

as the main oxidation products through equivalence and kinetic studies.

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Kinetic Studies of Tin and Germanium Atom Oxidation in the Gas Phase

J. R. Wiesenfeld* and M. J. Yuen†

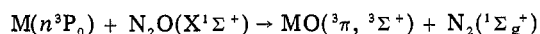
Department of Chemistry, Cornell University, Ithaca, New York 14853 (Received January 23, 1978)

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The removal of $\text{Ge}(3^3\text{P}_0)$ and $\text{Sn}(4^3\text{P}_0)$ following collisions with the oxidizing gases O_2 , Cl_2 , COS , N_2O , and NO_2 has been monitored using time-resolved atomic absorption analysis. Reaction rates have been measured for these processes which were initiated by pulsed photolysis under isothermal conditions ($T = 295\text{ K}$). In addition, the termolecular reaction of Sn and Ge atoms with NO in the presence of Ar has also been observed and characterized. The experimental results are discussed in terms of the detailed processes which might be expected to govern the course of such gas-phase metal atom oxidation reactions.

Introduction

The development of the general field of gas-phase kinetics has been paced by experimental studies of the chemistry of neutral atoms in the presence of strong oxidizers, first in flames¹ and more recently, in single-collision beams.² Interest in such reactions has heightened as the result of efforts to construct a visible chemical laser based on metal-oxidizer reactions such as



where M represents any group 4A atom. Consideration of spin conservation alone would predict the formation of the electronically excited MO molecule (the ground state of MO is $^1\Sigma^+$). This agrees with the observation³ of a high chemiluminescence quantum yield (ca. 0.5) arising from $\text{Sn} + \text{N}_2\text{O}$.

Previous experiments carried out in several laboratories have shown,^{4,5} however, that in spite of the high chemiluminescence quantum yield associated with the $\text{Sn} + \text{N}_2\text{O}$ reaction, the overall reaction rate constant is quite low,⁴ $k = (5.0 \pm 1.0 \times 10^{-13}) \exp[-(4000 \pm 200)/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The 4 kcal activation barrier may be accounted for by consideration of nonadiabatic effects along the reaction coordinate leading from $\text{Sn} + \text{N}_2\text{O}$ to molecular products.⁴ No simple explanation has been offered for the failure to observe similarly high quantum yields in the reaction of Ge with N_2O ,⁶ where the spin conservation rules should be even more strongly obeyed than in the case of Sn. Indeed, with the exception of several recent measurements of Ge atom reactivity,^{7,8} relatively little is known of the kinetic parameters characterizing the kinetic behavior of group 4A atoms in their ground state. The experiments reported here were undertaken both to obtain useful data for the development of potential chemical

TABLE I: Photolysis Sources and Reaction Vessels

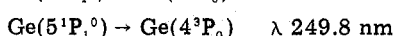
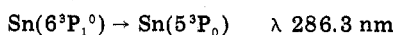
	Coaxial	Colinear
Input energy, J	400	425-500
Active length, cm	46	31
Vessel i.d., cm	3.2	3.2
Gases photolyzed	GeCl_4	SnCl_4 , $\text{Sn}(\text{CH}_3)_4$

lasers and to investigate the chemical reactivity of the group 4A metals, thus providing insight into the detailed mechanisms of such metal atom oxidation reactions.

Experimental Section

The description of the flash photolysis-atomic absorption spectroscopy apparatus used in these experiments has been published hitherto.^{4,9,10} The details of the photolysis equipment are presented in Table I. GeCl_4 was photolyzed in the coaxial vessel in order to provide sufficient far-UV radiation to yield Ge atom densities high enough (ca. 10^{-6} Torr) for analysis of single-shot experiments. $\text{Sn}(\text{CH}_3)_4$ served as the source gas in all experiments on Sn chemistry with the exception of $\text{Sn} + \text{Cl}_2$. Here, it was necessary to use SnCl_4 to avoid destruction of the source gas by the oxidant prior to photolysis. All studies of Sn reactions were carried out in the colinear reaction vessel.

The source of resonance radiation for detection of $\text{Sn}(5^3\text{P}_0)$ was, as previously,^{4,11} a sealed microwave-powered electrodeless discharge lamp (EDL), the temperature of which was controlled by an external heater. An EDL for Ge resonance radiation was constructed of 7-mm o.d. quartz tubing. A 4% mixture of GeCl_4 in Ar was flowed through the tube, a section of which was enclosed in a standard Evenson microwave cavity. The radiation emanating from the plasma immediately below the cavity was then focused through the reaction vessel and onto the entrance slit of a 0.5-m monochromator. Detection of the resonance transitions



* Author to whom correspondence should be addressed. Henry and Camille Dreyfus Teacher-Scholar; Alfred P. Sloan Fellow.

