

Absolute Rate Constants for the Reactions of Sulfur (3P_J) Atoms in Solution

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Abstract: The 248-nm laser flash photolysis of methyl isothiocyanate (MeNCS) was used to generate $S(^3P_J)$ ground state atoms in acetonitrile solution. The reaction of $S(^3P_J)$ atoms with the MeNCS precursor produces molecular diatomic sulfur $S_2(^3\Sigma_g^-)$ in its ground state, which possesses an absorption at ca. 270 nm. The first-order growth of this absorption was used to monitor the decay kinetics of the sulfur (3P_J) atoms and to measure the rate constants for their reactions with additives. The rate constants obtained for a number of olefins, e.g., $9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for ethyl vinyl ether, hydrogen donors, e.g., $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for tributyltin hydride, sulfur atom donors, e.g., $5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for carbon disulfide, and nucleophiles, e.g., $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for chloride ions, demonstrate that $S(^3P_J)$ atoms behave as reactive, yet very selective, intermediates in solution; the highest reactivity was observed toward nitrogen and phosphorus nucleophiles, e.g., 1.2 and $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for hydrazine and triethyl phosphite. The comparison with known nucleophilicity constants, e.g., for methyl iodide as electrophile, suggests further that $S(^3P_J)$ atoms act as potent but relatively soft electrophiles. The reaction modes between $S(^3P_J)$ atoms and the additives are assumed to involve abstractions of single atoms or addition to double bonds or lone electron pairs. The reaction rate constants for atomic sulfur $S(^3P_J)$ in solution are compared with previous gas phase data for $S(^3P_J)$ atoms and with the data for oxygen (3P_J) atoms in solution.

Introduction

The net result of many oxidation reactions can be formally described as the transfer of single atoms such as halogens, oxygen, or sulfur. However, it is not always straightforward to obtain mechanistic evidence that an “active” atomic species is actually involved in the elementary key step of the reaction. In solution, in particular, complexation and ionization, i.e., the intervention of a complexed atomic species and the participation of electron transfer, become quite often viable reaction pathways. Knowledge about the characteristic solution reactivity of atomic species is, thus, invaluable for the accurate description of several reaction mechanisms; it cannot be entirely gained by comparison with the gas phase reactivity of atoms, which has been more comprehensively investigated but is frequently restricted to molecules of very limited complexity.

The solution reactivity of atoms is now well-characterized for hydrogen,¹ fluorine,² chlorine,^{3–5} bromine,⁶ and iodine.⁷ Common denominators of the chemical behavior of halogen atoms are their high reactivity in hydrogen abstraction reactions (particularly F and Cl), and their tendency to form complexes with arenes and anions. The complexation reactions, which provide a pertinent example for the reactivity difference between an “active” and associated atom in solution, have been used to probe the lifetime and intervention of the halogen atoms by time-resolved transient absorption spectroscopy due to the intense

CT absorbance of such atom complexes.^{4,8,9} Recently, we have moved to group VIa of the periodic table by examining the reactivity of atomic oxygen in solution;¹⁰ in this case, the chemical reaction with acetonitrile as solvent has been employed to monitor the oxygen (3P_J) atom, since the resulting acetonitrile *N*-oxide absorbs at 330 nm, a wavelength readily accessible to time-resolved absorption spectroscopy. Oxygen (3P_J) atoms were found to be less reactive and more selective than fluorine atoms, but the resemblance with the halogen atom reactivity was still pronounced. In particular, the bivalent character of the oxygen atom, which has made their generation in solution more challenging, has not become a discriminating feature when compared to the monovalent halogen atoms.

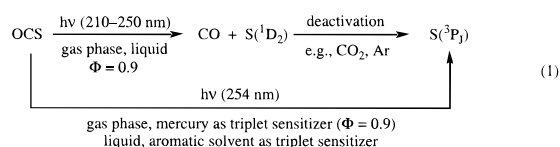
The group VIa element sulfur is characterized by a particularly rich multivalent organic and inorganic chemistry.¹¹ Again, since no quantitative data on the reactivity of atomic or active sulfur are available for solution, we have sought to find a suitable precursor to allow the photolytic generation of this atom, and also a suitable probe to follow its reaction rates by transient absorption spectroscopy. Fortunately, a vast number of gas phase studies have already been concerned with sulfur atoms, in which their relative or absolute reactivity, their reaction products, or the differences in excited state reactivity have been of primary interest. Moreover, some product studies in solution serve to obtain information on suitable precursors.

Gunning and Strausz have pioneered^{12–20} and reviewed^{21–24} the gas phase examination of atomic sulfur by using the

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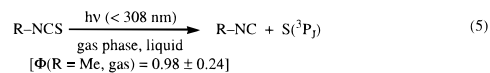
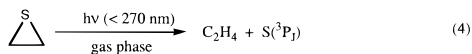
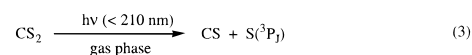
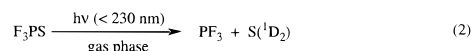
photolysis of carbonyl sulfide OCS (eq 1) as precursor for sulfur



atoms in their excited singlet (${}^1\text{D}_2$) and triplet ground state (${}^3\text{P}_1$), which are separated by 26.4 kcal mol $^{-1}$.²³ The products derived from photolysis of carbonyl sulfide have also been examined for photolysis in solution²⁵⁻²⁸ and in matrix,²³ indicating that the principal reactivity for excited and ground state sulfur atom formation remained the same, except for a less efficient product formation from S(${}^1\text{D}_2$) in matrices. While the direct photolysis of OCS affords primarily S(${}^1\text{D}_2$) with unit quantum yield,^{29,30} the addition of the triplet sensitizer mercury,³¹ or of deactivating colliders like CO $_2$ ^{32,33} or noble gases,³⁴ rendered the photolysis of OCS in the gas phase a selective source for ground state (${}^3\text{P}_1$) atoms.²⁴ Similarly, when the OCS photolysis was carried out in alcohols, acetonitrile, or aromatic solvents, no evidence for the reactions of excited S(${}^1\text{D}_2$) atoms could be obtained, but only the characteristic ground state S(${}^3\text{P}_1$) reactions were observed.^{35,36}

Another photolytic precursor for S(${}^1\text{D}_2$) is F $_3$ PS (eq 2), but this molecule had no particular advantages over OCS.^{19,37} Carbon disulfide (CS $_2$) is a selective precursor for ground state S(${}^3\text{P}_1$) atoms, but its photolysis proceeds only at wavelengths below 210 nm (eq 3).^{18,38,39} Another useful S(${}^3\text{P}_1$) precursor is ethylene episulfide (eq 4).⁴⁰⁻⁴² Sulfur dioxide produces S(${}^3\text{P}_1$) only in very low yield.⁴³ The photolysis of alkyl⁴⁴⁻⁴⁷ and aryl⁴⁸ isothiocyanates and isothiocyanic acid,⁴⁹ as well as the thiocy-

anato ion,⁵⁰ serves to generate selectively S(${}^3\text{P}_1$) atoms as well (eq 5). The precursors for S(${}^3\text{P}_1$) atoms have in common that intersystem crossing (ISC) in the singlet-excited precursor occurs before dissociation.



