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PYROLYSIS OF TETRAMETHYLTIN

BY

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A THESIS

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ABSTRACT

The pyrolysis of tetramethyltin has been studied in a toluene carrier flow system from 802°K to 907°K using pressures ranging from 10.6mm. to 52.4mm. An extensive study was also carried out in a packed vessel from 807°K to 940°K using pressures ranging from 16.7 to 28.4mm. The results obtained by product analysis were verified by measuring the undecomposed alkyl remaining. The agreement between these two analyses suggests 4 methyl radicals are released for every alkyl molecule which undergoes decomposition. The release of the first radical is rate controlling. Decomposition was found to be 1st order and rate constants calculated showed no dependence on total pressure, surface to volume ratio, toluene to alkyl ratio, or contact time. Some work was also done on $(k_a/k_r^{\frac{1}{2}})$ studies. The Arrhenius equation obtained was:

$$\log_{10}k_1 = 15.67 - (64{,}500/2.303RT)$$

where k_1 refers to the process

$$Sn(CH_3)_4 \longrightarrow Sn(CH_3)_3 + CH_3$$

The activation energy of this homogeneous process, 64.5 kcals/mole, may be equated to $D\left[(CH_3)_3{\cdot}Sn - CH_3\right]$.

ACKNOWLEDGEMENTS

To Dr. S.J.W. Price whose patience, encouragement and continual help have made this work possible.

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A - Frequency of the Arrhenius Equation.

D - Bond dissociation energy.

E - Arrhenius Activation Energy.

E_∞ - Arrhenius Activation Energy at infinite pressure.

h - Plank's constant.

K - Transmission Coefficient.

k_1, k_2 - Specific rate constants.

k - Specific rate constant at infinite pressure.

n - Number of atoms in a molecule.

R - Gas constant.

S - Number of degrees of freedom.

T - Absolute temperature.

v - Vibrational frequency.

CHAPTER I

INTRODUCTION

General Remarks

The metal alkyls of Group IV B, have been the subject of discussion for many researchers. Tetraethyl germanium has been studied by Geddes and Mack (1) who determined the decomposition to be first order with an observed activation energy of 51.0 kcals/mole. Tetramethyl lead was studied in a toluene carrier flow system by Price and Webster (2) who found its decomposition to be first order and the activation energy of the homogeneous process (Me_3 Pb - Me) to be 48.6 kcals/mole.

Of the related tin compounds, only dimethyltin-chloride has been studied using this system. The decomposition (3) was found to be first order and homogenous within a pressure independent region, with the strengths of the first two metal - carbon bonds found to be 56.1 and 34.0 kcals/mole knowing an average value of 45 kcals/mole. Tetramethyltin has a mean bond energy found by calorimetric procedures of $\bar{E}$ = 53.5 kcals/mole.(4) The kinetics of tetramethyltin decomposition have been studied by Waring and Horton (5) who reported the pyrolysis to be approximately first order and by Sathyamurthy et al (6)who reported an order of 3/2 and proposed a mechanism which agrees with this, but both investigations may be said to have dubious results as discussed in (7). The reaction is too complex to be studied in a simple manometric system. It is unlikely that the reported parameters have any relevance to the initial bond breaking reaction. The reaction was carried out in a static system and the rates were followed manometrically in a static system of crude apparatus.

This study will contain among other things ratio studies, contact time studies, pressure studies and surface to volume effects.

BOND DISSOCIATION ENERGIES BY THE KINETIC METHOD

The dissociation energy, $D(R_1-R_2)$ may be defined as the heat of reaction at absolute zero and in the ideal gas state of [1].

$$R_1R_2 \rightleftharpoons R_1 + R_2 \qquad [1]$$

This is based on the assumption that the activation energy of the reverse recombination reaction, E_{-1} is zero. Therefore with this assumption, we can say the bond dissociation energy is equal to the energy of the reaction.

There is considerable experimental justification for the assumption of zero energy of activation for the recombination. An energy of activation would imply that two atoms of appropriate spin would suffer some repulsion before combining. This would be a hump on the potential energy curve. Band spectrometric measurements show that usually no such potential maximum exists. The situation for polyatomic atomic molecules is much more complex, mainly because of the difficulties encountered in measuring the rates of recombination of radicals. A number of rates have been measured and the activation energy of recombination has been found to be zero, or nearly zero.(8-13)

If there is no potential energy barrier for the recombination of two radicals, the transition state theory predicts that the unimolecular rate constant is given by:

$$k_1 = K \frac{kT}{h} \frac{\phi^*(T)}{\phi\ (T)} e^{-H/RT} \qquad [2]$$

where ϕ (T) and ϕ^*(T) are the total partition functions for the normal molecule and activated complex, respectively. But since by assumption, that the dissociation energy at absolute zero and in the ideal gas state of the process R_1-R_2 is equal to the heat of reaction, we may write that $D = \Delta E$.

But also at absolute zero, $\Delta H = \Delta E$, equation [2] may be rewritten,

$$k_1 = K \frac{kT}{h} \frac{\phi^*(T)}{\phi\ (T)} e^{-D/RT} \qquad [3]$$

These total partition functions may be divided into their translational, rotational and vibrational aspects and if we assume that the rotational partition functions are both approximately equal to each other in both the normal molecule and the activated complex and that the vibrational partition function for all modes other than the one leading to dissociation are also approximately the same in both states, we get:

$$k_1 = K \frac{kT}{h} \left(1 - e^{-hV/kT} \right) e^{-D/RT} \qquad [4]$$

At low temperatures or when the vibrational frequency is high, as for strong bonds,

$e^{\frac{-hV}{RT}} \longrightarrow 0$ and equation [4] becomes

$$k_1 = K\,\frac{kT}{h}\,e^{-D/RT} \qquad [5]$$

$$\therefore\ \ln k_1 = \ln K\,\frac{kT}{h} + \ln T - \frac{D}{RT} \qquad [6]$$

$$\therefore\ \frac{d(\ln k_1)}{dT} = \frac{1}{T} + \frac{D}{RT^2}$$

$$= \frac{D + RT}{RT^2} \qquad [7]$$

At high temperatures or when the vibrational frequency is low,

$$e^{\frac{-hV}{k\,T}} \longrightarrow \frac{hV}{k\,T} \quad \text{because } \lim_{x \to 0}\,(1 - e^{-x}) = x$$

$$\therefore\ k_1 = K\,V\,e^{-D/RT} \qquad [8]$$

$$\therefore\ \ln k_1 = \ln KV - \frac{D}{R\,T} \qquad [9]$$

$$\therefore\ \frac{d(\ln k_1)}{dT} = \frac{D}{RT^2} \qquad [10]$$

Equations [6] and [9] are of the same form as the differential form of the Arrhenius equation with bond energy D replacing the activation energy E . Therefore, the limits as follows are placed on the experimental activation energy.

$$D \leq E \leq (D + RT)$$

If the experimental activation energy for unimolecular decomposition can be accurately determined, it should be a reasonable approximation to the bond dissociation energy. It should be noted that in the preceeding discussion, it was assumed that the experimental energy involved is the high pressure activation energy determined in the pressure independent region.

Other methods for the determination of bond dissociation energies (calorimetric, electron impact, spectroscopic methods et-cetra) are clearly outlined in a review by Szwarc. (14)

TOLUENE CARRIER TECHNIQUE

The toluene carrier technique is used to study unimolecular reactions that cannot be studied by a simple flow system. The radicals produced react preferentially with the carrier (toluene) rather than themselves. Experimental activation and bond energies may be determined, by measuring the unimolecular rate constants at various temperatures. Careful experimentation may lead to a high degree of accuracy but interfering side or competing reactions must be absent in order that the rate constant determined will be the unimolecular decomposition one.

