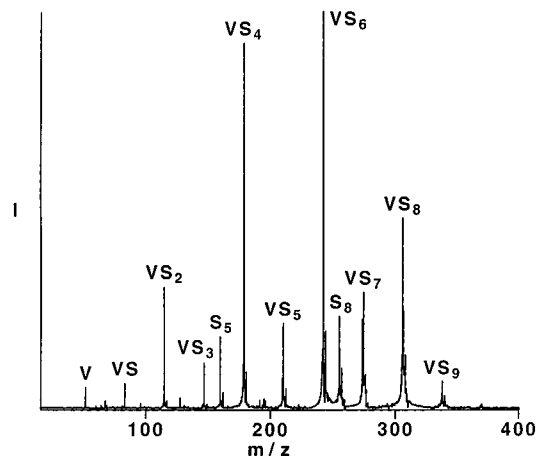
initial major ion, and [VS_6] $^+$ reach maximum intensities and then decay as [VS_8] $^+$ and [VS_7] $^+$ increase in intensity.

A full listing of the product ions for all of the transition metals except Tc is provided in Table 1. For most metals many [MS_y] $^+$ ions are detected, and Table 1 identifies separately those [MS_y] $^+$ ions which develop strong relative intensity at some stage during the time course. The general pattern of product development is similar to that displayed for Cu^+ , Ni^+ , and V^+ , in that the ions [MS_y] $^+$ with small y are formed in the early stages, followed by ions with increasing numbers of sulfur atoms: however each metal has different details for the identities, growth patterns, and further reactions of product ions. The first most intense ion for many metals is [MS_4] $^+$. This ion appears to be a precursor for larger ions such as [MS_8] $^+$ or [MS_{10}] $^+$ which grow in intensity as [MS_4] $^+$ reaches a maximum abundance and then diminishes. The smaller ions such as [MS] $^+$, [MS_2] $^+$, and [MS_3] $^+$ are often not observed or are of low intensity. The

Table 2. Periodic Distribution of Significant $[\text{MS}_y]^+$ Ions^a

group									
3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4, 10, 12	4, 8	4, 8	4, 8	4, 10	4, 10	4, 6	4, 10	4, 12	4
14	12	10	10	12	10	10	10	16	12
Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd
10, 14	6, 10	2, 4	4, 6		4, 8	4, 8	4, 10	4, 8	6, 12
14	12	10	12		12	12	10	16	12
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
12, 14	4, <i>b</i>	6, 8	6, <i>b</i>	4, 8	4, 8	4, 7	4	4	3
21		10	8	10	12	10	10	10	

^a The first row under each metal shows the y values for major products at some stage in the reaction sequence, with the smaller value of y being the initial major product. The second row under each metal lists the largest y value observed. ^b Spectrum dominated by $[\text{MS}_y\text{O}]^+$.

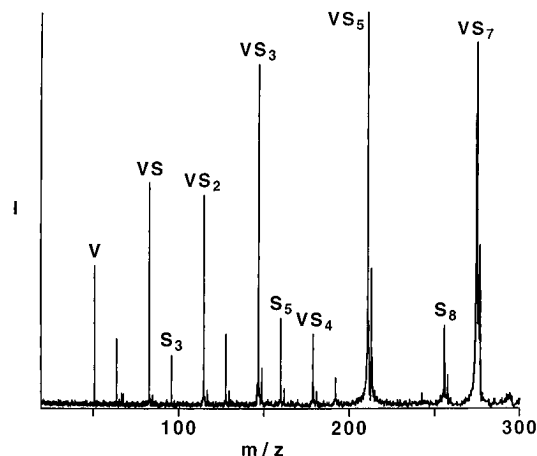
**Figure 6.** Mass spectrum of the mixture of products 2 s after isolation of $[\text{VS}_4]^+$ in the presence of 1×10^{-8} mbar of S_8 at ~ 25 °C.

$[\text{MS}_y]^+$ ions where y is odd are almost always of low relative intensity, with a few exceptions highlighted below. At long reaction times, high mass ions such as $[\text{MS}_{10}]^+$ or $[\text{MS}_{12}]^+$ have dominant intensities, but they are not necessarily the ions with highest mass. Table 2 shows the periodic distribution of the more intense $[\text{MS}_y]^+$ and the largest values of y for each metal.

