

**THE FREE-RADICAL AND ION CHEMISTRY OF VOLATILE SILANES, GERMANES  
AND PHOSPHINES**

Annual Informal Technical Report

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Work Done During Period September 1, 1989 - June 30, 1990

1. Ion-Molecule Reactions in SiH<sub>4</sub>-CO Mixtures. Synthesis of the SiC Radical in the Electric Discharge Chemistry

(K. P. Lim and F. W. Lampe, Int. J. Mass Spectrom. Ion Proc. 1990, in press)

The initial ion-molecule reactions characteristic of electric discharges in SiH<sub>4</sub>-CO mixtures, namely the reactions of C<sup>+</sup>, CO<sup>+</sup>, SiH<sub>2</sub><sup>+</sup>, SiH<sup>+</sup> and Si<sup>+</sup> with CO and SiH<sub>4</sub> have been studied in a tandem mass spectrometer over a kinetic energy range of 1-7 eV (LAB) and a pressure range of 1-10 millitorr. As is typical of systems involving positive ions and SiH<sub>4</sub>, the predominant reactions observed are hydride abstraction from SiH<sub>4</sub> by C<sup>+</sup> and CO<sup>+</sup>, both of which are highly exothermic and which occur with cross sections of 26 and 87 Å<sup>2</sup>, respectively at 2eV laboratory energy. Other dominant reactions that form C-Si bonds (and perhaps Si-O bonds), and which we think may play a very important role in the recently reported<sup>2,3</sup> synthesis of the SiC radical in CO-SiH<sub>4</sub> discharges and in interstellar space, are reactions of C<sup>+</sup> and CO<sup>+</sup> with SiH<sub>4</sub> that form CSiH<sup>+</sup>, the latter subsequently reacting by proton transfer with CO and perhaps with SiH<sub>4</sub> to form the CSi radical. The CSiH<sup>+</sup> ion also reacts with ND<sub>3</sub> and H<sub>2</sub> to form ND<sub>3</sub>H<sup>+</sup> and H<sub>3</sub><sup>+</sup>, which implies that in interstellar space CSi may be formed by reactions of CSiH<sup>+</sup> with any molecule present having a proton affinity<sup>4</sup> greater than 424 kJ/mol. The silicon-containing ions SiH<sub>x</sub><sup>+</sup> (X=0-3) are quite unreactive toward CO.

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2. Reactions of  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  Ions with  $\text{GeH}_4$

(K. P. Lim and F. W. Lampe, to be submitted to J. Phys. Chem.)

The reactions of gaseous ions derived from water with  $\text{GeH}_4$  have been studied in a tandem mass spectrometer over a kinetic energy range of 0.5-6.0 eV(LAB). The reactions observed, the branching percentages for the various channels and the standard enthalpy changes calculated from thermochemical data<sup>1</sup> are shown in Table I.

Table I

Reactions of Water-Derived Ions with  $\text{GeH}_4$  at 2eV(LAB)

	<u>% Total Reaction</u>	<u><math>\Delta\text{H}^\circ(\text{kJ})^{1-4}</math></u>
$\text{OH}^+ + \text{GeH}_4 \rightarrow \text{Ge}^+ + \text{H}_2\text{O} + \text{H}_2 + \text{H}$	3.2	-54
$\text{OH}^+ + \text{GeH}_4 \rightarrow \text{GeH}^+ + \text{H}_2\text{O} + \text{H}_2$	3.5	-147
$\text{OH}^+ + \text{GeH}_4 \rightarrow \text{GeH}_2^+ + \text{H}_2\text{O} + \text{H}$	27.5	-55
$\text{OH}^+ + \text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{H}_2\text{O}$	57.0	-159
$\text{OH}^+ + \text{GeH}_4 \rightarrow \text{GeOH}_2^+ + \text{H}_2 + \text{H}$	8.5	<0
$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{Ge}^+ + \text{H}_2\text{O} + 2\text{H}_2$	3.9	-42
$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}^+ + \text{H}_2\text{O} + \text{H}_2 + \text{H}$	2.6	-31
$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_2^+ + \text{H}_2\text{O} + \text{H}_2$	23.6	-43
$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{H}_2\text{O} + \text{H}$	66.1	-43
$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeOH}_2^+ + 2\text{H}_2$	1.9	<0