It is well-known that S(${}^1\text{D}_2$) atoms react with paraffins to undergo C-H insertion reactions and deactivation,^{13,26,32} while S(${}^3\text{P}_1$) atoms do not efficiently undergo this reaction with paraffins, alcohols, and acetonitrile (eq 6).^{35,36} Several relative^{33,34,42,51-53} and absolute⁵⁴⁻⁵⁶ rate constants for the vapor reactions of S(${}^1\text{D}_2$) have been reported over the years. The majority of the known absolute rate constants for sulfur atoms, however, refer to the gas phase reactions of ground state atoms S(${}^3\text{P}_1$) with alkenes^{17,18,57-59} and some halogenated olefins,¹⁵ alkynes,¹⁶ ethylene episulfide,^{15,18,60} carbon disulfide,⁵² and carbonyl sulfide.^{41,61} The absolute reaction rate constant between atomic sulfur and molecular oxygen in the gas phase has also received considerable attention^{43,62,63} due to its importance as an elementary process in the oxidation and combustion of sulfur compounds at elevated temperatures. The available absolute rate data for the gas phase are collected in Table 1, which contains in all cases the most recently published values for the gas phase along with some presently reported rate data in solution. Some relative rate data for Se(${}^3\text{P}_1$) have also been obtained from gas phase studies where OCSe and CSe $_2$ have been employed as precursors.⁶⁴⁻⁶⁸ The reactivity of tellurium atoms Te(${}^3\text{P}_1$) might also be of interest for

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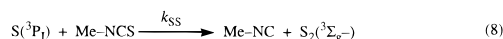
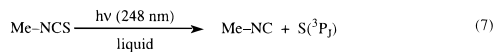
Table 1. Rate Constants for Reactions of Sulfur (3P_J) Atoms in the Gas Phase and in Solution

quencher	k_r ($10^8 \text{ M}^{-1} \text{ s}^{-1}$)		quencher	k_r ($10^8 \text{ M}^{-1} \text{ s}^{-1}$)	
	gas phase ^a	solution ^b		gas phase ^a	solution ^b
Me-NCS	120 ^c	4.2	R-CH=CH ₂	24 ^{g,h}	0.35 ⁱ
CS ₂	4.9 ^d	0.5	Me ₂ C=CMe ₂	240 ^j	3.3
COS	0.021 ^e	0.030	R-C≡CH	33 ^{h,k}	2.8 ⁱ
O ₂	10 ^f	<1.0			

^a The most recent value is given. ^b See Table 2 for details. ^c Reference 47. ^d Calculated from relative and absolute rate data in refs 52 and 61. ^e Reference 61. ^f Reference 62. ^g Reference 57. ^h R = ethyl. ⁱ R = *n*-hexyl. ^j Reference 59. ^k Reference 16.

comparative purposes; it has been studied with Me₂Te as a photolytic precursor.⁶⁹

As a continuation of the solution studies on atomic species,^{70,71} which have dealt with atoms in their ground states, our studies required a source of ground state sulfur atoms S(3P_J). The photolysis of methyl isothiocyanate (MeNCS) at 248 nm proved to be the most convenient source, and we have employed it to generate S(3P_J) atoms in solution (eq 7) and to measure the rate constants for their reactions with additives. As an important extension of the gas phase studies we have included some organic compounds with heteroatoms in our study, which might be of particular interest in organic chemistry. The rate data for atomic sulfur in solution can be compared with our recent data for oxygen (3P_J) atoms.¹⁰



The reaction of S(3P_J) atoms with the MeNCS precursor produces molecular diatomic sulfur S₂($^3\Sigma_g^-$) in its ground state (eq 8), which was used to monitor the kinetics of the sulfur (3P_J) atom reactions. The reaction sequence in eqs 7 and 8, which produces methyl isocyanide as the second stable product, is known to proceed with unit efficiency ($\pm 25\%$) on 308-nm photolysis in the gas phase at typical MeNCS pressures of 0.3 Torr.⁴⁷ Also in the solution photolysis at 254 nm, only products related to this reaction were observed, namely, methyl isocyanide, elemental sulfur (S₈); trapping products derived from methyl isocyanide or atomic sulfur could be isolated in high yields (eq 9).^{44,46}

Experimental Section

Acetone, acetonitrile, cyclohexane, methylene chloride, methanol, 2-propanol, tetrahydrofuran, and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) were Omnisolv grade (BDH) and used as received, except for Freon-113, which was passed once through alumina before the experiments. MeNCS, *tert*-butyl isothiocyanate, phenyl isothiocyanate,

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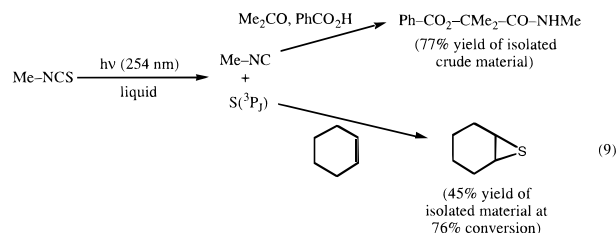
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carbon disulfide, Thiram (Aldrich), carbonyl sulfide, nitrous oxide, and high purity grade oxygen (Matheson Co.) were employed as received. Sublimation of MeNCS was carried out once, but since no change in extinction coefficient at 248 nm was noted, the commercial material was employed directly for the experiments. Most quenchers entered in Table 2 were also used as obtained in the highest available purity (Aldrich). 1-Octene and 1-octyne were distilled once prior to use. 2,3-Diazabicyclo[2.2.1]hept-2-ene (DBH) and 1,2-diethoxyethylene were synthesized according to well-known literature procedures; these compounds were identical with the samples used in other work.⁷²

The transient absorption traces and spectra were obtained with the nanosecond time-resolved laser flash photolysis setup available in our laboratory, which is similar to that described in detail elsewhere.⁷³⁻⁷⁵ The system was modified with a Tektronix 2440 digitizer and software developed in the LabVIEW 3.1.1 environment from National Instruments running on a PowerMacintosh computer. Lumonics EX-510 and EX-530 excimer lasers operated with Kr/F₂ and Xe/HCl gas mixtures provided 248-nm and 308-nm laser pulses of ca. 6-ns duration. The maximum energy doses per pulse, measured directly in front of the sample cuvette, were ca. 25 mJ at 248 nm and ca. 40 mJ at 308 nm; these were reduced in some control experiments. The time-resolved studies were done in Suprasil quartz cells with a 7-mm optical path. The cells allowed for a continuous flow of fresh sample through the photolysis region (ca. 0.2 mL per laser pulse), which was maintained by the gravity pressure of a reservoir containing ca. 50–200 mL of solution. The reservoir was deaerated by continuously bubbling oxygen-free nitrogen before and during the experiment; the nitrogen flow was reduced when the additives were volatile (e.g., ethyl vinyl ether). The flow system circumvents problems arising from transient absorptions due to photolysis products, which were found to become important with the presently studied systems. Optical absorption and steady state fluorescence spectra were obtained with HP-8451A diode array and Perkin-Elmer LS-50 luminescence spectrometers.

In the laser flash experiments, the concentrations of the substrates were typically adjusted to optical densities of ca. 0.4–0.8 at 248 nm. The extinction coefficient of MeNCS at 248 nm was found to be $650 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile (λ_{max} ca. 245 nm), which agrees well with the reported value of $630 \text{ M}^{-1} \text{ cm}^{-1}$ at the absorption maximum in dioxane (244 nm).⁷⁶ The concentrations of the quenchers were generally adjusted by adding subsequently appropriate amounts of the additives (or stock solutions) to the reservoir. In some cases (amines, hydrazines, cyclohexyl mercaptan, triethyl phosphite) fresh 50-mL solutions containing the additive were employed for each quencher concentration to minimize any depletion of the quencher through thermal chemical reaction with isothiocyanates. The effect of mercury was studied at only one concentration by using mercury-saturated cyclohexane, for which a concentration of 0.011–0.016 mM has been reported.⁷⁷ Gases as additives were bubbled directly through the reservoir. To examine the effect of oxygen as an additive, oxygen–nitrogen gas mixtures with different oxygen concentrations were prepared with a gas mixer (Air Products Co.). The concentration of carbonyl sulfide was monitored through its absorption at 248 nm, and a reduced flow of nitrogen was applied after bubbling with OCS. The extinction coefficient of OCS at this wavelength was taken as $5 \text{ M}^{-1} \text{ cm}^{-1}$; this value agrees with that recommended for the gas phase,³⁰ and it can be estimated from the absorption spectrum by comparison

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Table 2. Absolute Rate Constants for Reactions of Sulfur (3P_J) Atoms in Solution^a

quencher	k_r ($10^8 \text{ M}^{-1} \text{ s}^{-1}$)	quencher	k_r ($10^8 \text{ M}^{-1} \text{ s}^{-1}$)
alkenes/alkynes		nucleophiles	
acrylonitrile	<0.001	water	<0.00005
tetrachloroethylene	<0.001	acetonitrile ^g	<0.00002 ^c
1-octene	0.35 ^b	methanol	<0.0001
ethyl vinyl ether	0.97	diethylsulfite	0.0028
1-octyne	2.8	dimethylsulfoxide	<0.012
tetramethylethylene ^b	3.3	DBH ^h	1.3
diethoxyethylene	20	<i>n</i> -butyl isocyanide	4.0
hydrogen donors		cyclohexylmercaptan	10 ^b
Bu ₃ Sn-H [-D]	31 [34]	chloride ion ⁱ	13
cyclohexane	<0.00003 ^c	propyl sulfide	16
2-propanol	0.0046	mercury ^j	<20
tetrahydrofuran [-d ₈]	0.0055 [0.005] ^b	bromide ion ⁱ	31
methylene chloride	<0.00002 ^c	triethylamine	78
atom donors		DABCO ^k	110
Me-NCS	4.2 ^d	hydrazine ^l	120
COS ^b	0.030 ^e	1,1-dimethylhydrazine	170
carbonylsulfide	0.50	triethyl phosphite	210
O ₂	<1.0 ^f		