Reactions of Intermediates. These temporal evolutions of product ions raise questions about mechanism. In the middle stages of the standard reaction the cell contains many $[\text{MS}_y]^+$ ions, all able to react with S_8 , which complicates mechanistic interpretation. However, there is a straightforward experimental approach (experiment type B) for bypassing this complication and investigating directly and unambiguously the reactivities of *specific* intermediates $[\text{MS}_y]^+$.

Figure 6 shows the reaction of $[\text{VS}_4]^+$, which is isolated in the cell by ejecting all other ions, with S_8 for 2 s. Note that $[\text{VS}_4]^+$ reacts more rapidly with S_8 than does V^+ . The major products of this reaction are $[\text{VS}_6]^+$ and $[\text{VS}_8]^+$, and the minor products $[\text{VS}_5]^+$, $[\text{VS}_7]^+$, and $[\text{VS}_9]^+$. The intermediate $[\text{VS}_4]^+$ also undergoes dissociation, as shown by the presence of $[\text{VS}_2]^+$, $[\text{VS}_3]^+$, S_8^+ , and S_5^+ . Thus several processes are occurring as the complex $[\text{MS}_y]^+$ ions are formed and react further with S_8 . Studies with other intermediates such as $[\text{MoS}_4]^+$ give similar results.

Ions having odd values of y in $[\text{MS}_y]^+$ generally appear with low intensity, but $[\text{VS}_7]^+$ is an exception. Therefore this ion was isolated and allowed to collide with argon as collision gas, necessarily in the presence of S_8 ; the resulting spectrum is shown in Figure 7. In a very short time (0.2 s) the $[\text{VS}_7]^+$ ion dissociates to a series of $[\text{VS}_y]^+$ ions, with $y = 3$ and 5 being the most intense. There is also a series of S_n^+ ions including S_8^+ . No ions $[\text{MS}_y]^+$ were observed with y larger than 7.

**Figure 7.** Mass spectrum of the mixture of dissociation products 0.2 s after isolation of $[\text{VS}_7]^+$ in the presence of 1×10^{-7} mbar of Ar and 1×10^{-8} mbar of S_8 at ~ 25 °C.

Several other ions $[\text{MS}_y]^+$ have been dissociated in a similar manner and show the presence of sulfur ions as products. For example $[\text{CrS}_6]^+$ was isolated and reacted with S_8 in the presence of argon and gave the dissociation products, Cr^+ , $[\text{CrS}_2]^+$, and $[\text{CrS}_4]^+$ as major product ions with S_8^+ and S_5^+ as minor product ions.

It must be stressed that the reactions and products we are observing involve a time scale (up to 100 s) which is several orders of magnitude larger than those of conventional nontrapping mass spectrometry. This emphasizes the stability of these $[\text{MS}_y]^+$ species. However the long time scales do reveal secondary and competing reactions due to background water, forming products such as $[\text{YO}]^+$ and $[\text{YS}_6(\text{H}_2\text{O})]^+$. The transition metals of groups 3, 4, 5, and 6 react with adventitious water in the cell producing intense ions such as $[\text{MO}]^+$ and occasionally $[\text{MO}_2]^+$.²⁰ The normal background pressure after overnight bakeout of the cell was 1×10^{-9} mbar, but electron impact studies of the background showed that water was present.²¹

The disappearance of M^+ followed pseudo-first-order kinetics over several half-lives.²² In some cases two or three metals were studied simultaneously to obtain relative rates of reaction under identical conditions of sulfur vapor pressure. Some

(20) Investigation of the reaction of Ta^+ with the background indicates the formation of $[\text{TaO}]^+$ followed by $[\text{TaO}_2]^+$ and small amounts of $[\text{TaO}_2\text{H}_2\text{O}]^+$ at long reaction times.