$\text{H}_2\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeOH}_4^+ + \text{H}_2$	1.9	<0
$\text{H}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_2^+ + \text{H}_2\text{O} + \text{H}_2 + \text{H}$	5.7	+101
$\text{H}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{H}_2\text{O} + \text{H}_2$	88.5	-3
$\text{H}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_5^+ + \text{H}_2\text{O}^{\ddagger}$	5.8	+2
$\text{D}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_2^+ + \text{D}_2\text{O} + \text{HD} + \text{H}$	1.0	+101
$\text{D}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{D}_2\text{O} + \text{HD}$	93.1	-3
$\text{D}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_2\text{D}^+ + \text{D}_2\text{O} + \text{H}_2$	0.2	-3
$\text{D}_3\text{O}^+ + \text{GeH}_4 \rightarrow \text{GeH}_4\text{D}^+ + \text{D}_2\text{O}$	5.6	+2

As is common in reactions involving the attack of positive ions on silanes, the predominant process in all these reaction systems involving germane is hydride abstraction to form the germal ion  $\text{GeH}_3^+$ . The mass spectral distribution of the collision products is nearly independent of energy which suggests that the hydride transfer reaction to form  $\text{GeH}_3^+$  is a direct stripping process.

The dependence of the relative cross-section of the reactions in Table I on collision energy indicates that all reactions are exothermic and this is in accord with the bulk of the enthalpy changes calculated from thermochemical data. The apparent, glaring exceptions, namely the reactions of  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  to form  $\text{GeH}_2^+$  probably represent extraneous reactions due to the leakage of  $\text{H}_2\text{O}^+$  and  $\text{D}_2\text{O}^+$  through the Wien velocity filter.

Calibration studies are now in progress to establish absolute reaction cross-sections for these processes.

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### 3. Reactions of $\text{SiH}_x^+$ Ions with $\text{GeH}_4$

(K. P. Lim and F. W. Lampe, to be submitted to J. Phys. Chem.)

When  $\text{SiH}_x^+$  ions react with  $\text{SiH}_4$ , the predominant reaction observed is an overall hydride transfer process.<sup>1</sup> This overall process actually appears to proceed by two mechanisms,<sup>1,2</sup> one a process involving an ion-molecule collision complex and the other involving a direct stripping reaction. The relative contributions of the two mechanisms may be judged by the extent of H/D scrambling in the hydride transfer product of the reactions of  $\text{SiH}_x^+$  with  $\text{SiD}_4$ , namely  $\text{SiD}_3^+$ . Extensive scrambling has indicated significant participation of collision complexes, particularly in the reactions of  $\text{SiH}_2^+$  and  $\text{SiH}_3^+$  with  $\text{SiD}_4$ , at low collision energies. The relative contribution of the collision complex mechanism decreases with increasing relative kinetic energy of the reactants.<sup>1,2</sup>

We have initiated a study of the reactions of  $\text{SiH}_x^+$  ions with  $\text{GeH}_4$  to ascertain if the same mechanism obtains in this hetero-collision system.

Our preliminary results indicate that even at the lowest collision energy (i.e.  $\sim 0.4$  eV), very little if any H/D scrambling occurs when  $\text{SiH}^+$ ,  $\text{SiH}_2^+$  and  $\text{SiH}_3^+$  ions collide with  $\text{GeH}_4$ . The mass spectrum of the ionic products of the  $\text{SiH}_3^+ + \text{GeD}_4$  reaction can be produced quantitatively simply by adding 3 Daltons to the mass of each peak in the product-ion mass spectrum of the

$\text{SiH}_3^+ + \text{GeH}_3$  reaction. There may be somewhat more scrambling in the  $\text{SiH}_2^+/\text{GeD}_4$  reaction. These results, which are preliminary, suggest that the hydride transfer reaction in the  $\text{SiH}_3^+/\text{GeH}_4$  system proceeds almost exclusively by a direct stripping process.