The technique is based on the stability of the benzyl radical and the ease of the hydrogen abstraction reaction between many radicals and toluene. The benzyl radicals produced can combine in the reaction zone with R• to form a stable molecule, $C_6H_5CH_2R$. If the benzyl radical produced does not react in the hot zone under the experimental conditions used, it dimerizes outside to form dibenzyl. The production of dibenzyl proves that the decomposition is to two radicals rather than two molecules.

$$C_6H_5CH_3 \quad + \quad R \longrightarrow \underset{\text{benzyl radical}}{C_6H_5CH_2} \quad + \quad RH \qquad (1)$$

In the case of tetramethyltin, methyl radicals are produced. In the large excess of toluene, they can either recombine to form ethane or abstract a hydrogen atom from toluene to form a benzyl radical and a stable molecule.

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (2)$$

$$CH_3 + C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + CH_4 \qquad (3)$$

The benzyl from (3) can react in two common ways.

$$C_6H_5CH_2 + CH_3 \longrightarrow C_6H_5C_2H_5 \qquad (4)$$

$$2C_6H_5CH_2 \longrightarrow \underset{\text{dibenzyl}}{(C_6H_5CH_2)_2} \qquad (5)$$

This method is ideal for thermal studies of metal alkyls. Many other methods have proven unsatisfactory. The radicals produced in the initial bond rupture are too reactive to allow any thermal equilibrium method to be used. The molecules are too complex for the successful application of a spectroscopic method. Electron impact experiments will give only an upper limit of the dissociation energy. The derivation of dissociation energies from photochemical results would require a detailed knowledge of the mechanism by which the molecule absorbs energy.The complexity of the reactions in a static system is such that unambiguous interpretation of the results is almost impossible.

The technique enables reactant pressures and per cent decompositions to be varied greatly. In previous systems, reactant pressures .05 to 2.0mm. have been employed. Per cent decompositions can go from .1% to 98%.In calculating the rate constants from flow system data, the assumption is made that no mixing occurs in the reaction zone. The course of the reaction may then be studied by measuring the amounts of methane, ethane, ethylene and ethyl benzene.

Some limitations of the toluene carrier technique are as follows:

1. The alkyl bond to be investigated should be at least 10kcal/mole weaker than the C—H bond in the toluene side chain, and must of course be the weakest of the alkyl bonds.

2. It is assumed that each differential element of the volume flows through the reactor as though it were confined, at constant pressure, between two pistons, that is

plug flow. The problem of defining a residence time is a real one in tubular reactors. Ideally, every particle of the fluid should remain in the reactor the same amount of time, or the chemical reaction would not have proceeded to the same extent throughout the fluid.

3. Flow rates used must be such as to maintain thermal equilibrium and plug flow throughout the reaction zone.

4. If any surface reactions become significantly large, the rate constants determined will not be those for homogeneous unimolecular decomposition.

5. Any thermal decomposition of the toluene must be taken into account. Below 700°C. however, as all runs done in this work were, the toluene decomposition is less than 0.01% (16, 17). If the runs are done at decompositions where toluene decompositions would play a part, suitable corrections can be made. (18)

CHAPTER II

EXPERIMENTAL TECHNIQUE

Apparatus and Procedure

A schematic diagram of the toluene carrier flow system used in this work is seen in Fig. 1.

The vacuum source of the system was a two stage mercury diffusion pump backed by a two stage oil sealed rotary vane fore pump, Balzer Duo 5. All ground glass joints were lubricated with Dow Corning High Vacuum Silicone Stopcock Grease. Any heated taps were lubricated with Apiezon T Grease, while unheated ones had Apiezon N for lubrication. Due to the fact toluene tends to attack grease, Ace Glass greaseless Vitron "O" ring taps were used for the carrier inlet system of the main system.

An electric furnace was used to heat the reaction vessel. The furnace was constructed from a quartz cylinder three inches in diameter and twenty-four long with a wall thickness of one-quarter inch. The quartz cylinder was wound with Chromel-A Resistance ribbon 2mm. wide and .2mm. thick, having a resistance of 0.603 ohms per foot. The windings were cemented into place with Sauereisen Cement, Number 31. The spacing of the windings is shown in Fig. 2. The heating ribbon was tapped at seven points so that the temperature profile could be adjusted by shunt resistances. An inconel liner 2.5 inches in diameter, 12 inches long, and .25 inches thick was centered inside the quartz cylinder to even out the temperature profile.

The quartz tube was centered in a box (12x12x24 in.)