(21) Where $\text{M} = \text{Mo}, \text{Cu}, \text{Ag},$ and Zn , the $[\text{MS}_4]^+$ ions add H_2O . Isolation of $[\text{CuS}_4]^+$ and reaction with H_2S gave a product ion $[\text{CuS}_4\text{H}_2\text{S}]^+$. High mass ions present in the cell for long reaction times can also undergo reaction with water, e.g. the formation of $[\text{LaS}_{14}(\text{H}_2\text{O})]^+$. The studies of gas phase reactions of $[\text{MS}_y]^+$ ions will be reported in a separate publication.

preliminary measurements of absolute rates, that is rate of reaction relative to the collision rate, were obtained by comparison of the rates of reaction of M^+ and Ar^+ with S_8 under the same conditions: at $\sim 55^\circ C$ these ratios are Fe^+ 0.35, Au^+ 0.34, Cu^+ 0.30, Re^+ 0.25, W^+ 0.25, Ru^+ 0.20, Co^+ 0.17, Cr^+ 0.10, and Mo^+ 0.10. The relative reactivities of the M^+ ions, assessed as pseudo-first-order rates of disappearance, are complicated for some of the elements in groups 3, 4, 5, and 6 of the periodic table by their competitive formation of oxides. Overall, the variation of rates of reaction of M^+ with S_8 is not large.

The third row transition metal ions (except La^+) together with Zn^+ and Cd^+ , all form S_8^+ as the most intense product ion. S_8^+ is often accompanied by S_5^+ , and in the case of Hg^+ all the other S_n^+ ions ($n = 3-7$) are formed with S_8^+ .

Discussion

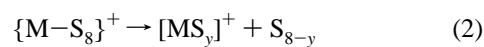
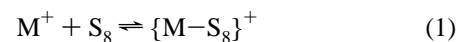
We first comment generally on the differences between our results for the $M^+(g) + S_8(g)$ reactions and the general experience of metal sulfur chemistry in condensed phases. A striking example is with mercury, conventionally chalcophilic in all oxidation states, and yet in the reaction $Hg^+(g) + S_8(g)$ the only detectable $Hg-S$ product is a trace of $[HgS_3]^+$, and the major products (S_n^+) do not contain mercury. Another surprise is the similarity of product distribution in these reactions covering a wide variety of metals.

General Mechanism. The pseudo-first-order kinetic reactivity of M^+ for at least several half-lives is significant and informative about the electronic state of M^+ . All reactions have been measured over long reaction periods, often well beyond the disappearance of M^+ . Many reactions have been tested with several different delay periods prior to isolation of M^+ . The independence of the pseudo-first-order rates from the length of the preperiod for collisional relaxation indicates that each M^+ reacts through only one electronic state, presumed to be the ground state. During the relaxation preperiod the M^+ ions undergo collision with S_8 (and also with argon), providing opportunity for the excited ions to either react to give ionic products which are ejected from the cell, or to relax by collision with the large S_8 molecule. During a period of 100 ms at pressures of 1×10^{-8} mbar, metal ions are estimated to have undergone at least 10 collisions, and probably more because the ions initially produced by laser ablation have large translational energies.

A second conclusion from the observed pseudo-first-order reactivity is that the variety of reaction products, including $[MS_y]^+$ and S_8^+ , are probably not being formed in parallel processes.

We propose a mechanism (see eqs 1 and 2) in which there is formation of an encounter complex $\{M-S_8\}^+$, which subsequently either dissociates to reactants or undergoes parallel and serial reactions to the products observed. It is postulated that none of the S-S bonds is yet broken in the encounter complex, which is not the same as the products $[MS_8]^+$ observed at later stages. It is significant that ions with the composition $[MS_8]^+$ are not observed in the very early stages of our reactions, consistent with the hypothesis that subsequent rearrangements

to products (eq 2) are comparatively fast. The different reaction

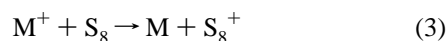


rates of the various metals would be consequent on details of the first rearrangement process, eq 2. The major product observed in the early stages is usually $[MS_4]^+$, suggesting that the most rapid of the processes, (2), involves metal-assisted scission of the S_8 cycle.

In separate work²³ we have investigated the reaction of Ca^+ with S_8 . The mechanism of eqs 1 and 2 applies, but the first observable product is the distinctive $[CaS_3]^+$, rather than $[MS_4]^+$ as seen with the transition metals. The following stages of the mechanism with Ca^+ were elucidated: $[CaS_3]^+$ can subsequently add S_8 to form $[CaS_{11}]^+$ in more than one isomer, as well as cleave S_8 to form $[CaS_9]^+$ and $[CaS_6]^+$ as abundant products.