Further investigation of this ion-molecule reaction system are continuing.

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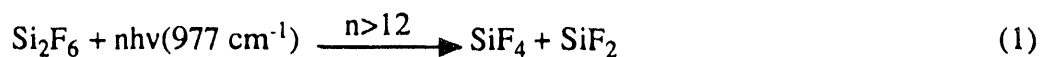
4. *The Infrared Multiple Photon Decomposition of  $\text{Si}_2\text{F}_6$*

(J. Biedrzycki and F. W. Lampe, Spectrochim. Acta **46A**, 631 (1990))

It has been reported<sup>1</sup> that the infrared multiple photon decomposition of  $\text{Si}_2\text{F}_6$  proceeds by an initial dissociation to  $\text{SiF}_2$  and  $\text{SiF}_4$ . We have examined this infrared laser photodecomposition in the presence of several substrate molecules to see if  $\text{SiF}_2$  produced in this manner is more reactive than that produced by pyrolysis of  $\text{Si}_2\text{F}_6$ .<sup>2,3</sup>

$\text{Si}_2\text{F}_6$ (20%) in  $\text{D}_2$  and  $\text{Si}_2\text{F}_6$ (30%) in  $\text{H}_2$  at total pressures in the range of 20-60 torr were irradiated with the R(22) line of a  $\text{CO}_2$ -TEA-laser, operating at 0.3 Hz and a fluence of about 0.5 J/cm<sup>2</sup>. The photolysis cell was coupled directly to a quadrupole mass spectrometer.

Very rapid infrared photodecompositions of  $\text{Si}_2\text{F}_6$  was observed with parallel formation of  $\text{SiF}_4$ , indicating that the expected primary decomposition (1) was taking place.

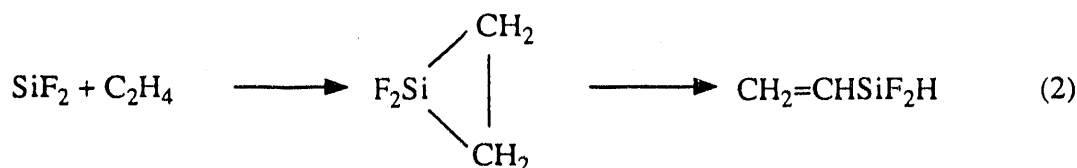


However, we could observe no products corresponding to the insertion of  $\text{SiF}_2$  in  $\text{H}_2$  or  $\text{D}_2$ . This is not surprising, if  $\text{SiF}_2$  from (1) does not contain much residual vibrational excitation, since "ab initio" calculations indicate a barrier of 270 kJ/mol for the insertion of ground state  $\text{SiF}_2$  into  $\text{H}_2$ .

The addition of  $\text{SiF}_2$  produced via (1) to the double bond of  $\text{C}_2\text{H}_4$  does, however, take place readily. The IR-Laser irradiation (as above) of  $\text{Si}_2\text{F}_6$  (16%) in  $\text{C}_2\text{H}_4$  at a total pressure in the range of 8-12.5 torr yielded new mass spectral peaks whose relative intensities were as follows:

m/z	91	92	93	94	95	112
R.I.	42	11	100	38	11	13

This spectrum is most likely due to difluorosilacyclopropane and/or difluorovinylsilane formed via (2), viz.



This would account for m/z 91-94. m/z 95 is principally due to isotopic contributions of  $^{29}\text{Si}$ ,  $^{30}\text{Si}$  and  $^{13}\text{C}$  but we have at present no explanation of the peak at 112 amu.