^a Data are $\pm 20\%$ in acetonitrile as solvent unless stated differently. ^b $\pm 30\%$. Value for 1-octene in Freon-113 as solvent. ^c Neat solvent. ^d Based on $\epsilon(248 \text{ nm}) = 650 \text{ M}^{-1} \text{ cm}^{-1}$. ^e Based on $\epsilon(248 \text{ nm}) = 5 \text{ M}^{-1} \text{ cm}^{-1}$. ^f See text. ^g Behaves as nucleophile toward oxygen (3P_J) atoms (ref 10). ^h 2,3-Diazabicyclo[2.2.1]hept-2-ene. ⁱ As tetraalkylammonium salt. ^j In cyclohexane. ^k 1,4-Diazabicyclo[2.2.2]octane. ^l As hydrate.

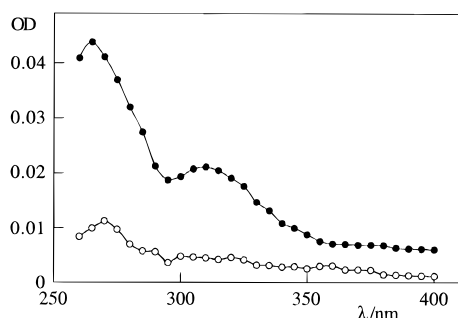


Figure 1. Transient absorption spectrum produced upon 248-nm laser flash photolysis of a solution of methyl isothiocyanate (1.5 mM) in deaerated acetonitrile recorded 4–6 μs after the laser flash. The angle of the incident laser beam relative to the monitoring beam was chosen as ca. 10° (●) or 90° (○). The front-face (10°) irradiation mode provides for higher transient concentrations in the monitored region of the cuvette and, hence, more intense absorptions.

with the reported extinction coefficient at 254 nm in organic solvents ($5 \text{ M}^{-1} \text{ cm}^{-1}$).³⁵ Saturation with nitrous oxide was achieved without flow of nitrogen. All measurements were done at room temperature.

Results

The 248-nm photolysis of MeNCS (ca. 0.2–3 mM) in various solvents (Freon-113, acetonitrile, cyclohexane, methylene chloride) produces a transient absorption with a maximum at ca. 270 nm (Figure 1), but no concomitant decay in the accessible 250–700-nm region. The transient traces display a step followed by a time-resolved monoexponential growth with a lifetime of several microseconds (Figure 2).

The signal intensity was highest in Freon-113 and lowest in cyclohexane; however, the step feature in the transient trace, which is attributable to the “immediate” formation of photo-products, was virtually absent in the latter solvent. The observation of a growth without a corresponding decay indicates the involvement of an “invisible” transient with absorption below 250 nm. This species enters into a chemical reaction to produce a visible transient, whose growth is monitored. We have previously exemplified that electronegative atoms of groups VIa and VIIa of the periodic table behave as invisible, yet highly reactive species,^{2,3,6,10} and since MeNCS was chosen as a precursor for sulfur (3P_J) atoms,^{44,46,47} the observed growth is attributed to a reaction of atomic sulfur (3P_J) with its precursor to produce molecular disulfur, $S_2(^3\Sigma_g^-)$, reaction 8. These

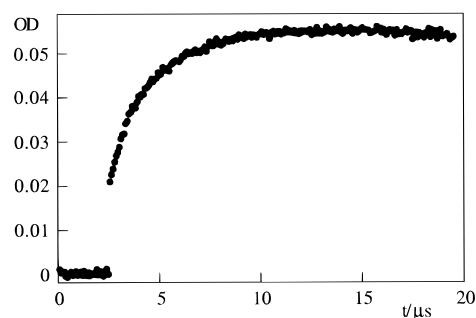


Figure 2. Initial step and first-order growth in transient absorption at 270 nm produced upon 248-nm laser flash photolysis of a solution of methyl isothiocyanate (1.5 mM) in deaerated acetonitrile.

assignments, the atomic nature and multiplicity of the invisible transient, and the production of $S_2(^3\Sigma_g^-)$ form the basis of the reported rate data and warrant a detailed discussion (see below).

Efforts were expended to optimize the conditions for generating $S(^3P_J)$ atoms. For example, the 248-nm photolysis of *tert*-butyl isothiocyanate in Freon-113 or acetonitrile yielded the same transient absorption pattern and growth traces, but the signal intensity was less than half that with MeNCS, indicating a less efficient elimination of $S(^3P_J)$. Finally, the use of phenyl isothiocyanate in acetonitrile, which was also expected to produce sulfur (3P_J) atoms,⁴⁸ did not produce any growth, but only bleaching of the substrate was observed. Attempts to sensitize the photolysis of MeNCS by adding acetone as triplet sensitizer and selectively exciting at 308 nm were unsuccessful. The transients produced on 248-nm photolysis of the sulfur atom precursor carbonyl sulfide in Freon-113 or acetonitrile resembled the photolysis of MeNCS, namely, the maximum of the absorption spectrum (ca. 280 nm) was in the same region, and a growth with a lifetime of several microseconds could be monitored at 260 and 310 nm. However, the step feature of the growth trace was much stronger than the time-resolved growth in the case of carbonyl sulfide, and a decay with a shorter lifetime than the growth was observed at ca. 290 and 390 nm. The more complex transient behavior displayed by carbonyl sulfide is supposedly due to the intervention of both excited singlet (1D_2) and triplet ground state (3P_J) sulfur atoms and their competing followup reactions.^{26–28,33,35,36,42,78}

Variations of the transient concentration produced on irradiation of MeNCS in acetonitrile (ca. 1.5 mM), either by changing the laser power instrumentally from 5 to 25 mJ/pulse, or by

variation of the angle of the incident laser beam from ca. 10° to 90° (the former provides for higher transient concentrations in the monitored region of the cuvette),⁷³ did not significantly ($\pm 15\%$) affect the growth kinetics. Conversely, the kinetics increased linearly with isothiocyanate concentration; many additives like olefins, amines, and sulfur compounds (*cf.* Table 2) shortened the growth lifetime.

Assignment of Transients. The assignment of the transient observed on photolysis of MeNCS in solution at room temperature as $S_2(^3\Sigma_g^-)$ is based on the location of its absorption maximum at 270 ± 5 nm, which coincides with that observed in the gas phase at high temperature⁷⁹ and also in low-temperature noble gas matrices.^{79–81} The extinction coefficient of $S_2(^3\Sigma_g^-)$, determined at the most intense gas phase band at 271.3 nm, is ca. 1×10^4 M⁻¹ cm⁻¹,⁴⁰ which should make possible its ready observation in solution, even if allowance for pressure broadening is made. The very long decay of this transient (millisecond time scale) and the insensitivity of its decay lifetime toward addition of many quenchers like oxygen, olefins, and dienes^{19,24,39,40,51} are also consistent with those of $S_2(^3\Sigma_g^-)$. More importantly, sulfur (3P_1) atoms in the gas phase are known to react with MeNCS to form $S_2(^3\Sigma_g^-)$ with unit efficiency (eq 2),⁴⁷ such that its observation is expected in solution as well. The assignment to $S_2(^3\Sigma_g^-)$ is also supported by two additional experimental observations. Firstly, the solution photolysis of carbonyl sulfide, another well-established source of S_2 in the gas phase,^{19,40} produces a transient absorption spectrum very similar to that produced from MeNCS. Secondly, the 248-nm photolysis of *tert*-butyl isoselenocyanate^{82,83} in acetonitrile or Freon-113 produces a transient growth with somewhat longer lifetime, and the absorption maximum lies at 310 nm; this transient is assigned to $Se_2(^3\Sigma_g^-)$. The observed bathochromic shift between $S_2(^3\Sigma_g^-)$ and $Se_2(^3\Sigma_g^-)$ is expected from the known absorption spectra^{84,85} and, thus, corroborates the proposed chemical reaction sequence for photolysis of isothio- and isoselenocyanates. Further studies on the isoselenocyanate as a source for Se(3P_1) atoms were discouraged by a very rapidly developing precipitation on the cell walls, supposedly elemental selenium, which led to severe shock waves in the transient traces, thus obstructing an accurate quantitative analysis. Nevertheless, the photochemical behavior of isothiocyanates and isoselenocyanates appears to be very similar.