† Chemistry Division, Argonne National Laboratory, Argonne, Ill. 60439.

TABLE II: Purification of Materials

	Source and grade	Vacuum distillation	Special handling
Sn(CH ₃) ₄	Ventron, ultrapure	Room temperature → liquid N ₂	Used as supplied
SnCl ₄	Ventron, ultrapure	Room temperature → liquid N ₂	
GeCl ₄	Ventron, ultrapure	Saturated NaCl-ice bath (−11 °C) → liquid N ₂	
Ar	Matheson Co., 99.9995%		Used vapor over ethanol slush
N ₂ O	Airco, grade 4.5	Pentane slush (−126 °C) → liquid N ₂	
NO	Matheson, research grade	Isopentane slush (−160 °C) → liquid N ₂	
NO ₂	Matheson, research grade	Chlorobenzene slush (−35 °C) → ethanol slush (−112 °C)	Before distillation, NO ₂ mixed with O ₂ (NO ₂ :O ₂ = 2:1) for several hours. Multiple freeze-thaw cycles to degas sample
COS	Synthatron Products, 99.9913%	Ethanol slush (−112 °C) → liquid N ₂	
O ₂	Airco		
Cl ₂	Fisher, high purity	Toluene-ethanol-pentane slush (−105 °C) → liquid N ₂	Used as supplied Passed over CaSO ₄ before distillation

was accomplished with a 1P21 photomultiplier. The use of the $5^1P_1^0 \rightarrow 4^3P_0$ transition minimized interference between closely spaced emission lines in the triplet spectrum. Transient absorption signals were displayed on a storage oscilloscope and photographed for analysis.

As in previous experiments involving detection of transient atoms by atomic absorption spectroscopy,¹² a modified form of the Beer-Lambert equation was used to relate the observed transmission of resonance radiation through the reaction vessel to the relative concentration of metal atoms, $[M(n^3P_0)]$, at time, t :

$$\ln(I_0/I_t) = \epsilon \{I[M(n^3P_0)]_t\}^\gamma \quad (I)$$

The constants and the technique for determining γ have been described in an earlier publication.¹⁰ In the present apparatus, γ values of 0.60 ± 0.05 and 0.75 ± 0.09 were obtained for the resonance transitions in Sn and Ge noted above. The larger value of γ for the transition in Ge suggests less self-reversal in the resonance emission emanating from the EDL for this atom. This seems reasonable in view of the smaller Einstein coefficient for the singlet-triplet transition in Ge as compared to the triplet-triplet transition in Sn ($gA[\text{Ge}(^1P_0 \rightarrow ^3P_0)] = 2.4 \times 10^8 \text{ s}^{-1}$, $gA[\text{Sn}(^3P_0 \rightarrow ^3P_0)] = 5.3 \times 10^8 \text{ s}^{-1}$).¹³

Due to potential difficulties associated with the possible presence of contaminants in the oxidants, considerable care was taken in the preparation of all materials (Table II). Mixtures were prepared in a mercury-free, glass vacuum line which could be evacuated to ca. 10^{-6} Torr. Pressures were measured using Wallace and Tiernan gauges. Dilute mixtures of source gases and oxidants were often required due to the high efficiencies of reaction. These were prepared by expansion from calibrated volumes. All reactive gases and mixtures were stored in darkened glass bulbs fitted with grease-free glass stopcocks. Research grade Ar (Matheson, 99.9995%) was used throughout as a buffer gas ($p = 30$ – 60 Torr) in the photolysis cell to prevent adiabatic heating of the reaction mixture as well as to ensure extremely rapid thermalization of the metal atoms produced by the initiating photolytic pulse.