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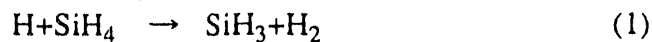
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5. Disproportionation and Combination of GeH<sub>3</sub>-Radicals

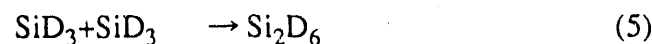
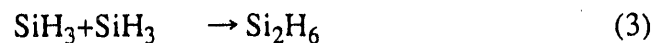
(D. Aaserud, M. V. Piserchio and F. W. Lampe, Work in Progress)

It has been shown<sup>1,2</sup> that, quite unlike CH<sub>3</sub> radicals, SiH<sub>3</sub> radicals undergo extensive disproportionation rather than combination in their bimolecular encounters. Indeed, Potzinger and co-workers have demonstrated that only at a total gas pressure exceeding ~3 atm are the probabilities of combination and disproportionation equal. One might expect that the bimolecular reactions of GeH<sub>3</sub>-radicals would be similar to those of SiH<sub>3</sub>-radicals but this has not previously been investigated experimentally.

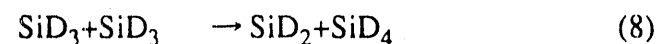
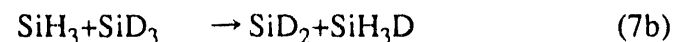
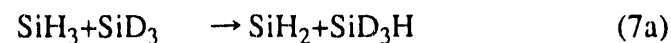
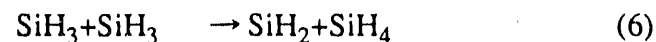
The domination of disproportionation in the silyl + silyl reaction was demonstrated by study of the isotopic composition of the disilane produced in the H-atom induced decomposition of SiH<sub>4</sub>-SiD<sub>4</sub> mixtures. Thus



If the reaction is exclusively combination then (1) and (2) are followed by

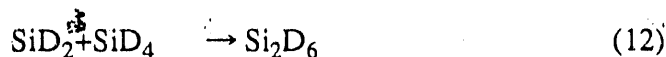
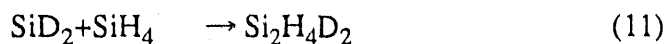
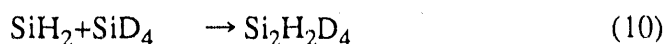
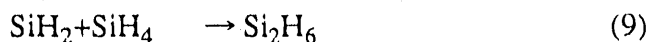


the point being that statistics favor silane-d<sub>3</sub>. On the other hand, if the reaction is exclusively disproportionation, viz.





followed by silyl insertion, i.e.



formation of disilane-d<sub>3</sub> is not possible. Experiment<sup>1</sup> showed that at pressures ~20-50 torr, disilane-d<sub>3</sub> was absent, within experimental error.

We have attempted to apply the same technique to the GeH<sub>3</sub>+GeD<sub>3</sub> reaction. However, the isotope distribution of natural Ge is such, i.e. <sup>70</sup>Ge(20.5%), <sup>72</sup>Ge(27.4%), <sup>73</sup>Ge(27.4%), <sup>73</sup>Ge(7.8%), <sup>74</sup>Ge(36.5%), <sup>76</sup>Ge(7.8%), that the extensive isotope corrections that must be made because of mass spectral fragmentation obscure the results.