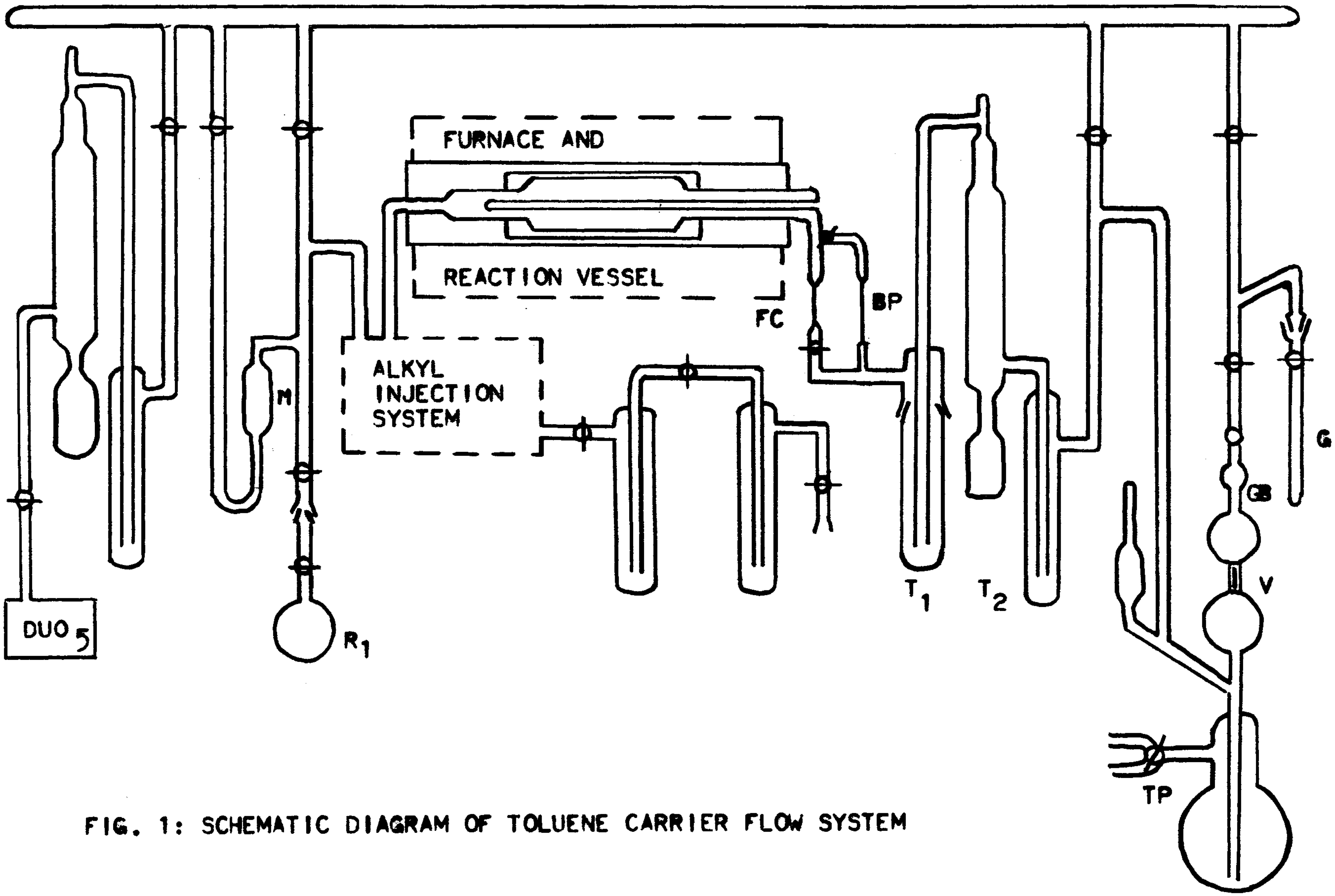

FIG. 1: SCHEMATIC DIAGRAM OF TOLUENE CARRIER FLOW SYSTEM

constructed of .25 inch asbestos with a .75 inch angle iron frame. The box had 3 inch diameter holes in both ends to accomodate the above described quartz cylinder. Powdered alumina was added to the box to act as insulation. The furnace was connected throug a Type W 20 HM Variac (Autotransformer) to the 220 volt A-C laboratory power source. The maximum operating temperature of the furnace was 1100°C.

The temperature of the furnace was controlled by a Sunvic Resistance Thermometer Controller Type RT. 2 . The temperature was measured with a chromel-P-alumel thermocouple inserted in the axial thermocouple well of the reaction vessel in conjunction with a Leeds and Northrup Millivolt Potentiometer Type 8691. The temperature of the reaction zone was kept within ± 2° with a steep fall off at the ends. See Fig. 3. A 10 ohm platinium resistance thermometer was mounted along the inside wall of the inconel liner as the sensing element for the Sunvic Controller.

The reaction vessels were made of fused quartz tubes 40mm. O.D., and 6 to 8 inches long. The ends were sealed to 20mm. O.D. quartz tubing which ended with graded quartz to Pyrex seals, a few inches beyond the ends of the furnace. An axial thermocouple well constructed of 10mm. O.D. tubing ran the length of the vessel.

The flow rate through the reaction zone was controlled by two methods. The first was by means of varying

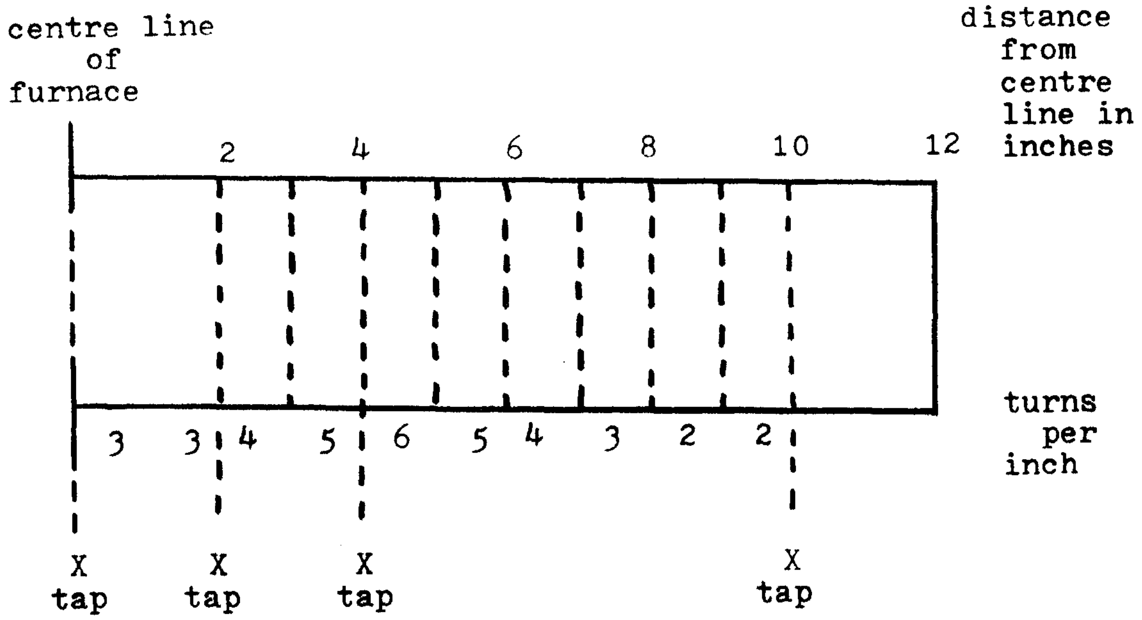

Fig.2 : Furnace block with taps for changing the temperature profile.

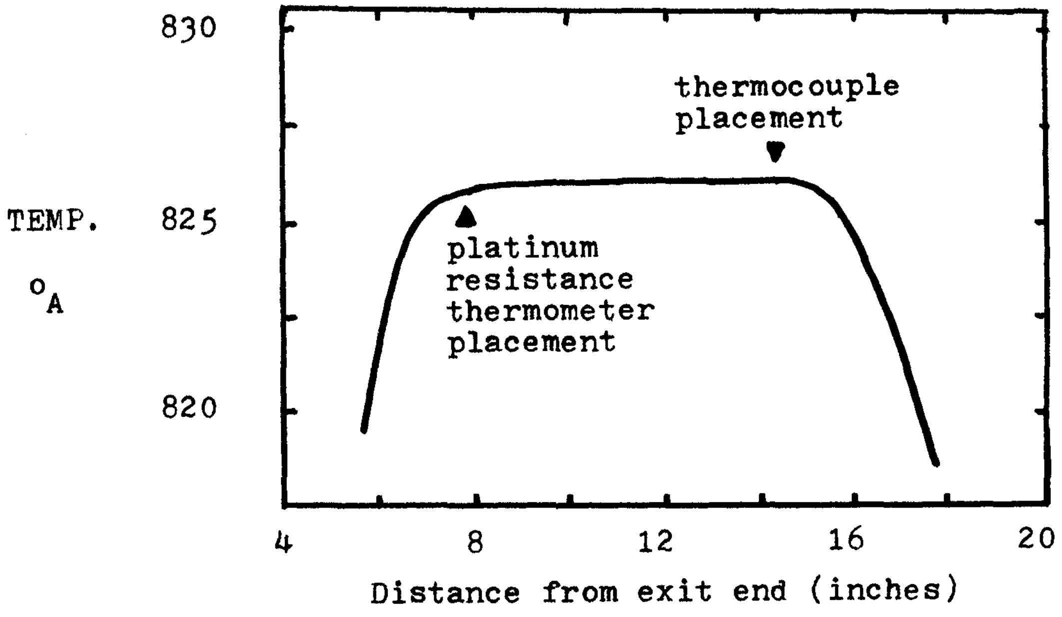

Fig. 3 : A Typical Temperature Profile

the length and inside diameter of the sealed in capillary at the outlet of the furnace. The second method was using an Edwards High Vacuum 10-turn Valve, in place of the capillary. A by-pass made of glass tubing was installed around the valve to prevent clogging of the Edwards Needle Valve. Tubing near the inlet and exit side of the reaction vessle was wound with Chromel "A" asbestos covered heating wire connected to a Variac. This allowed the tubing to be heated up to approximately 90°C when necessary.