Results

As experimental traces obtained in this laboratory have not previously been given for Ge absorption in kinetic experiments, Figure 1 presents typical transient profiles for the disappearance of Ge atoms following the flash photolysis of GeCl₄ in the absence and presence of an oxidant, N₂O. It may be seen that the signal-to-noise ratio

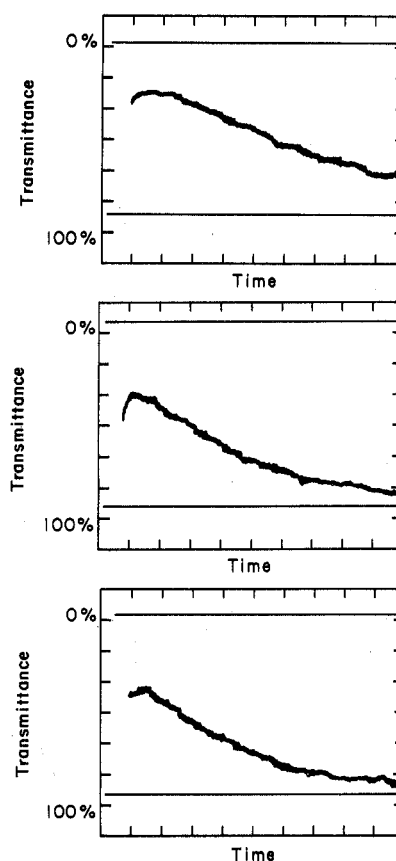


Figure 1. Oscilloscope traces showing temporal profile of transmittance of Ge-atom resonance radiation at 249.8 nm; time scale 0.2 ms/division; experimental conditions as follows: flash energy, 400 J, $P_{\text{GeCl}_4} = 8 \times 10^{-4}$ Torr, $P_{\text{total}} = 33$ Torr with Ar; (a, top) $P_{\text{N}_2\text{O}} = 0$; (b, middle) $P_{\text{N}_2\text{O}} = 1.7 \times 10^{-3}$ Torr; (c, bottom) $P_{\text{N}_2\text{O}} = 2.6 \times 10^{-3}$ Torr.

from these single-shot experiments is more than adequate for kinetic analysis.

The oxidant gases are present in great excess (at least $10^3\times$), hence the disappearance of metal atoms is expected to be pseudo-first order with respect to $[M]_t$ as demonstrated in Figure 2 for the case of Ge reaction with N₂O. The removal of metal atoms may be described by the relationship

$$\ln [M]_t = k't + \ln [M]_{t=0} \quad (II)$$

and substitution of (I) into (II) yields

$$\ln \ln(I_0/I_t) = \gamma k't + \gamma \ln [M]_{t=0} + \ln \epsilon + \gamma \ln I$$

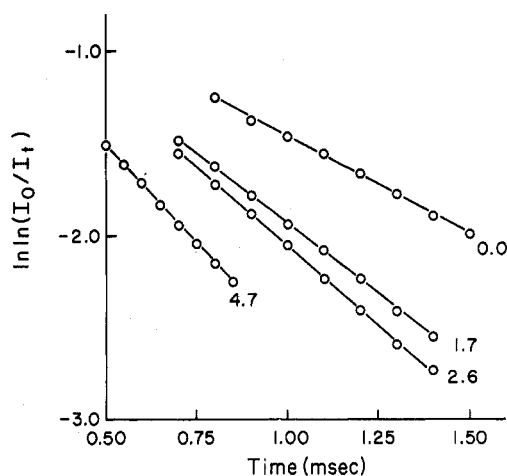


Figure 2. Semilogarithmic plots of $\text{Ge}(4^3\text{P}_0)$ removal in the presence of varying pressures of N_2O (shown in mTorr). Conditions are as in Figure 1.

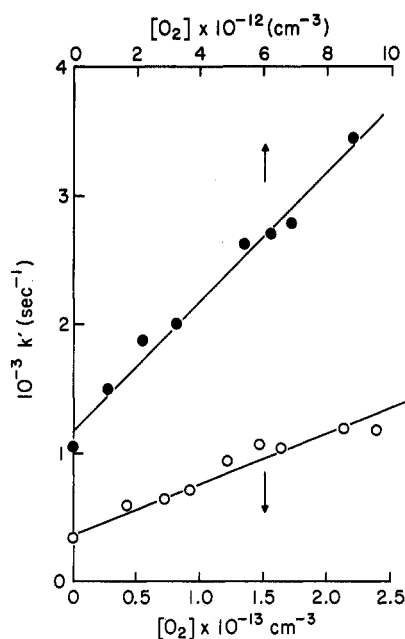


Figure 3. Plot of pseudo-first-order rate coefficients for removal of $\text{Ge}(4^3\text{P}_0)$ and $\text{Sn}(5^3\text{P}_0)$ as a function of O_2 density: (●) $\text{Ge}(4^3\text{P}_0)$; (○) $\text{Sn}(5^3\text{P}_0)$.