A very small amount of <sup>74</sup>GeO<sub>2</sub> that we were able to obtain was used to synthesize enough <sup>74</sup>GeH<sub>4</sub> and <sup>74</sup>GeD<sub>4</sub> to carry out one set of experiments. The deuterium isotope distribution in the digermanes, after correction for mass spectral cracking at 70eV ionizing energy, are as follows:

d <sub>0</sub>	=	58
d <sub>1</sub>	=	55
d <sub>2</sub>	=	25
d <sub>3</sub>	=	24
d <sub>4</sub>	=	50
d <sub>5</sub>	=	21
d <sub>6</sub>	=	5

These results are consistent with relative steady-state germylene concentrations of [GeH<sub>2</sub>]:[GeHD]:[GeD<sub>2</sub>]=6.2:2.2:1.0. The asymmetric distribution of isotopic germylens probably is due primarily to the H/D isotope effect in the primary reaction of H with GeH<sub>4</sub> and GeD<sub>4</sub>.

Although these results are very preliminary, the low concentration of  $\text{Ge}_2\text{H}_3\text{D}_3$  suggests that disproportionation is predominant, just as in the silyl + silyl reaction. Unfortunately, the one experiment essentially exhausted the small supply of  $^{74}\text{GeH}_4$  and  $^{74}\text{GeD}_4$  and we cannot continue these experiments until we obtain more  $^{74}\text{GeO}_2$ . In the renewal proposal accompanying this report we have requested funds to purchase sufficient  $^{74}\text{GeO}_2$  from Oak Ridge to complete the project.

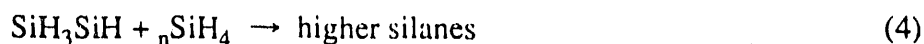
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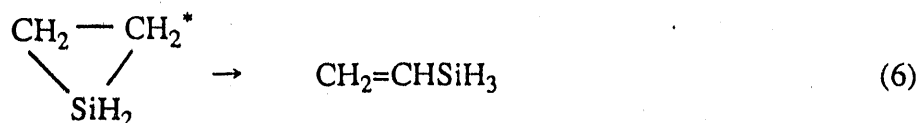
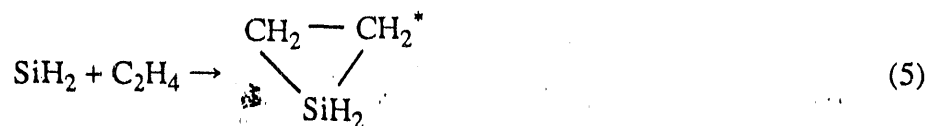
### 6. The Reactions of $\text{SiH}_2$ with $\text{C}_2\text{H}_4$

(J. R. Fisher and F. W. Lampe, J. Phys. Chem., to be submitted)

We have completed a study of the competition reaction of  $\text{SiH}_2$ , produced via the infrared multiple photon decomposition of  $\text{SiH}_4$ , with  $\text{C}_2\text{H}_4$  and  $\text{SiH}_4$  and have found that  $\text{SiH}_2$  produced in this manner reacts with  $\text{SiH}_4$  faster than with  $\text{C}_2\text{H}_4$  by a factor of 5.3. It is known<sup>1,2</sup> that the reaction of IR-laser produced  $\text{SiH}_2$  with  $\text{SiH}_4$  produces mainly  $\text{Si}_2\text{H}_6$ , with some higher silanes being formed via the reactions (1)-(4).



The reaction of  $\text{SiH}_2$  with  $\text{C}_2\text{H}_4$  leads essentially exclusively to  $\text{C}_2\text{H}_3\text{SiH}_3$ , presumably via the sequence



The rates of  $\text{SiH}_4$  depletion, and  $\text{Si}_2\text{H}_6$  and  $\text{C}_2\text{H}_3\text{SiH}_3$  formation as a function of the  $[\text{C}_2\text{H}_4]/[\text{SiH}_4]$  reactant rates is shown in Figure 1, and it is from such data that we are able to evaluate the rate constant ratio,  $k_1/k_5$ , to be 5.3 at 300K. Studies of the temperature dependence of this ratio indicate that there is an activation barrier for reaction of  $\text{SiH}_2$  with  $\text{C}_2\text{H}_4$  that is 3.3 kJ/mol greater than for insertion into the SiH bond of  $\text{SiH}_4$  (cf Figure 2).