All runs were carried out by essentially the same procedure. After the furnace was steady at the particular temperature and the vacuum had reached 10^{-4} mm. of Hg or better, the run could then begin. The toluene was stored in a detachable vessel R_1 which could be weighed prior to and after each run. A water bath was placed around the bulb to keep the desired pressure of toluene at a constant value. The toluene pressure was read on a mercury manometer along with a dioctylphthalate-mercury differential manometer (M in Fig. 1) with a 9.4 magnification factor as compared to the mercury manometer.

A small amount of alkyl was distilled from R_2 to the finger F_1 (Fig. 4). A fixed temperature bath in a Dewar flask was placed around F_1 to obtain a desired alkyl pressure. The alkyl vapour pressure was at all times greater than the toluene carrier pressure. The magnitude of the difference determined the concentration of the alkyl in the toluene

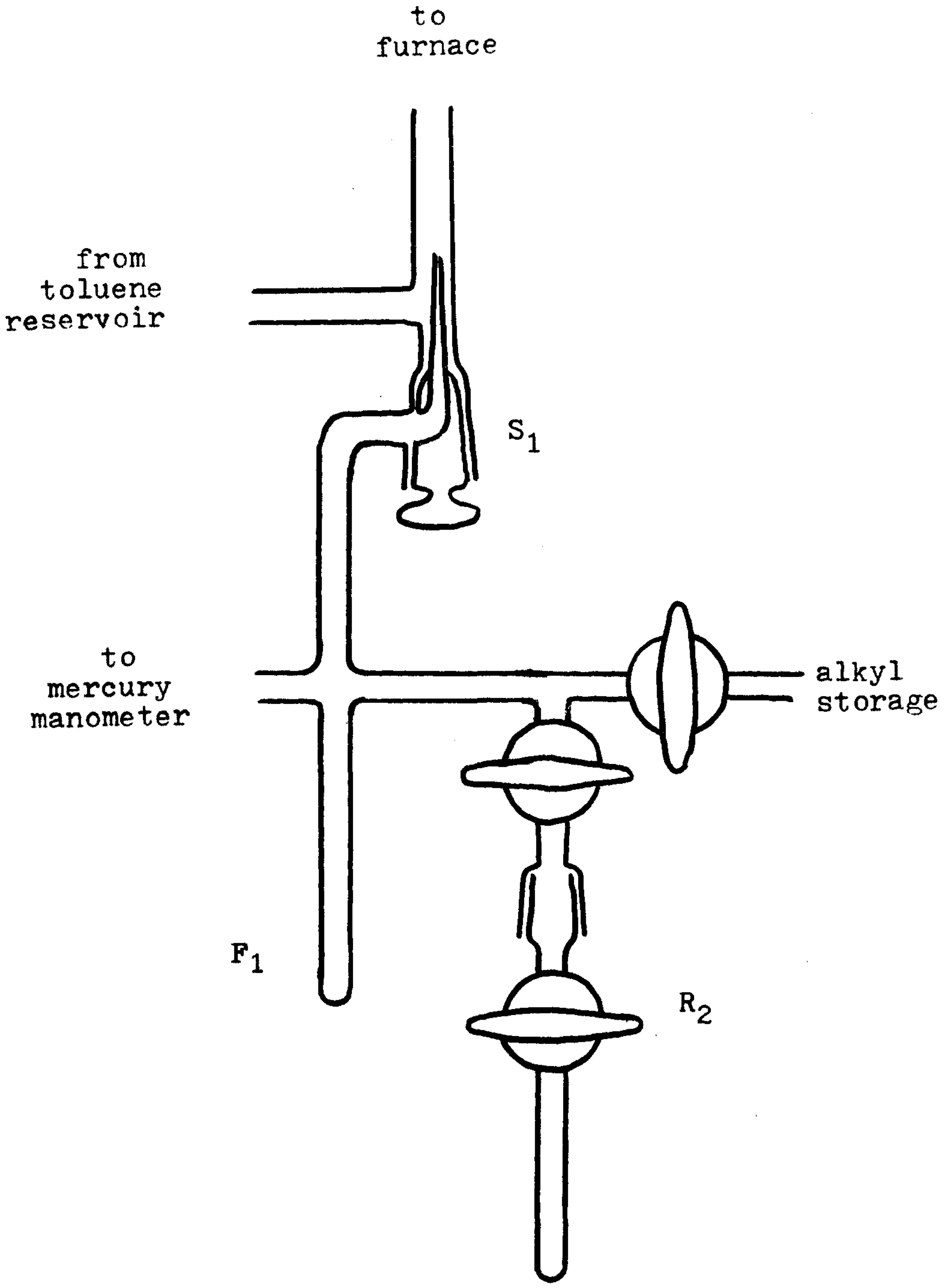

Fig.4 : Alkyl Injection System

stream.

The flow of toluene was commenced and the pressure, as measured by the mercury of differential manometer, was recorded. A pre-run flow of toluene was allowed for five minutes to help stablize flow conditions. After the pre-run of toluene, tap S_1 was opened and alkyl was admitted into the toluene stream. The flow of alkyl continued from 20 minutes to 55 minutes depending on the reaction conditions. This was followed by another 5 minute post-run of toluene. The alkyl remaining in F_1 was redistilled into R_2 and then both R_1 and R_2 were reweighed to determine the amounts of toluene and alkyl used.

Trap T_1, thermostated at -80°C. with an acetone dry ice sludge, collected the liquid products. For insurance Trap T_2, was maintained at -110°C. using an ethanol sludge to trap any liquid products which were not trapped out by T_1.The remaining gaseous mixture was transferred by means of a Toepler pump passed a non-return valve to a calibrated gas buret. After toepling for approximately seven minutes after the run, the P.,V.,T., data of the gaseous mixture were measured. Toepling was carried out continuously during the run to prevent any back diffusion due to build up of pressure from product formation.A sample of the gaseous products was then taken to a gas chromatograph for analysis.

During the run, the temperature of the vessel and pressures of the alkyl and toluene were monitored periodically, in most cases every five minutes. The readings for the entire run were averaged and these values were accepted as constant over the total run. Conditions were kept as constant as possible and only small deviations were noted through out the run.