The involvement of atomic sulfur (3P_1) in the solution phase photolysis of MeNCS is expected from preparative photoreactions at 254 nm, since both major reaction products of the photodissociation, methyl isocyanide and sulfur (3P_1) atoms, could be intercepted *in situ* with appropriate additives in ca. 70% and 50% isolated yield of trapping product.^{44,46,86} It is also significant that even prolonged irradiation of MeNCS

solutions at 254 nm does not produce complex product mixtures, but only methyl isocyanide and elemental sulfur, which indicates a relatively clean photochemistry.⁴⁴ In the gas phase, 308-nm photoinduced extrusion of sulfur (3P_1) atoms proceeds with unit quantum yield,⁴⁷ while at shorter wavelengths the C–N bond cleavage to afford the NCS radical and excited state isomerization to afford methyl thiocyanate were also detected^{87–89} (see below). Again, the photolysis of carbonyl sulfide in both the gas phase and solution^{21–28} is an alternative and efficient source of sulfur atoms, and since the transient spectra are comparable for the two different precursors, the production of sulfur atoms and the subsequent formation of S_2 seem to be a common denominator for both systems.

The triplet multiplicity (3P_1) of the sulfur atoms produced on MeNCS photolysis is also firmly established in both solution^{44,46} and the gas phase,⁴⁷ where the photolysis of methyl isothiocyanate in the presence of olefins yields only the characteristic triplet products (episulfides) and not the side products expected for singlet-excited S(1D_2) atoms (allyl mercaptans).^{13,26–28,32} Our experiments cannot rigorously exclude the production of S(1D_2) as a competing pathway or their intermediacy, but clearly the relatively slow (microsecond time scale) growth of the reaction product $S_2(^3\Sigma_g^-)$ is not in line with singlet-excited atoms, which are expected to be far more reactive toward both the precursor molecules and the solvent.^{33,34,42,51–55} In particular, the C–H bonds of alkanes are very reactive toward singlet-excited sulfur atoms,^{26,27,33,56} but the kinetics of the growth at 270 nm in cyclohexane are quite similar to Freon-113. It follows, that we are dealing with sulfur atoms in their triplet ground state (3P_1). The interaction between the ground state sulfur (3P_1) atoms and the additives must involve chemical reaction (see below). This is important to recognize, since the interaction of additives with electronically excited S(1D_2) atoms comprises physical deactivation (ISC to the triplet ground state) in addition to chemical reactions.^{23,24,27,32,34,40,42}

Control experiments employing 2,3-diazabicyclohept-2-ene as additive demonstrated that the invisible state is not an electronically excited singlet or triplet state with an energy above 80 or 63 kcal mol⁻¹, i.e., the corresponding excited state energies of the azoalkane additive;⁹⁰ the quenching effect on the growth lifetime (ca. 10^8 M⁻¹ s⁻¹) fell short of that expected ($> 10^9$ M⁻¹ s⁻¹) for an exothermic energy transfer process.^{91,92} An acetonitrile solution containing MeNCS was also saturated with nitrous oxide, but the transient characteristics remained unchanged, which renders photoionization or the observation of a photochemically reduced transient as carriers, contributors, or precursors of the signal unlikely.⁹³

It is difficult to imagine any other system but S(3P_1) atoms and $S_2(^3\Sigma_g^-)$ as precursor and carrier of the observed transient growth, especially since the preparative photochemistry in solution appears to be quite clean (eq 9).^{44,46} Methyl isocyanide, the other fragment of the photodissociation, is a quite stable molecule, which does not absorb in the spectral region examined.⁴⁷ One could argue that the transient may not be $S_2(^3\Sigma_g^-)$, but rather an intermediate resulting from addition of a sulfur (3P_1) atom to the methyl isocyanide, e.g., Me–N=CSS, which would have to convert relatively slowly to $S_2(^3\Sigma_g^-)$, and

(78) The photolysis of carbon disulfide at 308 nm has also been studied in solution but provided no evidence for the formation of sulfur (3P_1) atoms, as was expected from gas phase data.^{18,38,39} Also the 308-nm photolysis of Thiram, an organosulfur pesticide and postulated precursor for sulfur atoms (*cf.* Crank, G.; Mursyidi, A. J. *Photochem. Photobiol. A: Chem.* **1992**, *68*, 289, did not provide evidence for the involvement of atomic sulfur.

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(86) Some secondary chemistry occurred when cyclohexene was added, since the resulting episulfide undergoes a slow thermal reaction with the precursor⁴⁶ as well as secondary photolysis at the irradiation wavelength of 254 nm,^{40–42} these side reactions suggest that the actual efficiency for sulfur (3P_1) atom extrusion might be higher than implied by the yield of isolated trapping product.

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of course, would have to absorb in the same region. Although the formation of a related species ($S=CSS$) has been proposed in the approximately thermoneutral ($\Delta H_f^\circ = +0.5 \text{ kcal mol}^{-1}$)⁹⁴ reaction with carbon disulfide,^{18,52} the intermediacy of such a long-lived adduct in the case of MeNCS is quite unlikely in view of the high exothermicity of the sulfur abstraction ($\Delta H_f^\circ = -25.5 \text{ kcal mol}^{-1}$).⁹⁴ Moreover, a previous suggestion⁶³ of an intermediate for the related reaction sequence for production of $S_2(^3\Sigma_g^-)$ from sulfur (3P_J) atoms and carbonyl sulfide for OCS ($\Delta H_f^\circ = -27.9 \text{ kcal mol}^{-1}$)^{94,95} has not been substantiated, but a concerted process has been favored.^{30,41,61} Even if the transient absorption corresponded to another primary adduct of sulfur atoms, the observed growth of the transient would still reflect the kinetics of atomic sulfur (3P_J), and thus, our quantitative analysis and conclusions with respect to their reactivity toward the examined additives would not change. Conversely, one might suggest that the observed formation of $S_2(^3\Sigma_g^-)$ does not directly derive from the bimolecular reaction with atomic sulfur (3P_J), but from a unimolecular rearrangement of this primarily formed adduct, Me-NCSS or Me-NS-CS, which would then have to be formed immediately ($<50 \text{ ns}$) on the experimental time scale. Clearly, such a mechanism is not in accord with the observed dependence on MeNCS concentration, which is indicative of a bimolecular reaction.

It has been proposed that the $S(^3P_J)$ atoms generated in the gas phase flash photolysis of OCS (17–100 Torr)^{19,40} or in the conventional photolysis of OCS in solution (0.8 M)³⁵ form $S_2(^3\Sigma_g^-)$ predominantly by bimolecular recombination rather than by reaction with OCS. This interpretation was questioned, and it was concluded that the reaction of $S(^3P_J)$ atoms with OCS ($>17 \text{ Torr}$) is sufficiently fast to compete with sulfur (3P_J) atom recombination, even in flash photolysis experiments.^{24,41,43,58,61,63} Similarly, our rate data (Table 2) and the observed clean first-order kinetics (Figure 2)^{43,63} suggest that atom recombination is not important even at the relatively high local concentration of sulfur (3P_J) atoms in our flash photolysis experiments using MeNCS. Furthermore, control experiments, in which the transient concentrations were intentionally varied through the energy dose (5–25 mJ/pulse) or the irradiation angle,⁷³ did not indicate any significant effect ($<10\%$) on the growth kinetics.⁴³ Assuming a maximum recombination rate constant of ca. $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, (cf. Table 2), adding a spin-statistical factor of 4/9 to account for the probability of an irreversible triplet-triplet reaction,⁹⁶ and multiplying with a typical transient concentration of ca. $1 \times 10^{-5} \text{ M}$,⁹⁷ provides an estimated (initial) recombination rate constant of ca. $1 \times 10^5 \text{ s}^{-1}$, which is slower than the reaction with the MeNCS precursor at the employed 1.5 mM concentration ($6 \times 10^5 \text{ s}^{-1}$). For similar reasons, the back-reaction between methyl isocyanide and sulfur (3P_J) atoms (reaction 5) cannot contribute significantly to the observed first-order growth, since the reaction with isocyanides is not diffusion-controlled (Table 2). It is also significant that any removal of sulfur (3P_J) atoms, e.g., by additives, will reduce the relative importance of the recombination reaction; the rate constants for the reactions of sulfur (3P_J) atoms are obtained under such favorable conditions (see below).