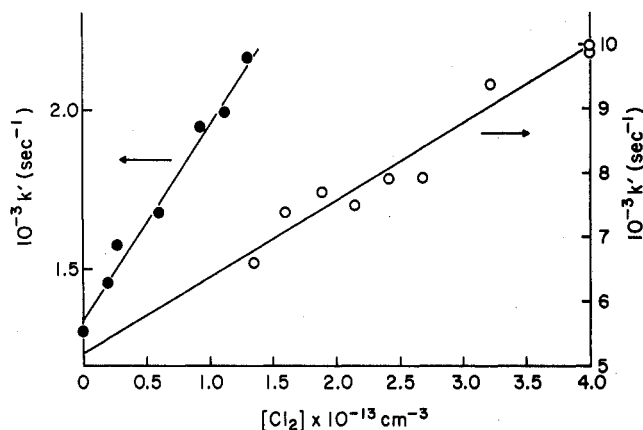


Figure 4. Plot of pseudo-first-order rate coefficients as a function of Cl_2 density. Legend as in Figure 3.

Thus, the slopes of the semilogarithmic plots (Figure 2) must be divided by γ to yield k' , the first-order rate coefficient

$$k' = k_{\text{Ox}}^{\text{M}}[\text{Ox}] + K$$

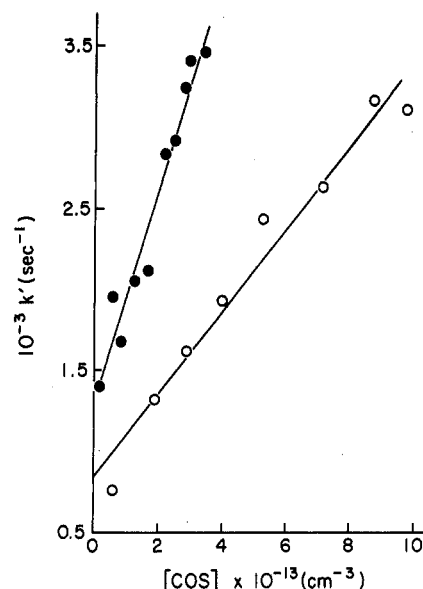


Figure 5. Plot of pseudo-first-order rate coefficients as a function of COS density. Legend as in Figure 3.

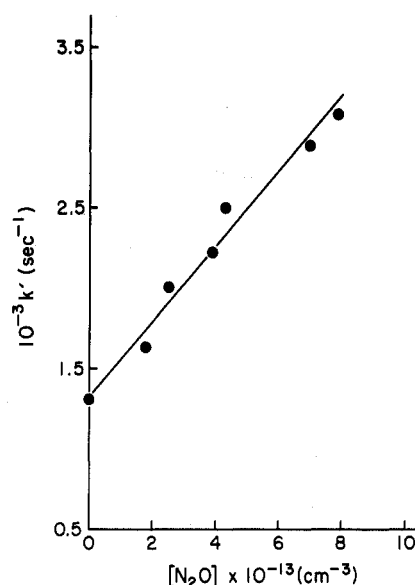


Figure 6. Plot of pseudo-first-order rate coefficients for removal of $\text{Ge}(4^3\text{P}_0)$ as a function of N_2O density.

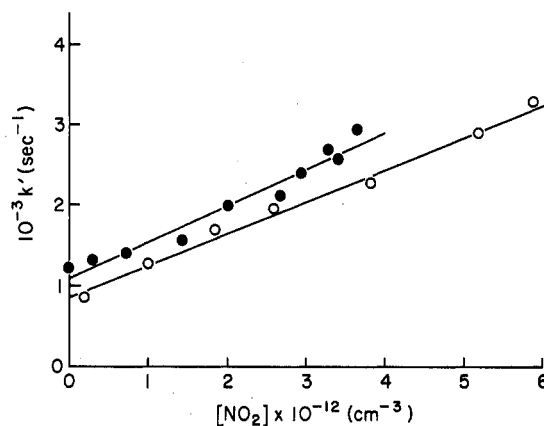


Figure 7. Plot of pseudo-first-order rate coefficients as a function of NO_2 density. Legend as in Figure 3.