The gas chromatographic analysis was carried out using a Perkin Elmer 154 gas chromatograph equipped with a 1/4 inch, 6 foot silica gel column. The column temperature was set at 80°C. and a helium flow rate of 7 pounds per square inch. Fig. 5 shows the injection system used for the gas analysis. The sample vessel G was placed in position shown with a steel bar resting on the break seal and this region evacuated. The "U" tube between C_2 and C_3 was also evacuated and then isolated. The break seal was broken by raising the steel bar with a magnet and dropping it, allowing the gas to go into the upper section of the vessel. A new type gas vessel was tried for the last twenty runs. It is seen in Fig. 5. It saved a great deal of glass blowing and worked just as efficiently as the former all glass type with the break seal. A part of the gas sample was then transferred to the gas buret and the pressure measured using a cathatometer. C_2 was then opened and the mercury raised to force the sample into the "U" tube. C_2 was then opened to allow helium to flow into the "U" tube and C_3 was simultaneously connected so that it connected the "U" tube to the column. Calibration curves were constructed

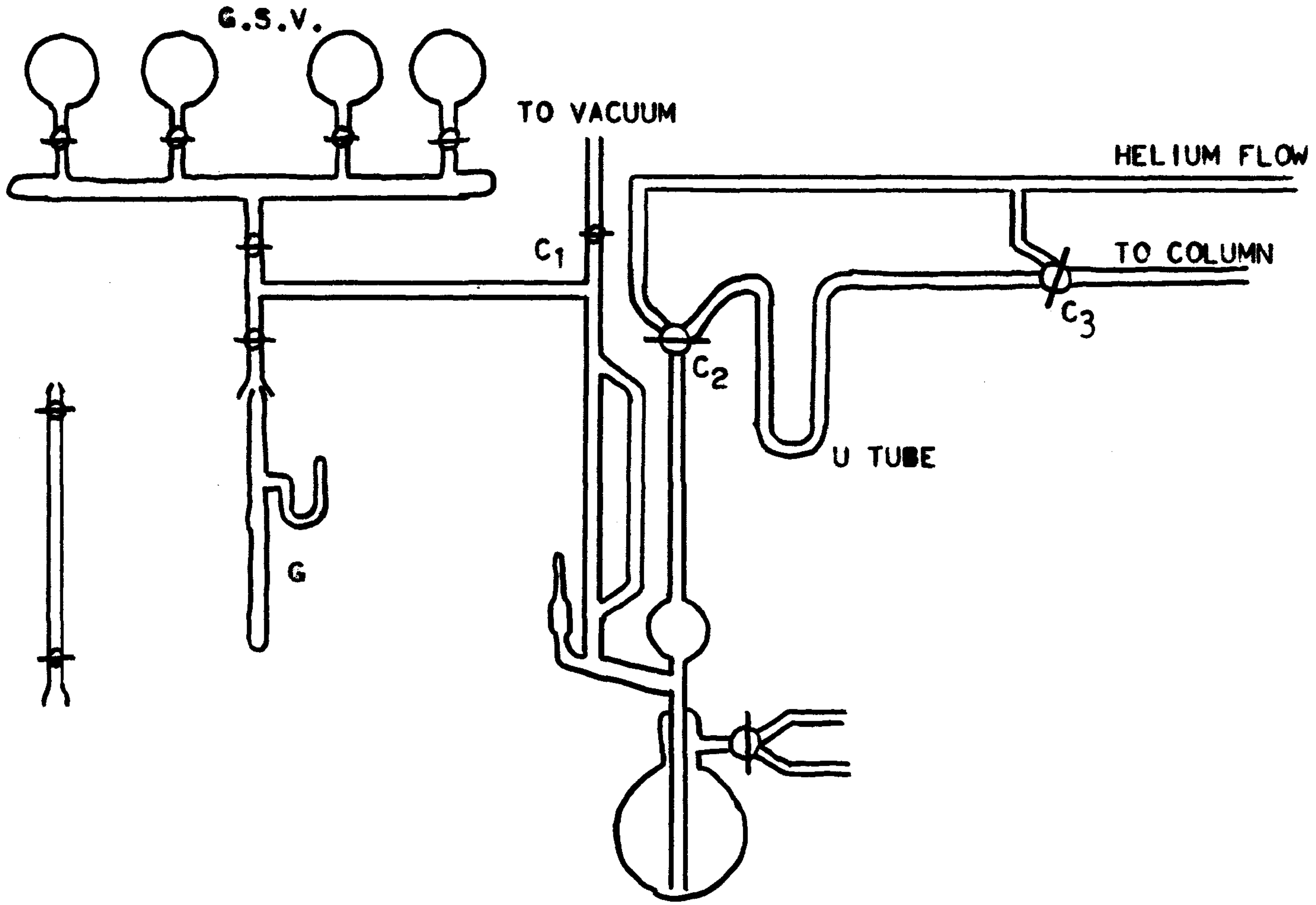

FIG. 5: SCHEMATIC DIAGRAM OF THE INJECTION SYSTEM USED FOR GAS ANALYSIS.

using pure gases from the gas storage vessels (G.S.V.) with each set of analysis so that the peak heights could be used for analysis. As many samples as possible were run for each run gas vessel and the results were averaged.

The liquid sample collected in traps T_1 and T_2 if any managed to get by T_1, were redistilled back to trap T_1 and analyzed on a Perkin Elmer 800 gas chromatograph equipped with a flame ionization detector. A .02 inch I.D. 150 foot open tubular column coated with polypropylene glycol (Perkin Elmer R) was used. Nitrogen was used as a carrier gas and the column maintained at 60°C. Synthetic mixtures containing the components present in the liquid samples were made by accurately weighing each component in a known tared 25ml. volumetric flask, with a long neck and a ground glass top. From these calibration mixtures, which contained the same relative amounts of the various components, calibration curves were constructed. For each batch of samples, the curves were checked and since the mixtures were of the approximate strength as the standards, a peak height comparison could be used to determine the composition of the liquid samples.

Preparation of Materials

A. TOLUENE

The toluene used was that of Eastman Organic Chemicals, Number X325 which was made from sulfonic acid. It was dried by refluxing over sodium ribbon for 24 hours under vacuum and then degassed by repeated bulb to bulb degassings or distillations.

B. Tetramethyltin

The tetramethyltin was commercially available from Alfa Inorganics, Inc., Number SN-145. It was checked for purity on the gas chromatography unit and degassed and purified by bulb to bulb distillations. The vapour pressure curve was checked against that of Bullard and Haussman (15) and found to correspond. The melting point from literature was -54.8°C. and the boiling point was found to be 78°C. The refractive index of 1.4409 and a specific gravity of 1.2904 agreed with those found in (5).

CHAPTER III

Experimental Results and Discussions

PYROLYSIS OF TERTAMETHYLTIN

The labratory data from experiments on the pyrolysis of tetramethyltin giving the experimental conditions and product analysis are found in Tables I and IB. Liquid products were found to contain only $SnMe_4$ and ethylbenzene; significant amounts of xylenes were not observed over the total experimental scope. The gas products were mainly methane with lesser amounts of ethane and ethylene. Small amounts of colourless needlelike crystals were seen in the bypass area of the exit of the furnace. It was found to melt about 50°C. but no effort was made to purify this product as only small amounts were present after a series of twenty runs. It was concluded to be dibenzyl (m.p. 56°C.) from the melting point and from basic toluene carrier flow system theory.

The vapour pressures of the starting commercial tetramethyltin as compared to literature values are shown in Fig.6 and Table II. It was found to coincide almost exactly.