More intriguing is the possible involvement of NCS radicals derived from C–N bond cleavage, which are detected upon vacuum-UV,⁸⁷ and also in the 248-nm photolysis of MeNCS

in the gas phase.^{88,89,98} Unfortunately, no quantum yields for this process are available. This contrasts the unit quantum yield for C=S bond cleavage to generate sulfur (3P_J) atoms upon 308-nm photolysis of MeNCS.⁴⁷ Apparently, C=S bond cleavage represents the primary decomposition pathway at lower excess energies, while higher energies make C–N bond cleavage possible.⁹⁹ We suspect that C–N bond cleavage is feasible from higher vibrational levels ($v > 0$) of the singlet-excited state, while ISC to the triplet state, which undergoes $S(^3P_J)$ extrusion, is the major fate of the $v = 0$ state. One would intuitively expect that the latter pathway prevails in solution, where rapid transfer of excess vibrational energy to the solvent molecules is favorable. This notion is experimentally manifested in the product studies in solution, which were done at 254 nm and revealed only products related to C=S bond cleavage.^{44,46} It is also important that the photolysis of OCS in solution, although more complex in its transient kinetics, gives rise to a very similar transient absorption spectrum ($\lambda_{\text{max}} = 280 \text{ nm}$), which cannot be related to NCS radicals. It should be noted that allyl isothiocyanate, for which C–N bond cleavage should be more favored than in alkyl isothiocyanates, is a comparably efficient source for sulfur (3P_J) atoms in solution.⁴⁶ In conclusion, the observed growth cannot be related to the reaction of NCS radicals.¹⁰⁰ The strongest support for $S(^3P_J)$ atoms and the proposed mechanistic scheme comes from the rate constants measured from the effect of additives on the growth lifetime (Table 2). The comparison of the rate data with those available for the gas phase (Table 1), and with those available for the solution reactions of other atoms (cf. Discussion) are consistent with the interception of sulfur (3P_J) atoms.

Measurement of Reaction Rate Constants. The effects of additives on the transient kinetics were quantitatively examined in acetonitrile as solvent. Although the transient traces were strongest in Freon-113 as solvent, acetonitrile was preferable for practical reasons and provided for a better comparison with the rate constants measured for $O(^3P_J)$ atoms in solution. The experimental conditions for monitoring the time-resolved growth were optimized by using front-face irradiation, which resulted in signals with better intensity (by a factor of 4–5, cf. Figure 2), and by monitoring at 260 nm, where the initial step was less pronounced. The less intense transient spectral band at 310 nm (Figure 1), which was observed in acetonitrile, followed the same kinetics ($\pm 10\%$), including its response to additives (see below), and, thus, is related to the same precursor or carrier. The concentrations of MeNCS were generally chosen as ca. 1.5 mM, which resulted in a reasonable balance between good signal intensity and sufficiently long lifetime for the growth (ca. 1.5–2 μs); the latter were required to enable the accurate measurement of the kinetics over a relatively wide range of additive concentrations.

The kinetics of $S_2(^3\Sigma_g^-)$ formation reflects the decay kinetics of $S(^3P_J)$ atoms; under the experimental conditions and in the relevant time regime (see above), the growth of $S_2(^3\Sigma_g^-)$ derived from the pseudo-first-order reaction of $S(^3P_J)$ atoms with excess MeNCS (eq 8) such that the monoexponential growth lifetime (Figure 2) reflects the lifetime of $S(^3P_J)$. Hence, the rate constants for the reactions of $S(^3P_J)$ atoms with various additives (eq 10) can be determined by monitoring the growth lifetime of $S_2(^3\Sigma_g^-)$ as a function of additive concentration. According

(94) The thermodynamic data cited in this work were calculated from the standard heats of formation contained in ref 95, i.e., H_f° (kcal mol⁻¹) for OCS (-34.0), CO (-26.4), S₂ (30.7), S (66.2), MeNCS (31.0), MeNC (41.0), CS₂ (28.0), CS (64.0), ethylene episulfide (19.6), and ethylene (12.5).

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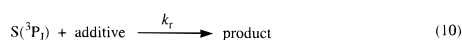
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(99) From an energetic point of view, C=S and C–N bond cleavage require very similar amounts of energy, namely, 76.2 and 77.7 kcal mol⁻¹ (refs 87 and 94).

(100) Only very few rate data for the NCS radical in solution are known, and the examined reactants differ from those presently examined, e.g., 1 and $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for triethanolamine and thiocyanato anion in water.¹ Hence, no comparison of the rate data can be made to further exclude the intervention of NCS radicals.

to eq 11, the experimental rate constant for $S_2(^3\Sigma_g^-)$ formation



$$k_{\text{exp}} = k_0 + k_{SS} [\text{MeNCS}] + k_r [\text{additive}] \quad (11)$$

(k_{exp} , cf. Figure 2) is dependent (i) on the decay rate constant of $S(^3P_J)$ atoms in the absence of MeNCS and additive (k_0), (ii) on the rate constant for reaction with the precursor (k_{SS} , eq 8) and its concentration, and (iii) on the rate constant for reaction with the additive (k_r , eq 10) and its concentration. Hence, when the MeNCS concentration is kept constant, the rate constant for formation of $S_2(^3\Sigma_g^-)$ varies linearly with concentration of the additive and allows the determination of the reaction rate constant k_r (eq 10). The rate constants in Table 2 were obtained by linear regression analysis according to eq 11; in general, 4–7 different concentrations of additive were selected in order to allow a variation of the experimental growth lifetimes by a factor of at least 4 (up to ca. 0.4 μs).

In most cases, the signal intensity, which was measured through the absorbance of the plateau region of the growth trace (Figure 2), decreased with increasing quencher concentration. Quantitative analysis of the effect on the signal intensities (Stern–Volmer quenching) resulted in quenching rate constants, which were generally within $\pm 25\%$ of the values obtained from the growth kinetics. Such behavior is expected for the interception of a single precursor [$S(^3P_J)$ atoms] for the monitored transient growth and the formation of transparent products. However, there were a few exceptions, where the signal intensity decreased more or less rapidly than expected from the quenching effects on the transient kinetics. For example, in the case of the amines and hydrazines, increased quencher concentrations resulted in faster growth kinetics, but the signal intensity remained similar or increased slightly. Such an observation is indicative of the formation of absorbing products from the reaction between $S(^3P_J)$ atoms and the quenchers (competitive transient absorption).

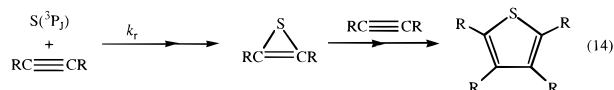
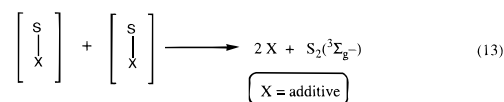
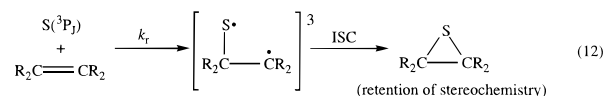
In contrast, the addition of 1-octene and molecular oxygen decreased the signal intensity, but only a small or no effect on the growth kinetics was observed. The faster interception of the sulfur (3P_J) atom precursor, e.g., the triplet-excited MeNCS, or the formation of byproducts, e.g., SO or $O(^3P_J)$, produced from the reaction of $S(^3P_J)$ with O_2 , might complicate the kinetic analysis in these special cases. Possible problems in the time-resolved kinetic analysis of the $S(^3P_J)$ – O_2 system (gas phase) have been addressed previously.⁴³ Addition of water or methanol also leads to a substantial decrease of the signal intensity with no concomitant shortening of the growth lifetime. Only 10% of these additives could be added, which provides only an upper limit for the reaction rate constants of these protic additives; beyond this concentration signals were too weak to allow reliable analysis. The situation was similar for 2-propanol and tetrahydrofuran, but an effect on the growth lifetime was observed in these cases due to the lower concentrations required. Due to its low solubility (ca. 0.015 mM),⁷⁷ no significant effect of dissolved mercury was observed in cyclohexane as solvent, leading again only to an upper limit for the rate constant (Table 2).