The bimolecular rate constant, k_{Ox}^{M} , for reaction of metal, M , with oxidant, Ox , may be determined by varying the oxidant density while measuring the overall first-order rate coefficient. The term K is associated with reaction of the metal with the source gas or trace impurities in the argon

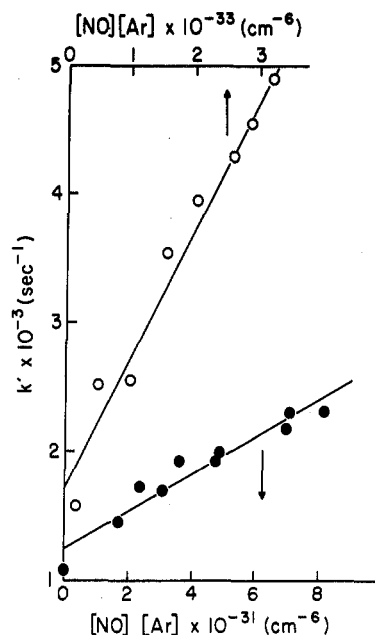


Figure 8. Plot of pseudo-first-order rate coefficients for the recombination of $\text{Ge}(4^3\text{P}_0)$ and $\text{Sn}(5^3\text{P}_0)$ with NO in the presence of Ar. Legend as in Figure 3.

buffer, both of which are kept at constant pressures, as well as diffusion of the metal atoms to the walls of the reaction vessel. Plots of k' vs. $[\text{Ox}]$ are presented in Figures 3–7 for reactions of Ge and Sn with O_2 , Cl_2 , COS, N_2O , and NO_2 .

In the case of Sn and Ge reactions with NO, a dependence of the overall removal rate on total pressure was noted. This suggested that these processes proceeded via a three-body recombination described by the rate law

$$-d[\text{M}]/dt = k_{\text{Ox,Ar}}^{\text{M}}[\text{M}][\text{Ox}][\text{Ar}]$$

Pseudo-first-order rate coefficients, k' , were obtained over a range of argon pressures, $p_{\text{Ar}} = 30$ –55 Torr, and plotted against $[\text{NO}][\text{Ar}]$ (Figure 8). The termolecular rate constant for recombination in the presence of Ar

$$k' = k_{\text{Ox,Ar}}^{\text{M}}[\text{NO}][\text{Ar}] + K$$

may be obtained from the slope of this plot.

The bimolecular rate constants (295 K) determined for the reaction of Sn and Ge with Cl_2 , O_2 , N_2O , COS, and NO_2 are presented in Table III. The termolecular rate constants for recombination of Sn and Ge with NO are $1.02 \pm 0.04 \times 10^{-30}$ and $1.4 \pm 0.1 \times 10^{-29}$, respectively. As may be seen from these tables, agreement with previous experiments reported by Husain and co-workers⁷ is not as good as might be desired, the present values being approximately a factor of 2 larger for $k_{\text{O}_2}^{\text{Ge}}$ and $k_{\text{N}_2\text{O}}^{\text{Ge}}$. Both values of $k_{\text{N}_2\text{O}}^{\text{Ge}}$ obtained by time-resolved atomic absorption spectroscopy are significantly larger than the measured rate reported in a flow experiment where Ge atoms were produced in a hollow cathode discharge.⁸ Also, these workers⁷ have only given a bimolecular rate constant for the removal of Ge by NO at an argon pressure of 25 Torr, $3.8 \pm 0.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, at which pressure the value of $k_{\text{NO,Ar}}^{\text{Ge}}$ ($1.4 \pm 0.1 \times 10^{-29}$) would yield an apparent bimolecular rate constant of $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, again considerably faster than reported by the Cambridge group.⁷ No explanation can be offered for this systematic difference in measured rates.

Discussion

The linearity of the semilogarithmic plots of absorbance vs. time suggests that the photolysis of the source gases

TABLE III: Bimolecular Rate Constants for the Reaction of Tin and Germanium Atoms with Oxidants (295 K)

Oxidant	Ge	Sn
Cl_2	$6.1 \pm 0.3 \times 10^{-11}$	$5.3 \pm 0.2 \times 10^{-11}$
O_2	$2.5 \pm 0.1 \times 10^{-10}$	$1.05 \pm 0.08 \times 10^{-11}$
	$1.2 \pm 0.1 \times 10^{-10a}$	
COS	$3.4 \pm 0.2 \times 10^{-10}$	$1.29 \pm 0.01 \times 10^{-11}$
N_2O	$9.9 \pm 0.9 \times 10^{-12}$	6.2×10^{-16c}
	$5.8 \pm 0.8 \times 10^{-12b}$	
	$6.7 \pm 2.5 \times 10^{-13d}$	
NO_2	$4.6 \pm 0.4 \times 10^{-10}$	$4.0 \pm 0.2 \times 10^{-10}$

^a Reference 7b. ^b Reference 7a. ^c Extrapolated from data in ref 4. ^d Reference 8.

used in these studies leads primarily to the production of ground state metal atoms. Therefore, the kinetic data obtained were not affected by the deactivation of higher-lying, optically metastable atomic states by collision with the oxidant.