The thermal decomposition of tetramethyltin was studied over the temperature range 802°K to 907°K and pressures from 1.06cm. to 5.24cm. The results are presented in Table III. The rate constants were calculated from the

TABLE I
THE PYROLYSIS OF TETRAMETHYLTIN
FUNDAMENTAL DATA

RUN	P. (mm.)	Temp (^{o}K)	TIME* (min.)	TOLUENE (gm.)	ALKYL (moles x 10^{-3})	TOL/ALK (molar ratio)	CH_4	C_2H_6 (moles x 10^{-4})	C_2H_4	Eth ϕ
Sn 1	16.17	817	5,20,5	6.00	.3824	114/1	.671	.0102	.0041	.113
Sn 2	18.72	822	5,20,5	7.00	2.3181	17/1	3.388	.1415	.0900	1.009
Sn 10	21.21	822	5,20,5	6.90	1.1983	42/1	2.084	.0436	.2858	.690
Sn 5	21.87	822	5,20,5	7.00	1.5670	32/1	2.145	.1046	.0549	.587
Sn 23	21.81	822	5,20,5	6.90	1.4835	38/1	2.763	.0117	.0058	.300
Sn 11	21.91	822	5,50,5	13.80	2.0416	61/1	4.240	.0261	.0261	.479
Sn 7	22.57	822	5,20,5	5.50	1.5188	23/1	3.855	.0902	.0644	.612
Sn 6	22.88	822	5,20,5	7.50	.9342	58/1	1.568	.0220	.0135	.199
Sn 12	23.19	822	5,50,5	14.60	1.9695	67/1	2.698	.0375	.0312	.509
Sn 9	23.74	822	5,20,5	4.30	1.4293	22/1	4.212	.1429	.1044	.688
Sn 22	18.09	822	5,21,4	5.55	1.3622	31/1	1.800	.0539	.0404	.699
Sn 64	22.55	838	5,27,8	3.50	.1146	299/1	.106	.0014	.0009	.029
Sn 66	23.02	839	5,35,5	10.55	.1420	628/1	.813	.0031	.0021	.085
Sn 65	22.52	845	5,35,5	10.15	.5558	154/1	2.967	.0330	.0181	.325
Sn 67	23.18	851	5,20,5	6.80	.5748	86/1	4.066	.0872	.0581	.751
Sn 87	15.44	861	5,45,5	7.80	.0710	977/1	.585	.0052	.0052	.129
Sn 79	11.39	862	5,20,5	8.15	.1431	412/1	.811	.0066	.0006	.096
Sn 82	13.62	862	5,30,5	3.13	.1632	156/1	.213	.0339	.0148	.272
Sn 78	15.06	862	5,30,5	14.25	.1051	1446/1	.879	.0075	.0019	.089
Sn 83	15.43	862	5,20,5	4.35	.4031	78/1	3.171	.0846	.0507	.678
Sn 80	14.44	864	5,20,5	4.30	.1359	229/1	1.423	.0163	.0131	.202
Sn 81	15.27	864	5,25,5	3.90	.1901	159/1	2.354	.0328	.0164	.368
Sn 84	15.38	864	5,20,5	4.13	.5614	53/1	4.648	.1494	.1217	.843
Sn 85	15.47	864	5,20,5	4.33	.2941	107/1	4.289	.0429	.0490	.389
Sn 86	15.50	864	5,20,5	4.39	.1515	209/1	1.470	.0227	.0189	.182
Sn 96	35.56	864	5,21,5	19.05	.2349	607/1	1.627	.0129	.0097	.0495
Sn 95	23.93	865	5,20,5	1.23	.6610	13/1	16.363	1.4497	1.3231	1.740

Sn 98	40.62	866	5,28,7	1.80	.5480	23/1	15.401	.8070	.8638	1.800
Sn 97	52.41	866	5,20,5	3.70	.1498	178/1	4.061	.0795	.0901	.370
Sn 94	10.64	867	7,23,5	4.67	.1845	180/1	1.491	.0202	.0156	.308
Sn 93	14.87	867	5,20,5	3.87	.2304	121/1	2.502	.0453	.0330	.530
Sn 88	20.14	867	5,20,5	5.70	.3199	129/1	3.491	.0475	.0475	.849
Sn 91	20.18	867	5,20,5	11.27	.2975	274/1	1.967	.0270	.0222	.266
Sn 92	20.21	867	5,20,5	18.73	.3215	422/1	1.393	.0742	.0824	.299
Sn 89	20.21	867	5,20,5	4.07	.3148	93/1	4.563	.0912	.0738	1.152
Sn 69	22.99	867	5,40,5	11.60	.2315	435/1	3.093	.0222	.0197	.331
Sn 68	23.11	867	5,30,5	8.80	.4451	161/1	5.607	.0668	.0487	.836
Sn 90	20.23	868	5,20,5	1.93	.2136	65/1	4.963	.2095	.1599	1.409
Sn 76	14.67	876	5,20,5	11.85	.2679	320/1	2.074	.0228	.0137	.257
Sn 77	13.11	877	5,36,4	15.00	.3277	453/1	2.691	.0219	.0156	.396
Sn 70	22.50	896	5,25,5	5.75	.2505	178/1	6.541	.0904	.0506	1.354
Sn 75	16.74	908	5,30,5	18.63	.2700	562/1	5.215	.0576	.0323	.899
Sn 73	17.66	908	5,35,5	12.88	.1148	169/1	13.832	.2654	.1475	3.478
Sn 74	17.84	908	5,30,5	9.12	.3691	179/1	8.278	.0199	.0129	2.399

* Time refers to prerun, alkyl run, and post run.

For gas products and ethylbenzene, expressed in moles x 10^{-4}.

These runs were done in the unpacked vessel.

TABLE I B
THE PYROLYSIS OF TETRAMETHYLTIN
FUNDAMENTAL DATA PACKED VESSEL

RUN	P (mm.)	TEMP (°K)	TIME * (min.)	TOLUENE (gm.)	ALKYL (moles x 10^{-3})	TOL/ALK (molar ratio)	CH_4	C_2H_6 (moles x 10^{-4})	C_2H_4	Eth φ
Sn 63	22.72	803	5,35,5	3.10	.3931	67/1	.923	.0162	.0121	.350
Sn 50	16.71	807	5,35,5	7.15	1.2694	78/1	.698	.0125	.0080	.222
Sn 25	17.43	813	5,20,5	12.40	1.6479	55/1	.616	.0179	.0019	.246
Sn 13	17.71	817	5,20,5	14.10	2.8310	36/1	9.095	.0092	.0029	.644
Sn 14	20.29	817	5,20,5	14.40	3.9017	27/1	1.633	.0627	.0348	.658
Sn 15	21.71	817	5,20,5	15,80	3.0985	44/1	1.699	.0428	.0179	.506
Sn 46	16.29	818	5,50,4	8.95	.5262	200/1	.718	.0071	.0059	.161
Sn 48	16.71	818	5,60,5	10.80	.4479	243/1	.607	.0054	.0045	.106
Sn 47	17.57	818	6,54,5	11.00	.4736	210/1	.693	.0065	.0054	.311
Sn 27	20.86	818	5,50,5	29.85	.7666	341/1	.482	.0049	.0049	.162
Sn 29	16.71	822	5,25,5	13.70	.5077	209/1	.322	.0020	.0020	.098
Sn 30	16.86	822	5,25,5	11.55	.5715	157/1	.390	.0029	.0029	.132
Sn 28	17.00	822	5,40,5	19.85	.4249	406/1	.273	.0055	.0029	.119
Sn 26	20.86	822	5,40,5	26.00	.3344	676/1	.511	.0193	.0193	.092
Sn 16	17.00	824	5,23,5	12.90	3.6740	27/1	2.387	.0963	.0368	.820
Sn 17	22.00	824	5,20,5	16.10	2.0649	56/1	1.386	.0376	.0156	.528
Sn 45	16.14	826	5,35,5	6.60	.7331	130/1	1.455	.0162	.0129	.297
Sn 46	16.29	826	5,35,5	12.60	1.9762	54/1	1.235	.0218	.0218	.356
Sn 43	16.14	834	5,30,5	6.00	1.2431	39/1	2.799	.0855	.0657	.565
Sn 42	16.14	834	5,50,5	9.90	1.0843	82/1	2.553	.0521	.0405	.439
Sn 41	16.29	834	5,20,5	4.40	.3786	84/1	1.105	.0229	.0216	.203
Sn 18	16.71	836	5,20,5	10.50	2.6885	26/1	3.541	.1709	.0579	1.218
Sn 33	17.86	836	5,25,5	14.65	.9892	114/1	1.008	.0130	.0106	.078
Sn 21	22.71	836	5,21,4	18.90	.5460	319/1	.593	.0084	.0055	.213
Sn 19	23.43	836	5,40,5	30.30	1.3186	196/1	1.392	.0288	.0144	.342
Sn 24	23.00	836	5,30,5	23.30	2.6617	71/1	2.599	.0491	.0866	.429
Sn 31	15.00	837	5,25,5	11.75	.5228	174/1	.672	.0398	.0398	.109
Sn 32	17.43	837	5,25,5	14.95	.8159	142/1	.833	.0176	.0068	.135
Sn 36	15.00	848	5,25,5	11.85	.5242	175/1	1.073	.0026	.0022	.182