One disadvantage of MeNCS compared to carbonyl sulfide as precursor for sulfur atoms is its thermal reactivity, which leads to the formation of stable products in the case of protic nucleophiles.¹⁰¹ Thus, care had to be taken to avoid the depletion of MeNCS or of the additive. The reactions with alcohols or water occur only at elevated temperatures with

reasonable rates,¹⁰¹ and we observed no significant change in the UV spectrum of MeNCS within the time scale of the experiments (up to 1 h). In the case of the nitrogen-, sulfur-, and phosphorus-containing additives, the measurements were performed immediately after addition to minimize the exposure time to typically 5–10 min, and for each concentration a fresh solution was prepared. These precautions were considered sufficient when compared with the reported second-order rate constants for the reactions with amines (e.g., 3.2 $\text{M}^{-1} \text{min}^{-1}$, for *n*-butylamine),¹⁰¹ which suggest reaction times of several hours under the selected experimental conditions (1.5 mM MeNCS solutions and 10^{-5} – 10^{-4} M concentrations of additives).

Discussion

The presently reported rate constants for the bimolecular reactions of $S(^3P_J)$ atoms (Table 2) characterize $S(^3P_J)$ atoms as highly reactive, yet very selective, electrophiles. The highest reactivity is observed with amines, hydrazines, and phosphites, and the corresponding rate constants are characteristic for diffusion-controlled reactions (ca. $10^{10} \text{M}^{-1} \text{s}^{-1}$). For olefins and alkynes, gas phase studies have established the highly diastereoselective formation of episulfides (eq 12).^{15–18,57–59,102} This reaction is 59 kcal mol^{-1} exothermic for ethylene.⁹⁴ The reactivity of $S(^3P_J)$ atoms toward olefins is highest for electron-rich derivatives, such as vinyl ethers, and lowest for electron-deficient ones, such as tetrachloroethylene and acrylonitrile, where no effect on the decay kinetics of $S(^3P_J)$ atoms was observed within the experimentally accessible concentration range. This reactivity order establishes a high electrophilicity toward olefins. The latter has already been deduced from gas phase studies for alkylated and halogenated derivatives.^{15,33} Moreover, the reactions of $O(^3P_J)$ atoms with olefins¹⁰ follow the same trend with electron-donating properties of the olefins, but the absolute rate constants are at least 2–3 orders of magnitude higher, as is expected from the differences in electrophilicity and bond energies. No accurate correlation between the ionization potentials of the olefins¹⁰³ and the reaction rate constants from Table 2 was observed, supposedly due to the large structural variations and the complex effects of olefin substituents on the preexponential Arrhenius factors and activation energies; the latter have been discussed previously in gas phase studies.^{15,17} In summary, the observed reactivity pattern towards olefins is consistent with the involvement of sulfur (3P_J) atoms.



One followup reaction of the primary adducts (X) with sulfur atoms, which always needs to be considered, is their bimolecular recombination to form $S_2(^3\Sigma_g^-)$ and regenerate the additive (eq 13); i.e., the additive serves as a mediator for sulfur (3P_J) atom

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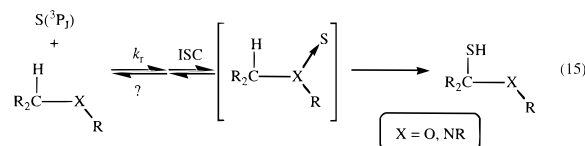
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recombination. In the case of the episulfide adducts (eq 12) this reaction is probably not important, except for the very electron-deficient olefins³³ or the related episelenides.^{50,64–68} The adducts of alkynes and sulfur (3P_J) atoms (thiirenes), on the other hand, are expected to be unstable toward further addition to another molecule of alkyne, a reaction which may lead to thiophene derivatives (eq 14).^{16,20} It should be noted that S(3P_J) atoms rapidly (e.g., $2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for ethylene episulfide, gas phase)^{15,18,60} abstract sulfur from episulfides to yield $S_2(^3\Sigma_g^-)$ and regenerate the olefin (for other examples of sulfur abstraction reactions see below); this reaction has been shown to complicate the time-resolved kinetic analysis of the gas phase addition reaction (eq 12), resulting in apparently too high reaction rate constants,⁵⁸ since the product (episulfide) is a more efficient scavenger of sulfur (3P_J) atoms than the olefin. In our solution study, where problems related to the buildup of reaction products should be minor due to the use of a flow system, no evidence for interference by this reaction was obtained; i.e., no deviation from clean first-order kinetics was observed in the presence of olefins.

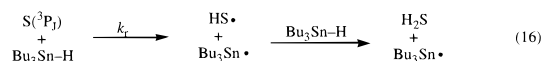
A pronounced difference between sulfur and oxygen (3P_J) atoms is their reduced reactivity toward abstractable hydrogen atoms. For example, while oxygen (3P_J) atoms,¹⁰ and also fluorine² and chlorine⁵ atoms, rapidly abstract hydrogen from solvents like methylene chloride, chloroform, and cyclohexane, no reactivity is observed for sulfur (3P_J) atoms (eq 6, Table 2); i.e., only an upper limit for the reaction rate constants can be given. Bromine atoms, for comparison, do not show significant chemical reactions with cyclohexane either.⁶ These data can be reconciled in terms of the diatomic binding energies (kcal mol⁻¹) between the atomic species and hydrogen,¹⁰³ namely, O–H = 102, S–H = 82, F–H = 136, Cl–H = 103, and Br–H = 87. These values render the hydrogen abstraction from cyclohexane, which possesses C–H bonds of 95.5 kcal mol⁻¹ bond energy,¹⁰³ exothermic for oxygen, fluorine, and chlorine, but endothermic for sulfur and bromine. Thus, since hydrogen abstraction from C–H bonds remains exothermic on going from fluorine to chlorine atoms, but changes from exothermic to endothermic on going from oxygen to sulfur (3P_J) atoms, it can be explained that the reactivity difference (for non-diffusion-controlled reactions) between the two upper group VIIa halogen atoms is only 2 orders of magnitude,² while for the two upper group VIa elements, it is at least 3 or 4 orders of magnitude as judged from the comparison for cyclohexane and methylene chloride; oxygen (3P_J) atoms abstract hydrogen from these reactants with rate constants of $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁰

It should also be noted that the reactivity of bromine atoms toward C–H bonds increases dramatically on going from alkanes to alcohols,⁶ although the C–H bond energies of alcohols (e.g., 94 kcal mol⁻¹ for methanol)¹⁰³ are quite similar to those of cyclohexane.¹⁰³ Polar effects have been held responsible for this contrast;⁶ product (HBr) stabilization through hydrogen bonding may also be important. For sulfur (3P_J) atoms (Table 2), an upper limit of $10^4 \text{ M}^{-1} \text{ s}^{-1}$ applies for the sulfur (3P_J) atom reaction with methanol, while for bromine atoms this value is $10^6 \text{ M}^{-1} \text{ s}^{-1}$.⁶ The reduced reactivity of sulfur (3P_J) atoms can again be understood in thermodynamic terms; i.e., the S–H bond strength lies ca. 5 kcal mol⁻¹ below the strength of the H–Br bond (see above). However, when 2-propanol and tetrahydrofuran are employed as additives (Table 2), which possess weaker C–H bonds (91–92 kcal mol⁻¹)¹⁰³ than methanol and cyclohexane, the lifetime of sulfur (3P_J) atoms is shortened, and the rate constants for chemical reaction are now ca. $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Table 2). This result resembles that, for bromine atoms, where an increase in reactivity by 1–2 orders

of magnitude has been established for 2-propanol relative to methanol.⁶ In view of the pronounced reactivity of sulfur (3P_J) atoms toward lone-electron pairs (see below), one needs to consider an alternative stepwise C–H insertion reaction mechanism with alcohols and ethers, in which the rate-determining step is addition to the oxygen lone pairs (eq 15); this speculative mechanism could account for the insignificant isotope effects. Clearly, the observed low reactivity toward hydrogen donors supports the involvement of sulfur (3P_J) atoms.