The temporal evolution of products for the transition metals usually involves $[MS_4]^+$ transforming to $[MS_y]^+$ with y even: the more stable products have $y = 6, 8,$ and 10 . These results parallel the measurements of Freiser et al^{7c} on the decomposition of ions $[FeS_y]^+$ by loss of S_2 . The ions with odd values of y are often less intense than those with y even, with a few exceptions such as $[MS_7]^+$ for $M = V, Mn, Zr, Rh,$ and Ta , and $[AgS_{13}]^+$. Details of the numerous transformations of the many intermediates $[MS_y]^+$ in our reactions are accessible through experiments in which the intermediates are trapped alone and monitored: these details are too voluminous to include in this overview paper.

Formation of S_8^+ . Table 1 shows that S_8^+ is observed for some but not all metals. The simplest process which could account for S_8^+ is electron transfer, eq 3. However we believe



that with the possible exception of $M = Ir$, reaction 3 is not occurring as such in our experiments. Simple charge transfer would be a resonant process, requiring that the ionization energies of M and S_8 be close, $IE(M) \geq IE(S_8)$. The ionization energy of S_8 has been reported as 9.04 eV.²⁴ Of the transition metals, all except four have first ionization energies considerably smaller than that of S_8 , so that reaction 3 would be endothermic. Three metals, Hg (10.44 eV), Zn (9.39 eV), and Au (9.225 eV) have ionization energies too far above that of S_8 for resonant charge transfer and could be expected to react similarly to Ar^+ , producing several S_n^+ ions. The rate of the reaction of Au^+ with S_8 is slower than the reaction of Ar^+ with S_8 (ratio 0.34:1), and the reaction produces $[AuS_y]^+$ ions as well as S_8^+ and S_5^+ , all disfavoring the occurrence of reaction 3. Of the third row transition metals, the sequence Hf to Os and Pt , all have ionization energies lower than that of S_8 . Only Ir has an IE (9.02 eV) close to that of S_8 , and therefore reaction 3 could occur for Ir^+ . For the other metals the observed formation of S_8^+ must involve processes other than just equation 3.

The temporal data also indicate that reaction 3 is not occurring in those systems where S_8^+ is an observed product. Resonant charge transfer is expected to be very rapid, causing similarly rapid depletion of M^+ by the excess of S_8 . However M^+ is not rapidly depleted, and the formation of the S_8^+ is not coupled kinetically with the diminution of M^+ . For instance, S_8^+ is

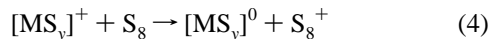
(22) The time points in the kinetic measurements could be affected by small variations in the pressure of S_8 and the temperature. The precise pressure of S_8 could vary from experiment to experiment as the cell could not be kept at a constant temperature, and so the first-order kinetic rates are approximate.

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present when there are unreacted Au⁺ ions after 10 s, and unreacted Zn⁺ after 50 s. The presence of both Re⁺ and S₈⁺ is evident also in Figure 2.

The rate of formation of S₈⁺ is comparable with the rate of formation of the [MS_y]⁺ ions, suggesting that charge transfer processes of the type shown in (4) provide a possible mechanism



for generation of S₈⁺. The [MS_y]⁺ ion or ions responsible for S₈⁺ formation according to (4) are therefore not expected to appear in the spectra. It is notable that for the third row transition metals W to Au, where S₈⁺ is a major product, the [MS₂]⁺ ion is absent or of low abundance, suggesting that this could be the species undergoing reaction 4. We do not yet have data on the ionization energies of [MS_y]⁺ ions. We have direct evidence to support the occurrence of reaction 4 for [PtS]⁺. This ion is very weak in the product distribution with Pt⁺, but we were able to isolate it in the cell, and observed that it reacted rapidly within 1 s, with concomitant formation of S₈⁺. A similar result was obtained with [PtS₂]⁺.

The relative absence of [HgS_y]⁺ products from the reaction of Hg⁺ with S₈ can be accounted for by the removal of a key early intermediate through efficient charge transfer (eq 4). Perhaps [HgS₄]⁺ as an early product, or even {Hg–S₈}⁺, undergoes efficient electron transfer on collision with S₈ and thereby interrupts the normal development of [HgS_y]⁺ products. Neutral [HgS_y]⁰ products may be formed but not observed in these experiments.