TABLE IB
(CONTINUED)

Sn 34	17.57	848	5,25,5	14.55	1.1961	94/1	2.082	.0566	.0385	.397
Sn 35	17.86	848	5,25,5	14.75	.7113	161/1	1.172	.0284	.0216	.208
Sn 37	17.71	850	5,20,5	4.95	.4021	89/1	1.931	.0465	.0169	.380
Sn 40	23.43	850	5,20,5	7.75	.6754	86/1	2.532	.0468	.0220	.919
Sn 38	25.14	850	5,40,5	16.20	.5826	242/1	2.066	.0034	.0091	.320
Sn 39	28.14	850	5,20,5	4.15	.3931	76/1	3.724	.0731	.0366	.848
Sn 51	18.71	870	5,20,5	6.75	.4205	116/1	2.550	.0448	.0344	.675
Sn 52	18.57	879	5,20,5	6.30	.4065	112/1	4.674	.1021	.0699	1.152
Sn 58	21.30	886	5,25,5	7.40	.6548	88/1	9.721	.3378	.1853	2.171
Sn 57	20.94	886	5,45,5	11.80	.3908	336/1	5.376	.0586	.0644	.836
Sn 53	19.29	900	5,20,5	5.80	.3942	107/1	7.827	.2098	.1368	1.305
Sn 55	20,87	900	5,20,5	6.55	.2812	166/1	5.595	.1009	.0820	.928
Sn 56	21.01	900	5,45,5	11.75	.1499	697/1	3.482	.0193	.0348	.436
Sn 54	19.29	926	5,20,5	5.95	.3668	118/1	6.577	.1339	.0967	2.380
Sn 59	21.29	941	5,25,5	7.40	.4110	140/1	11.798	.3524	.1957	3.074
Sn 60	21.39	941	5,35,5	9.95	.2248	374/1	7.035	.8190	.0819	1.511
Sn 62	22.16	941	5,20,5	6.90	.5150	97/1	14.100	.5058	.2759	4.160
Sn 61	22.99	941	5,35,5	11.20	.1124	842/1	3.775	.0330	.0377	.503
Sn 49	17.29	818	5,50,5	13.70	4.9209	107/1	.212	.0070	.0050	.053

* Time refers to prerun, alkyl run and post run.

Gas products and ethylbenzene expressed in moles x 10^{-4}.

first order equation:

$$k = \frac{2.303}{t_c} \log \frac{100}{100-x}$$

where x represents the per cent decomposition. The contact time was evaluated from the expression

$$t_c = \frac{V}{22416} \times \frac{P}{760} \times \frac{273}{T} \times \frac{1}{F}$$

where V in cc. represented the volume of the reaction vessel, P in mm. the overall pressure during the run, T in ^{o}K the temperature of the reaction zone, and F in moles/sec. was the molar flow rate through the reaction zone. The per cent decomposition was calculated from:

$$\%\text{Decomp.} = \frac{\text{moles } CH_4 + 2\text{moles } C_2H_6 + 2\text{moles } C_2H_4 + \text{moles Et}\phi}{4 \text{ moles alkyl}}$$

Methyl radicals produced by thermal decomposition of metal alkyls in a toluene carrier flow system may abstract hydrogen atoms from either the side chain or the ring of toluene, or they may recombine to give ethane.

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \text{ or } C_6H_4CH_3 \quad \text{(a)}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad \text{(r)}$$

The rate expression for these reactions may be written as:

$$\frac{d\,[CH_4]}{dt} = k_a\,[CH_3][C_6H_5CH_3]$$

$$\frac{d\,[C_2H_6]}{dt} = k_r\,[CH_3]^2$$

from which:

$$\frac{k_a}{k_r^{\frac{1}{2}}} = \frac{d[CH_4]/dt}{(d[C_2H_6]/dt)^{\frac{1}{2}}[C_6H_5CH_3]}$$

when
$$\frac{d[CH_4]}{dt} = \frac{\text{moles } CH_4}{V \times t}$$

and moles CH_4 is the number of moles of methane produced in the run, V is the volume of the reaction vessel in cc., t is the length of alkyl run in seconds. Similarly,

$$\frac{d[C_2H_6]}{dt} = \frac{\text{moles}([C_2H_6]+[C_2H_4])}{V \times t}$$

C_2H_4 is included because it arises from a reaction of C_2H_6. (See reactions 9,10).

The toluene concentration assuming ideal gas conditions is given by:

$$[C_6H_5CH_3] = \frac{n}{v} = \frac{P}{RT} = \frac{Pmm./760}{82.057\ T^oK}$$

Thus the expression for $k_a/k_r^{\frac{1}{2}}$ becomes, in terms of experimental parameters

$$\frac{k_a}{k_r^{\frac{1}{2}}} = \frac{\text{moles } CH_4 \times 760 \times 82.06 \times T}{\text{moles } (C_2H_6 + C_2H_4)^{\frac{1}{2}}\ (v \times t)^{\frac{1}{2}}\ P}$$

This derivation of $k_a/k_r^{\frac{1}{2}}$ is based on the assumption that the methyl radicals are produced uniformly over the reaction zone and at a constant rate. If the partial pressure of the alkyl is kept constant throughout

TABLE III
THE PYROLYSIS OF TETRAMETHYLTIN
RESULTS

Run #	$10^3/T$		$k_a/k_r^{\frac{1}{2}}$	t_c (sec.)	% dec. (g)	% dec.(a)	log k (sec^{-1})
Sn 1	1.2240	s	390.82	1.496	5.31	4.96	-1.4382
Sn 2	1.2154	s	425.64	1.877	5.24	5.92	-1.5422
Sn 10	1.2165		413.50	1.696	6.09	6.67	-1.4314
Sn 5	1.2173	a	277.42	1.725	4.86	3.65	-1.5387
Sn 23	1.2176		340.33	1.745	5.22	5.76	-1.5125
Sn 11	1.2161		605.59	1.752	5.91	4.14	-1.4589
Sn 7	1.2158	b	491.50	2.541	7.86	8.30	-1.4916
Sn 6	1.2158		412.01	1.682	4.92	4.23	-1.5233
Sn 12	1.2164		317.49	1.753	4.24	6.30	-1.6062
Sn 9	1.2158		403.47	3.045	9.44	6.10	-1.4874
Sn 22	1.2180		357.07	1.800	4.93	4.69	-1.5512
Sn 64	1.1940	a	278.14	4.130	30.68	34.63	-1.0519
Sn 66	1.1916	a	426.93	1.769	15.98	13.39	-1.0068
Sn 65	1.1841		511.77	1.788	15.27	19.62	-1.0329
Sn 67	1.1748		538.96	1.816	22.22	29.48	-0.8592
Sn 87	1.1614	c	292.12	1.911	25.88	25.89	-0.8050
Sn 79	1.1604		996.67	.736	16.09	15.31	-0.6224
Sn 82	1.1701		689.00	3.052	38.41	29.45	-0.7992
Sn 78	1.1701	d	581.65	.834	23.47	22.95	-0.4940
Sn 83	1.1701		662.66	1.866	25.54	24.88	-0.8010
Sn 80	1.1578		681.76	1.763	31.00	34.53	-0.6769
Sn 81	1.1577		738.24	2.398	37.09	38.94	-0.7139
Sn 84	1.1686		688.95	1.957	26.86	26.29	-0.7963
Sn 85	1.1685		620.58	1.877	25.71	23.38	-0.8005
Sn 86	1.1581	c	551.74	1.855	28.62	19.82	-0.7404
Sn 96	1.1571		352.56	.996	18.32	17.46	-0.6921
Sn 95	1.1554		488.97	10.194	89.45	97.28	-0.6563