As expected from the above thermodynamic arguments, hydrogen abstraction becomes efficient whenever the bond strength of the donor X–H bond lies below that of the S–H bond. Thus, sulfur (3P_J) atoms react rapidly with the potent hydrogen donor tributyltin hydride (Table 2), since the Sn–H bond strength is ca. 8 kcal mol⁻¹ below that of S–H.¹⁰³ Owing to the significantly higher H–S bond strength in H₂S compared to HS (91 versus 82 kcal mol⁻¹),¹⁰³ the resulting HS radical should be more reactive toward hydrogen abstraction than the sulfur (3P_J) atom³⁶ (cf. also the reactivities of an oxygen (3P_J) atom and hydroxyl radical)¹⁰ and will rapidly abstract another hydrogen from the stannane (eq 16). The reaction with the

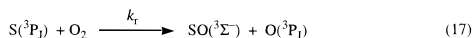


stannane constitutes the only exothermic hydrogen abstraction reaction which has been examined. The absence of a deuterium isotope effect in the latter case (Table 2) is probably due to the high absolute value of the rate constant (close to diffusion control). Isotope effects in this reactivity domain fall far below the expected values (e.g., ca. 3.6 for Sn–H bonds).¹⁰⁴ For example, singlet-excited acetone reacts with tributyltin hydride with a rate constant of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and the observed deuterium isotope effect is only 1.28.¹⁰⁴ Thus, if allowance is made for a somewhat smaller isotope effect due to the higher rate constant in the case of the sulfur (3P_J) atoms ($3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the isotope effect might well lie below the accuracy presently accessible.

Another characteristic of sulfur (3P_J) atoms is their ability to abstract divalent atoms such as sulfur or oxygen from appropriate substrates (OCS, MeNCS, CS₂, molecular oxygen) in a reaction mechanism, which has been investigated in detail for the gas phase with respect to its Arrhenius parameters.^{30,41,43,61–63} The reaction can proceed in a concerted, spin-allowed manner to produce $S_2(^3\Sigma_g^-)$ and $SO(^3\Sigma^-)$ as ground state products (cf. eq 8). The order of rate constants for the reaction of sulfur (3P_J) atoms with MeNCS, CS₂, and OCS in solution (MeNCS \gg CS₂ > OCS, Table 2) does not follow the order of exothermicity for sulfur abstraction (–25.5, +0.5, –27.9 kcal mol⁻¹) and, thus, cannot be entirely explained on a thermodynamic basis. It appears more likely that the nucleophilicity of the additives determines the reaction rate (see below), namely, the electron-donating properties of the sulfur lone pairs. Thus, the exchange of the imino fragment in MeNCS by oxygen in OCS is expected to reduce the nucleophilicity of the double-bonded sulfur, and results in a significantly lower rate constant for the abstraction reaction. Following this argument, one would expect that CS₂ is the most reactive molecule, which is not the

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case. Probably, since the reaction is no longer strongly exothermic for carbon disulfide (see above), the higher nucleophilicity is offset by the less favorable thermodynamics. It should also be noted (*cf.* Results) that the reaction between sulfur (3P_1) atoms and CS_2 might not be concerted but might lead to an intermediate ($S=CSS$);^{18,52} the latter is not thought to decay by unimolecular decomposition to CS and $S_2(^3\Sigma_g^-)$, but by bimolecular reactions. The reaction between sulfur (3P_1) atoms and molecular oxygen in the gas phase produces sulfur monoxide $SO(^3\Sigma^-)$ and oxygen (3P_1) atoms in a ca. 6 kcal mol⁻¹ exothermic reaction (eq 17).^{43,62,63} Due to problems in the



course of the kinetic analysis with molecular oxygen as additive in solution (*cf.* Results), only an upper limit for the corresponding rate constant could be given (Table 2); the problems may be partly due to the production and followup reactions of the more reactive¹⁰ oxygen (3P_1) atom in this reaction. Obviously, the rate constant for reaction of sulfur (3P_1) atoms with molecular oxygen falls far below the rate constant determined for fluorine and oxygen (3P_1) atoms,^{2,10} as would be expected for the relatively small exothermicity. No evidence for the formation of SO_2 or SOO was obtained.

The most interesting facet of sulfur 3P_1 atom reactivity is observed with many common organic nucleophiles as additives, and much efforts was expended in this direction (Table 2). Clearly, the reactivity pattern toward nucleophiles confirms once more the electrophilicity and selectivity of sulfur (3P_1) atoms. Qualitatively, it is interesting to observe that soft sulfur nucleophiles such as mercaptans or dialkyl sulfides are efficient scavengers of sulfur (3P_1) atoms, but when the nucleophilic sulfur center is rendered less electron rich and harder through oxidation as in diethyl sulfoxide or in dimethyl sulfoxide, the reactivity is much suppressed (Table 2). However, such relatively hard nitrogen nucleophiles such as amines are also very reactive,¹⁰⁵ but deactivation of the nucleophilic site like in the azo group ($-N=N-$), *cf.* the rate constant for 2,3-diazabicyclohept-2-ene (DBH) in Table 2, reduces the reactivity considerably. The higher rate constant measured for bromide relative to chloride is also expected from nucleophilicity arguments (solvation, softness).^{106,107}

From a more quantitative point of view, it should be noted that the reactivity order for different nucleophiles resembles the order observed for other electrophiles. Methyl iodide and *trans*-[Pt(py)₂Cl₂] have been employed^{106,107} to define nucleophilicity scales for a moderately soft and very soft electrophile (Table 3). The overall comparison is much better for methyl iodide as electrophile, which tends to suggest that sulfur 3P_1 atoms are moderately soft electrophiles, but not very soft (like the platinum complex). As would be expected for the large variances in structure and reactivity of sulfur (3P_1) atoms and methyl iodide (*cf.* the absolute rate constants given for hydrazine in Table 3), there are also some discrepancies. For example, the rate constant for triethyl phosphite, which presents the highest value contained in Table 2, appears to be too high. Whether this is interpreted as a hint toward higher softness is uncertain.

(105) The very high rate constants for the amines, but also for the anionic nucleophiles (Table 2), might be in part due to the importance of CT interactions (e.g., $R_3N^{\delta+} \cdots \delta^-S$). However, the rate constant for reaction between sulfur (3P_1) atoms and triethylamine in the nonpolar solvent cyclohexane was only ca. 20% lower than in acetonitrile, which does not suggest that CT interactions are the major denominators of the reactivity toward amines.

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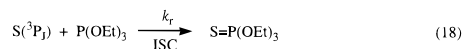
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Table 3. Comparison of Rate Constants for Reactions of Sulfur (3P_1) Atoms and Typical Electrophiles with Selected Nucleophiles

reactant (X)	nucleophilicity constant η^a		
	$S(^3P_1)^b$	CH_3I^c	<i>trans</i> -[Pt(py) ₂ Cl ₂] ^c
methanol	0.0 ^b	0.0	0.0
R-NC	4.6	"very low"	6.4
Cl ⁻	5.1	4.4	3.2
R-S-R	5.2	5.3	4.6
Br ⁻	5.5	5.8	4.1
NEt ₃	5.9	6.7	"very low"
H ₂ N-NH ₂	6.1 ^d	6.6 ^e	4.0 ^f
P(OR) ₃	6.3	5.2	7.3

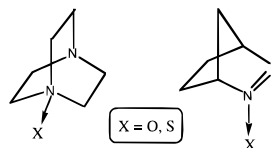
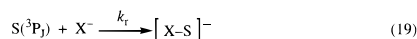
^a $\eta = \log[k_r(X)/k_r(\text{MeOH})]$. ^b From Table 2; the value for methanol was taken as $1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. ^c References 106 and 107. ^d Absolute rate in acetonitrile: $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. ^e Absolute rate in methanol: $0.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. ^f Absolute rate in methanol: $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Probably, the apparently too high rate constant is a consequence of the higher thermodynamic driving force due to the very high bond strengths between phosphorus and the group VIa elements, e.g., $D(P=O) = 143 \text{ kcal mol}^{-1}$ and $D(P=S) = 106 \text{ kcal mol}^{-1}$ in diatomics and $D(P=O) = 130 \text{ kcal mol}^{-1}$ in $O=PF_3$.¹⁰³ For comparison, the rate constant for reaction between oxygen (3P_1) atoms and triethyl phosphite ($3.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is also the highest among the neutral additives examined.¹⁰ Clearly, the reaction of sulfur (3P_1) atoms with phosphites yields trialkyl thiophosphates as quite stable products (eq 18);⁴⁴ the latter are



not expected to undergo the bimolecular decomposition reaction in eq 13. Similar, supposedly less persistent "oxidation products" are expected from the addition of sulfur (3P_1) atoms to diethyl sulfoxide and dimethyl sulfoxide (see also eq 20 below).