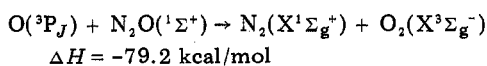
The remainder of this discussion is concerned with consideration of the oxidation of the metal atoms by specific classes of oxidants.

N_2O , CO_2 , and COS. As these molecules are all valence-shell isoelectronic, their chemistry upon collision with Sn and Ge molecules may be discussed within the context of a simple model including nonadiabatic effects which was developed in an earlier publication.⁴ The thermochemistry of these reactions to produce the corresponding metal oxides or sulfides

	ΔH , kcal/mol
$\text{Sn} + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2$	-84
$+ \text{CO}_2 \rightarrow \text{SnO} + \text{CO}$	+3
$+ \text{COS} \rightarrow \text{SnS} + \text{CO}$	-39
$\text{Ge} + \text{N}_2\text{O} \rightarrow \text{GeO} + \text{N}_2$	-118
$+ \text{CO}_2 \rightarrow \text{GeO} + \text{CO}$	-30
$+ \text{COS} \rightarrow \text{GeS} + \text{CO}$	-59

clearly shows that ground state products are, in all cases other than $\text{Sn} + \text{CO}_2$, energetically accessible to the reactants. As the ground state of MO and MS is $^1\Sigma^+$, conservation of spin would require that an excited state of the metal oxide or sulfide be formed. The low-lying triplet states of these molecules are all about 2–3 eV above the ground state, so exothermic adiabatic paths are available to the reaction of Sn or Ge with N_2O . No electronically excited products would be expected for the reaction of either atom with CO_2 or COS.

The very slow reaction of Sn with N_2O has been shown^{4,5} to be the result of a 4-kcal activation barrier in the reaction coordinate leading to product molecules. The presence of this barrier has been ascribed⁴ to the avoided crossing between states correlating diabatically with $\text{Sn} + \text{N}_2\text{O}(^1\Sigma^+)$ and $\text{Sn} + \text{N}_2\text{O}(^3\Sigma^+)$. A similar effect has been noted¹⁴ for the reaction



which displays a 25-kcal activation barrier. The magnitude of the activation energy associated with such reactions should be primarily determined by the energy gap between the ground state of the product molecule, e.g., $\text{SnO}(\text{X}^1\Sigma^+)$, and the lowest excited state correlating with the metal atom and $\text{O}(2^1\text{D}_2)$, SnO^* , where the identity of this excited state is unknown. In addition, the exothermicity of the reaction will play a role as the manifold of electronic states of the product molecule will be fixed in relation to the reactants by this single parameter. Thus, the $\text{Ge} + \text{N}_2\text{O}$ reaction might be expected to proceed more rapidly than $\text{Sn} + \text{N}_2\text{O}$ due to its greater exothermicity.

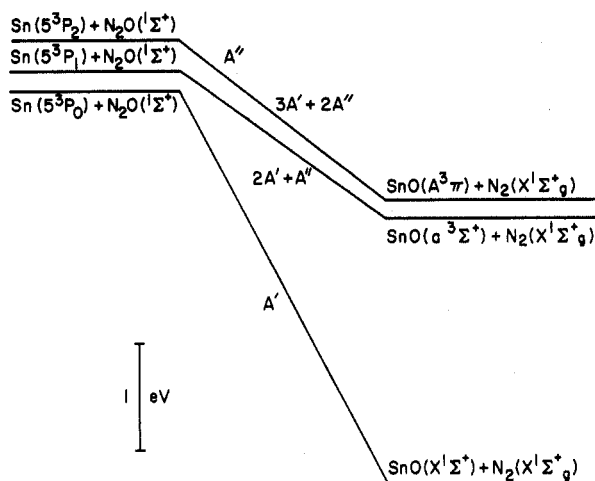
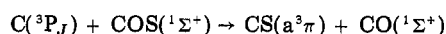


Figure 9. Adiabatic correlation diagram for the reaction $\text{Sn} + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2$ under the assumption of (J, Ω) coupling in reactants and products.