It is unlikely that S₈⁺ is formed by dissociation from larger [MS_y]⁺ ions. The ion [VS₇]⁺, when isolated and allowed to react with S₈, generated S₈⁺ which cannot be formed by simple dissociation. Similarly [CrS₆]⁺ could not dissociate to give the observed S₈⁺.

Most Stable and Largest Products. After long reaction times the most abundant ion is often [MS₈]⁺ or [MS₁₀]⁺ or [MS₁₂]⁺ or [MS₁₄]⁺, but these ions may not be the highest mass ions (Tables 1 and 2). For example, La⁺ reacts to form [LaS₁₄]⁺ as the most abundant ion at reaction times of 100 s (long after the disappearance of La⁺) but the highest mass ion is [LaS₂₁]⁺. It is probable that with higher concentrations of sulfur (not obtainable under our experimental conditions) larger ions might be observed. The stability of the ions observed in our experiments is shown by their longevity and sustenance of multiple collisions in the ICR cell.

Periodicity. One general conclusion from this study is that there is no marked dependence of the distribution of the product ions [MS_y]⁺ with the position of M in the periodic table. Fe⁺ reacts faster than most of the other transition metals including some of the third row transition metals, and yet the largest ion observed is [FeS₁₀]⁺, whereas the slower reacting ion Mo⁺ forms [MoS₁₂]⁺. The elements early in each period react faster than those towards the end of the period, but this conclusion is complicated by the reaction of the oxophilic metals with the background water, which is at least 1 order of magnitude lower in pressure than the S₈. Although comparative reaction rates have not been measured under identical conditions, it appears that the rate of reaction of Ca⁺ with S₈²³ may be as fast as those of Fe⁺ and Sc⁺. In the context of the mechanism proposed above, the relative rates and the product distributions for the various transition metals will be determined by the properties of the intermediate collision complex. It is readily conceivable that different directions of collision with the anisotropic S₈ molecule will be favorable for different metals and that the subsequent rearrangement reactions could be quite dependent on the electronic properties of the metal. Further elaboration

of this point depends on computational modeling in progress using density functional methods.

Structures. The structural possibilities for the coordination in [MS_y]⁺ are numerous, extending from (a) M bound to intact S_n monocycles (4 ≤ n ≤ ca. 12), through (b) M chelated by polysulfide S_n (n ≥ 2), to (c) M coordinated by isolated S atoms. Stereochemically allowable variation in the lengths and conformations of the S_n chains and cycles, together with combinations of these coordination types, permits many hypotheses. We use gradient corrected density functional theory to optimize the geometries of postulated structures and to evaluate relative energies of isomers. Mapping of the geometry–energy surfaces for the products described here, together with mapping of the geometry–energy surfaces for the intermediates {M–S₈}⁺ which we believe are influential in affecting the relative rates and product distributions, will be reported separately. We have already described and partially evaluated possible structural types for [MS₄]⁺, [MS₈]⁺, and [MS₁₂]⁺ for selected first row transition metals.¹⁴ The ion [CuS₄]⁺ has been calculated to have the lowest energy when Cu is incorporated into a CuS₄ chelate ring, while [MS₄]⁺ ions for earlier first row transition metals have lowest energy structures with S₂ units imposing various coordination stereochemistries at M.

There is a significant precedent for coordinated monocyclic sulfur in [Ag(S₈)₂]⁺ (AsF₆)⁻, prepared by the reaction of elemental sulfur with AgAsF₆ in liquid SO₂, and characterized crystallographically.²⁵ The sandwich structure is comparable with that which we propose for the gas-phase ions [CuS₁₆]⁺ and [AgS₁₆]⁺. The crystal structure of Cs₃Te₂₂, recently reported,²⁶ contains Cs⁺ similarly surrounded by two puckered crown-shaped Te₈ rings.