These results are in satisfactory agreement with the absolute rate constant measurements of Jasinski and coworkers<sup>3</sup> for the depletion of  $\text{SiH}_2$ .

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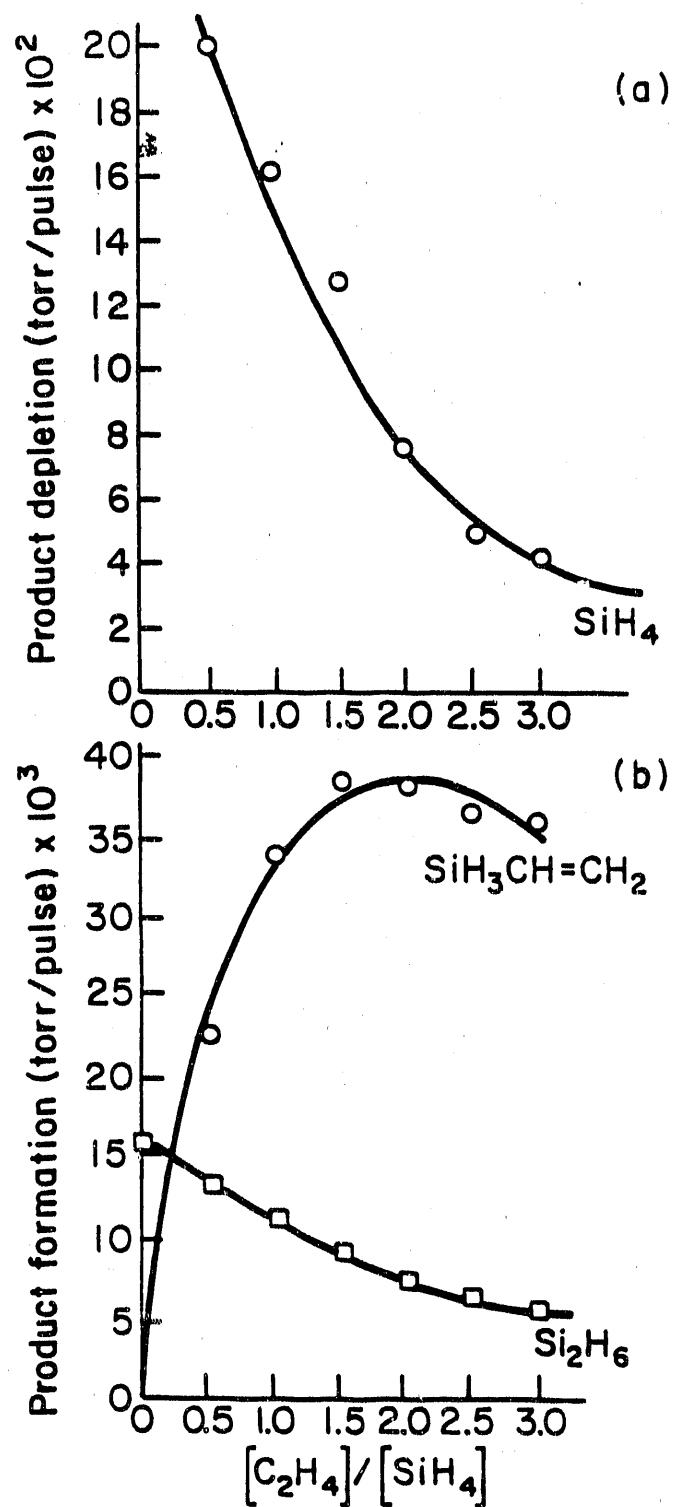


Figure 1: Plot of the (a) reactant silane depletion and (b) disilane and vinylsilane production versus the  $[C_2H_4]/[SiH_4]$ .