An alternative explanation¹⁵ of the activation energy associated with the $\text{Sn} + \text{N}_2\text{O}$ reaction is possible if it is the $\text{Sn}(5^3\text{P}_1)$ state which reacts to form electronically excited $\text{SnO}(^3\Sigma^+, ^3\pi)$. The $^3\text{P}_1$ level lies 4.8 kcal/mol above the ground state. Consideration of this mechanism requires the construction of an adiabatic correlation diagram¹⁶ with the assumption of J, Ω coupling in reactants and products (Figure 9). Indeed, the $J = 1$ level is seen to correlate with $\text{SnO}(a^3\Sigma^+)$. However, why would not the $J = 0$ ground level react efficiently with N_2O to form $\text{SnO}(^1\Sigma^+)$? This would greatly reduce the quantum yield of the overall process, the thermal population of $J = 1$ being only 25% even at 1000 K.

Yet another difficulty with this scheme arises from consideration of the $\text{Ge} + \text{N}_2\text{O}$ reaction. Application of a similar argument to $\text{Ge}(4^3\text{P}_1)$, which lies 1.6 kcal above $^3\text{P}_0$, would require a preexponential factor of 9×10^{-11} for this reaction, over two orders of magnitude greater than that for the corresponding $\text{Sn} + \text{N}_2\text{O}$ reaction,⁴ even if the slower value of $k_{\text{N}_2\text{O}}^{\text{Ge}}$ reported by Chowdhury and Husain⁷ were correct. Further experimental studies of the temperature effect on the $\text{Ge}(4^3\text{P}_1) + \text{N}_2\text{O}$ reaction would help to resolve this question. Also, direct determination of the chemiluminescence quantum yields of the $\text{Sn}(5^3\text{P}_1) + \text{N}_2\text{O}$ reaction would serve to elucidate the mechanism of these interesting reactions.

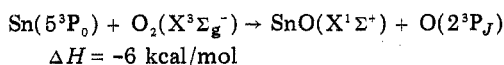
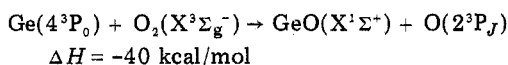
The collisional removal of Sn and Ge atoms by COS and Ge by CO_2 must, due to the thermochemistry, result in the formation of ground state products only. The reaction of $\text{M}(n^3\text{P}_0)$ with these molecules to form ground state SnS and GeS is adiabatic (correlation diagram similar to that shown in Figure 9) in the context of total angular momentum conservation. The enhanced rate of COS oxidation of both metals and the higher reactivity of Ge with COS (with respect to Sn) can be ascribed in simplest terms to the greater exothermicity of the appropriate reactions. However, a report of laser action¹⁷ following the reaction



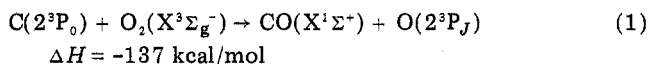
along with the high quantum yield of the $\text{Sn} + \text{N}_2\text{O}$ reaction suggests that spin conservation must play a significant role in the oxidation of group 4A atoms. Perhaps, in the absence of an exothermic, spin-allowed pathway to products, a relatively long-lived collision complex may permit multiple crossing of a region of nonadiabatic coupling with the lower-lying surface, thus leading to the formation of ground state products.¹⁸

O_2 . The reactions of Sn and Ge with O_2 are both quite

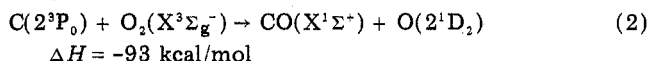
efficient, that of Ge being ca. 25 times faster than that of Sn. Both reactions are exothermic



as is the analogous reaction



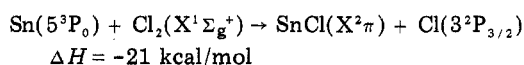
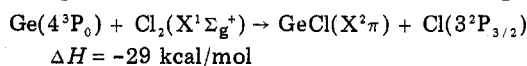
In an examination of the CO infrared chemiluminescence from this reaction, Thrush et al.¹⁹ observed no vibrational excitation above $v = 17$ which corresponds to an exothermicity of 93 kcal/mol. They concluded that this was due to concomitant formation of electronically excited oxygen atoms, $\text{O}(2^1\text{D}_2)$



The failure of this reaction to produce the more exothermic products was ascribed¹⁹ to an activation barrier in reaction 1 which would proceed via electronically excited $\text{CO}_2(^3\text{B}_2, ^3\text{A}_2)$, the lowest-lying states of CO_2 which correlate with reactants and products of (1). Thus, while the products of (2) are less exothermic with respect to reactants than those of (1), the surface along which (2) proceeds, namely, that of $\text{CO}_2(X^1\Sigma_g^+)$, is far lower in energy (by ca. 240 kcal) than either of the triplets. The ground state, $\text{CO}_2(X^1\Sigma_g^+)$, correlates with reactants and $\text{CO}(X^1\Sigma^+) + \text{O}(2^1\text{D}_2)$.