Significance and Conclusions. Metal polysulfide chemistry has a long history, which has seen distinct stages of development. The conditions for formation of metal polysulfide complexes began with aqueous polysulfide solutions (in an analytical context) which allow a small number of metals to form soluble molecular metal polysulfide complexes.^{15a} In the 1980s the use of non-aqueous media and the consequent increase in the thermodynamic activities of the polysulfide anions in solution allowed the synthesis of a plethora of soluble molecular complexes for virtually all metals.^{15b,c,d} Also during this period the systematic exploration of non-aqueous melts yielded a diverse set of new metal polychalcogenide compounds, more commonly nonmolecular in structure.²⁷ Each of the above preparative techniques used essentially the reaction type Mⁿ⁺ + S_y²⁻ (or E_y²⁻ for other chalcogens). A variant preparative reaction explored by Rauchfuss involved combination of the elements, M + S₈ in non-aqueous solution in the presence of heterocyclic amines, in which the elements undergo redox reactions to form molecular metal polysulfide complexes with coordinated amine.¹⁶

The coordination of S₂, S₃, S₄, S₅, S₆, S₇, S₈, and S₉ is well-known in anionic metal polysulfide solids,^{15,28,29} solutions^{29,30}

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and in neutral coordination and organometallic compounds.^{31–33} Most metal polysulfide systems are either anionic or neutral with coordinated polysulfide,^{15,32} whereas our studies involve *cations* which are not common in solution. There is only one characterized compound having cyclosulfane S₈ coordinated in a cation, namely [Ag(S₈)₂]⁺ mentioned above. Further, our experiments reveal no analogs of the di- and polymetallic complexes which are common with sulfide and polysulfide ligands in solutions and crystals.¹⁵ These normally occur as anions, such as [Mo₂S₈]²⁻,³⁴ [Mo₃S₁₃]²⁻,³⁵ [W₃S₁₀]²⁻,³⁶ [Re₂S₁₆]²⁻,³⁷ [Fe₂S₁₂]²⁻,³⁸ [Pd₂S₂₈]⁴⁻,³⁹ or [Cu₆S₁₇]²⁻,⁴⁰ but it is easy to conceive of related cations obtained by removal of one or two terminal polysulfide ligands. However our experimental conditions do not favor the association processes required for polymetallic complexes.

In the chronological progression of M/S_y synthetic chemistry, the influence of the solvent has been significant and variable. In the experiments reported here we have moved to the extreme of no solvent. We describe the intrinsic reactivity for the combination M⁺ + S₈. The principal conclusion in this context is that the transition metals are not very different in their reactivities and in their product distributions. This emphasises the interpretation that the variabilities of the known M/S_y chemistry in condensed phases are essentially consequences of the influences of the condensed phase and are not intrinsic to

the metal. This same comment applies to the occurrence of metal oxidation states: the well-known variations of formal oxidation states from M⁺ throughout the transition elements are consequences of the condensed medium in which the metal occurs. In M⁺/S_y chemistry there are some variations correlating with the electron population of the metal, but they are not as might be expected from variations in condensed phase chemistry. We do observe that the balance between oxophilicity and chalcophilicity across the transition series, with the early groups being oxophilic, is superficially similar in the gas phase and in solution. However this comparison is complicated by the fact that the metals which are oxophilic in the condensed phase are in much higher formal oxidation states than the M⁺ of our experiments.

Having made this somewhat fundamentalist interpretation of our gas phase M⁺/S_y chemistry, what is its relevance given that most practical M/S_y chemistry involves condensed phases? The relevance is the provision of a reference state against which the influences of various media can be assessed and deployed. For instance, our results suggest that M⁺ + S₈ (or M²⁺ + S₈) reactions in liquid SO₂ similar to that already mentioned for Ag⁺,²⁵ could yield a class of compounds still unrecognized. We emphasise that the majority of the [MS_y]⁺ products we report are not fleeting entities, but are long-lived and survive multiple collisions. It is entirely feasible that they will be stable in inert solvent systems.

It is possible to investigate the gas phase reactivity under conditions which are closer to those of the condensed phase, namely with other ligands on the metal.⁴¹ We have observed that some [MS₄]⁺ ions coordinate water, and in the reaction of Cu⁺ with S₈ in the presence of H₂S, [CuS₄H₂S]⁺ is formed.²¹ Other potential donor molecules are currently under investigation and there may be an extensive coordination chemistry of these [MS_y]⁺ ions.

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