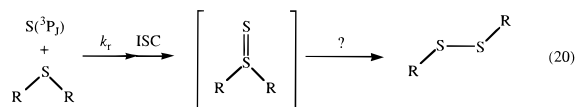
The rate constants measured for the reaction of sulfur (3P_1) atoms with chloride and bromide ions (1.3 and $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Table 2)¹⁰⁵ fell below the diffusion-controlled rate constants (10^{10} – $10^{11} \text{ M}^{-1} \text{ s}^{-1}$) observed for the reactions of oxygen (3P_1) and bromine atoms. The lower reactivity of sulfur (3P_1) atoms is probably attributable to their lower electron affinity¹⁰³ (see also below). The reaction yields sulfur-halogen radical anions as primary adducts (eq 19), which might be unstable toward



bimolecular reaction to form $S_2(^3\Sigma_g^-)$ and regenerate the halide ions (eq 13). Due to the relatively high rate constants measured even for the weakly nucleophilic halide ions (Table 3) and because of the restriction to acetonitrile as solvent for tetraalkylammonium salt based nucleophiles (acetonitrile/water = 9/1 can be employed, but the signal intensity is much reduced), we have not examined the reactions of more potent^{106,107} anionic nucleophiles (e.g., sulfite or cyanide), which will presumably occur under diffusion control (ca. $10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

The reaction mode of $S(^3P_1)$ atoms with nitrogen nucleophiles, i.e., hydrazines, triethylamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), or the azoalkane 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), is particularly interesting. Addition to the nitrogen lone pairs should give rise to *N*-sulfide products. The corresponding *N*-oxides, e.g., the *N*-oxides derived from DABCO and azoal-

kanes (see above), can be isolated,^{108,109} such that there is little reason to doubt that the corresponding *N*-sulfides do not possess a certain thermodynamic stability as well. However, due to the much weaker N–S bond strength with reference to the N–O bond,¹¹⁰ it seems quite likely that the *N*-sulfides decompose by bimolecular reaction (eq 13), or rearrange by insertion into the relatively weak C–H (for the amines) or N–H (for the hydrazines) bonds (eq 15). A search was made to substantiate the appearance of the *N*-sulfides derived from DABCO by transient absorption spectroscopy. However, no transient absorption was observed in the visible region of the spectrum, and the changes in the UV transient spectrum (at ca. 300 nm) were too uncharacteristic to allow an unequivocal discrimination from the $S_2(^3\Sigma_g^-)$ spectrum. Interestingly, even at a DABCO concentration high enough to quench ca. 90% of the sulfur (3P_J) atoms, a UV spectrum similar to that of $S_2(^3\Sigma_g^-)$ remained. A similar observation, namely, the absence of any characteristic visible absorption, was made for dipropyl sulfide as additive. For sulfides and mercaptans, one would also expect addition to the sulfur lone pairs. The resulting adducts, whose transient absorptions were sought for, are supposedly not stable and will either react intermolecularly or rearrange to disulfides (eq 20, or according to eq 15).



The reactions between sulfur (3P_J) atoms and isocyanides or mercury are better defined, and the addition products (mercury sulfide and alkyl isothiocyanates) are stable compounds. Unfortunately, the low solubility of mercury allowed only the determination of an upper limit for the rate constant (Table 2), which indicates merely that the reaction occurs slower than diffusion. The reaction with mercury was of interest due to its wide applications as an efficient scavenger of sulfur in organic and inorganic chemistry (see, for example, reference 44). The addition to isocyanides, on the other hand, was important due to its possible importance as a removal pathway for sulfur (3P_J) atoms generated in the laser flash photolysis of methyl isothiocyanate; i.e., it constitutes the thermal reversal of the formation reaction (eqs 5 and 7). The rate constant falls far below diffusion control and, thus, cannot contribute significantly to the observed decay of sulfur (3P_J) atoms (*cf.* Results).

The comparison of the solution and gas phase reactivity data is restricted to seven reactants (Table 1). With the exception of the data for alkynes, there is a satisfactory agreement between the (relative) order of rate constants, which provides strong support for the assignment to sulfur (3P_J) atoms. For example, the reactivity of additives which are capable of transferring divalent atoms to the sulfur (3P_J) atom (see above) follows the same order in solution and in the gas phase, namely, $MeNCS > (O_2 >) CS_2 > OCS$. Quantitatively, with the exception of OCS, the rate constants in acetonitrile solution are lower, by 1 or 2 orders of magnitude, than the values in the gas phase. This

discrepancy cannot be related to the restriction of diffusion in solution, since all gas phase values fall below the values expected for diffusion-controlled reactions in acetonitrile (ca. $3 \times 10^{10} M^{-1} s^{-1}$). We propose tentatively that the reactivity of atoms like halogens, oxygen, and sulfur is inherently different in solution, where the atoms are stabilized through CT interactions with the solvent molecules, i.e., partial electron donation to the sulfur (3P_J) atom; this stabilization need not to involve stoichiometric complexation.¹⁰ In considering this explanation, two aspects of CT complexation of atoms need to be recalled: (i) The efficiency of CT interactions increases with the electron affinity of the atom;^{8,103} the latter is 2.08 eV for sulfur, i.e., higher than for oxygen (1.46 eV) and hydroxyl (1.83 eV), but lower than for fluorine (3.40 eV), chlorine (3.62 eV), bromine (3.37 eV), and iodine (3.06 eV). (ii) CT complexes between halogen atoms or hydroxyl and water are well characterized.^{4,8,9} Since the ionization potentials of the solvents used, namely, acetonitrile (12.2 eV), cyclohexane (9.8 eV), and Freon-113 (12.0 eV) lie below that of water (12.6 eV),^{4,103} CT interactions may be significant not only for halogen atoms, but also for sulfur (3P_J) atoms. It should also be noted that the very small rate constants estimated for the reactions of sulfur (3P_J) atoms with olefins (10^2 – $10^4 M^{-1} s^{-1}$) in aromatic solvents can be accounted for by efficient CT interactions, as was already proposed in the original paper.²⁵ Interactions between atomic or radical species and the solvent can moderate radical reactivity¹¹¹ and might further contribute to the observed variations between the gas phase and solution phase reactivity of sulfur atoms. To which degree such “solvent complexation” affects the bimolecular reactivity cannot be predicted *a priori* and requires experimental data such as those supplied in Tables 1 and 2.

Conclusions

The reduced reactivity of $S(^3P_J)$ atoms in solution as compared to fluorine,² chlorine,^{3–5} and oxygen¹⁰ atoms is accompanied by an increase in selectivity toward the reactants, which establishes $S(^3P_J)$ atoms as strong but relatively soft electrophiles. While the reaction mechanisms and the final products of the addition reactions of $S(^3P_J)$ atoms with several organic nucleophiles will require more detailed attention, the present solution rate constants confirm the notion that the chemistry of atomic sulfur is more complex than that of oxygen and halogen atoms. Hence, while the abstraction of hydrogen atoms is a common denominator in the reactions of oxygen and fluorine atoms,^{2,10} the reactions of sulfur $S(^3P_J)$ atoms appear to involve competitive primary reaction pathways (e.g., abstraction of hydrogen or divalent atoms *versus* addition), and various follow-up reactions of the adducts (e.g., rearrangement or dimerization).

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