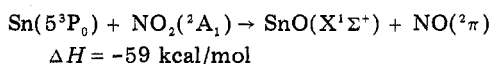
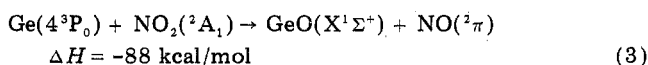
Similar arguments can, of course, be made for the reactions of Sn and Ge with O_2 , although the relative stabilities of the singlet and triplet surfaces of the MO_2 molecules are not known. The production of $\text{SnO}(X^1\Sigma^+) + \text{O}(2^1\text{D}_2)$ and $\text{GeO}(X^1\Sigma^+) + \text{O}(2^1\text{D}_2)$ are, respectively, endothermic by 51 and 4 kcal. As both reactions are very rapid, not even a 4-kcal activation barrier could be present and ground state oxygen atoms must be produced. As noted above, such rapid rates would require efficient nonadiabatic transitions from the low-lying singlet surface correlating with $\text{MO}(X^1\Sigma^+) + \text{O}(2^1\text{D}_2)$. This would be the case if a long-lived collision complex, MO_2 , permitted multiple crossings of an appropriate region of nonadiabaticity before dissociating back into reactant species. Indeed, observation of the angular distribution of reaction products in $\text{Sn} + \text{O}_2$ suggests that such a long-lived complex is formed.²¹ It may be presumed that the greater depth of the GeO_2 well and, hence, enhanced stabilization of the complex, leads to the more rapid rate constant observed for the $\text{Ge} + \text{O}_2$ reaction.

Cl_2 . The reactions of Sn and Ge with Cl_2



are both exothermic and symmetry allowed. Conservation of spin requires that the reactions proceed via the electronically excited state surface of $\text{MCl}_2(^3\text{B}_1)$ which lies approximately 65 kcal above the ground state, $^1\text{A}_1$, in both cases.²² As the $^3\text{B}_1$ state is at a lower energy than either set of reactants, the reactions are expected to be rapid.

NO_2 . Both Ge and Sn may react with NO_2 to yield a metal oxide and nitric oxide



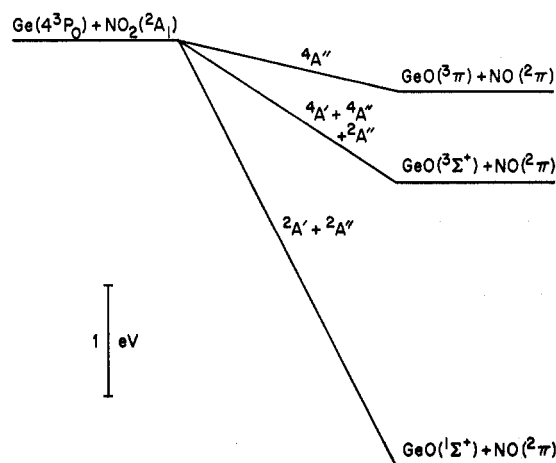
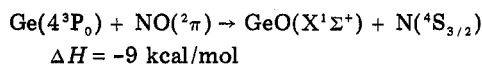


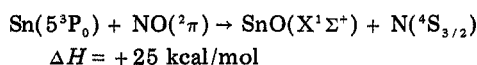
Figure 10. Adiabatic correlation diagram for the reaction $\text{Ge} + \text{NO}_2 \rightarrow \text{GeO} + \text{NO}$ for (l,s) coupling.

Reaction 3 is sufficiently exothermic to yield electronically excited GeO; emission from the $^3\pi$ and $^3\Sigma^+$ states has been observed.⁶ These excited states correlate adiabatically with $\text{Ge} + \text{NO}_2$ (Figure 10). Insufficient energy is available for production of $\text{SnO}(^3\Sigma^+, ^3\pi)$; no emission is observed.²³

NO. The reaction of Ge with NO



is slightly exothermic while that of Sn



is highly endothermic. The experiments showing third-order behavior suggest that in both cases, however, reaction proceeds via the formation of a bound MNO molecule, which has not, to date, been identified. Emission following the mixing of Ge with NO has been observed,⁶ and must

arise from reactions involving relatively energetic (and possibly long-lived) intermediates.

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