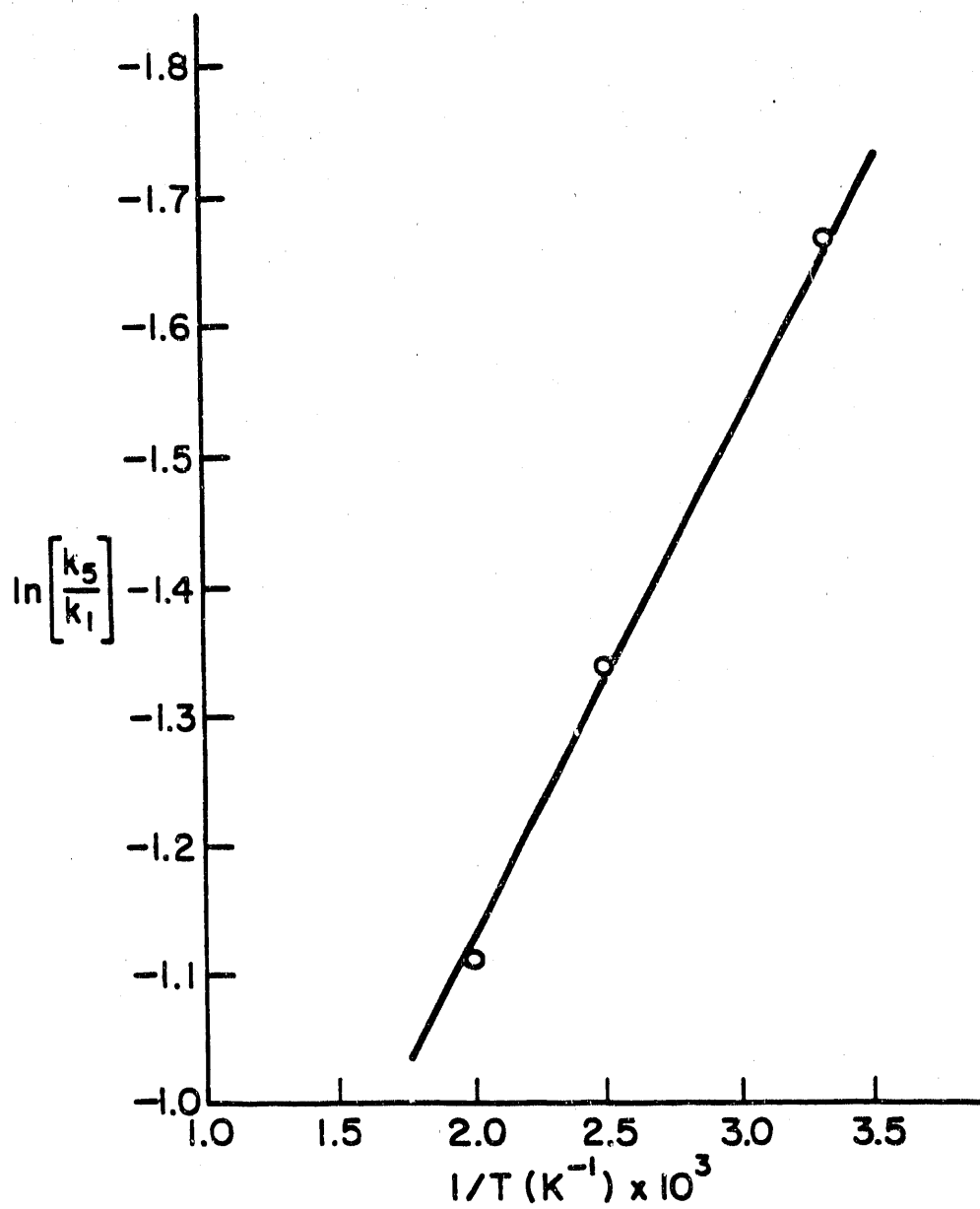


Figure 2: Arrhenius plot of  $k_5/k_1$  versus  $1/T$ .

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