TABLE III
(CONTINUED)

Sn 98	1.1550		322.29	13.791	93.71	94.85	-0.6976
Sn 97	1.1550		224.06	7.421	79.58	76.13	-0.6694
Sn 94	1.1537		823.69	1.391	25.34	25.30	-0.6775
Sn 93	1.1537		716.71	2.011	34.61	38.01	-0.6753
Sn 88	1.1537		670.63	1.849	35.41	34.23	-0.6263
Sn 91	1.1537		660.51	.937	19.49	22.66	-0.6357
Sn 92	1.1538		655.16	.566	13.41	14.26	-0.5946
Sn 88	1.1537		670.63	1.849	35.41	34.23	-0.6263
Sn 89	1.1534		662.60	2.598	48.00	50.62	-0.5991
Sn 69	1.1537		553.86	1.728	37.87	40.39	-0.5600
Sn 68	1.1537		695.19	1.832	37.49	42.84	-0.5910
Sn 90	1.1521	b	481.79	5.479	83.22	86.31	-0.4870
Sn 76	1.1413		891.19	.641	22.46	22.85	-0.4018
Sn 77	1.1403		892.76	.678	24.13	19.70	-0.3901
Sn 70	1.1158	a	853.85	2.310	81.60	84.37	-0.1351
Sn 75	1.1011		1059.50	.598	57.99	49.07	+0.1600
Sn 73	1.1016		1150.60	1.028	70.62	73.90	+0.0763
Sn 74	1.1016		3205.20	.977	72.76	75,27	+0.1249

Not all the above runs were used in calculation of experimental parameters. Some were left out due to experimental problems.

a = air in vessel, b = bad analysis either gas or liquid
c = temperatiu re fluctuation d = unexplainable result.
s = surface effect due to first usage of vessel.

TABLE IIIB
THE PYROLYSIS OF TETRAMETHYLTIN
RESULTS

Run #	$10^3/T$		$k_a/k_r^{\frac{1}{2}}$	t_c(sec.)	% dec. (g)	% dec. (a)	log k (sec^{-1})
Sn 63	1.2461		201.20	6.214	84.59	85.35	-1.8470
Sn 50	1.2389		291.60	.825	18.93	15.86	-1.6348
Sn 25	1.2300		416.21	.537	13.45	5.07	-1.5984
Sn 13	1.2247	s	7161.50	.478	8.61	14.80	-0.7246
Sn 14	1.2247	s	352.53	.536	1.58	.82	-1.5249
Sn 15	1.2244		390.30	.523	1.88	4.82	-1.4406
Sn 46	1.2225		326.33	1.067	4.30	4.88	-1.3854
Sn 48	1.2222		282.58	1.265	4.09	1.62	-1.4818
Sn 47	1.2232		293.17	1.315	5.43	1.30	-1.3721
Sn 27	1.2183		196.75	.546	2.16	.93	-1.3969
Sn 29	1.2165		365.53	.538	2.10	3.64	-1.4020
Sn 30	1.2162		418.65	.567	2.33	4.09	-1.3796
Sn 28	1.2160		166.95	.539	2.40	3.35	-1.3453
Sn 26	1.2165	b	118.68	.505	5.08	2.58	-1.0857
Sn 16	1.2136		484.24	.546	2.36	2.59	-1.3588
Sn 17	1.2142		386.57	.515	2.44	3.54	-1.3203
Sn 45	1.2114	b	539.97	.806	6.17	3.09	-1.1020
Sn 46	1.2225		326.33	1.067	4.29	4.88	-1.3854
Sn 43	1.1988		497.47	1.336	7.37	5.53	-1.2414
Sn 42	1.1990		449.10	1.215	7.32	6.57	-1.2032
Sn 41	1.1982		439.66	1.377	9.22	3.99	-1.1531
Sn 18	1.1956		606.40	.591	4.52	5.46	-1.1067
Sn 33	1.1962	a	448.53	.528	2.88	5.00	-1.2592
Sn 21	1.1973		255.60	.492	3.82	7.83	-1.1007
Sn 20	1.1965		306.02	.488	3.42	2.45	-1.1468
Sn 24	1.1959		525.66	.489	2.95	1.26	-1.2126
Sn 31	1.1959	a	194.54	.553	4.50	2.82	-1.0795
Sn 32	1.1955		374.55	.505	3.11	3.29	-1.2027
Sn 36	1.1792		423.28	.541	6.40	7.14	-0.9126

TABLE IIIB
(CONTINUES)

Sn 34	1.1787		477.32	.516	5.58	4.77	-0.9534
Sn 35	1.1792		364.70	.517	5.20	4.87	-0.9861
Sn 37	1.1762		602.47	1.307	15.16	18.25	-0.9005
Sn 40	1.1765		573.45	1.105	13.86	13.00	-0.8695
Sn 38	1.1781		388.44	.947	10.61	12.93	-0.9262
Sn 39	1.1767		556.04	2.479	30.47	26.95	-0.8338
Sn 51	1.1498		689.26	.990	20.12	24.44	-0.6443
Sn 52	1.1377		873.67	1.042	37.95	36.74	-0.3390
Sn 58	1.1292		818.40	1.178	49.40	53.21	-0.2378
Sn 57	1.1292		707.61	1.152	52.11	54.62	-0.1942
Sn 53	1.1117		1015.20	1.148	62.30	72.85	-0.0707
Sn 55	1.1121		992.80	1.119	61.22	53.48	-0.0723
Sn 56	1.1130		698.29	1.133	67.16	66.16	-0.0076
Sn 54	1.0797	b	1079.70	1.087	64.19	66.37	-0.0247
Sn 59	1.0628	b	1031.60	1.108	97.12	94.97	+0.5084
Sn 60	1.0628		946.40	1.064	98.69	99.15	+0.6102
Sn 62	1.0630	a	599.27	1.061	96.23	99.83	+0.4901
Sn 61	1.0630		718.76	1.016	98.31	98.83	+0.6033
Sn 49	1.2225	a	306.31	1.085	13.57	16.36	-0.8716

Not all the above runs were used in calculation of experimental parameters. Some were left out due to obvious experimental problems.

a = air in vessel, b = bad analysis either gas or liquid
c = temperature fluctuation d = unexplainable
s = surface effect due to first usage of vessel

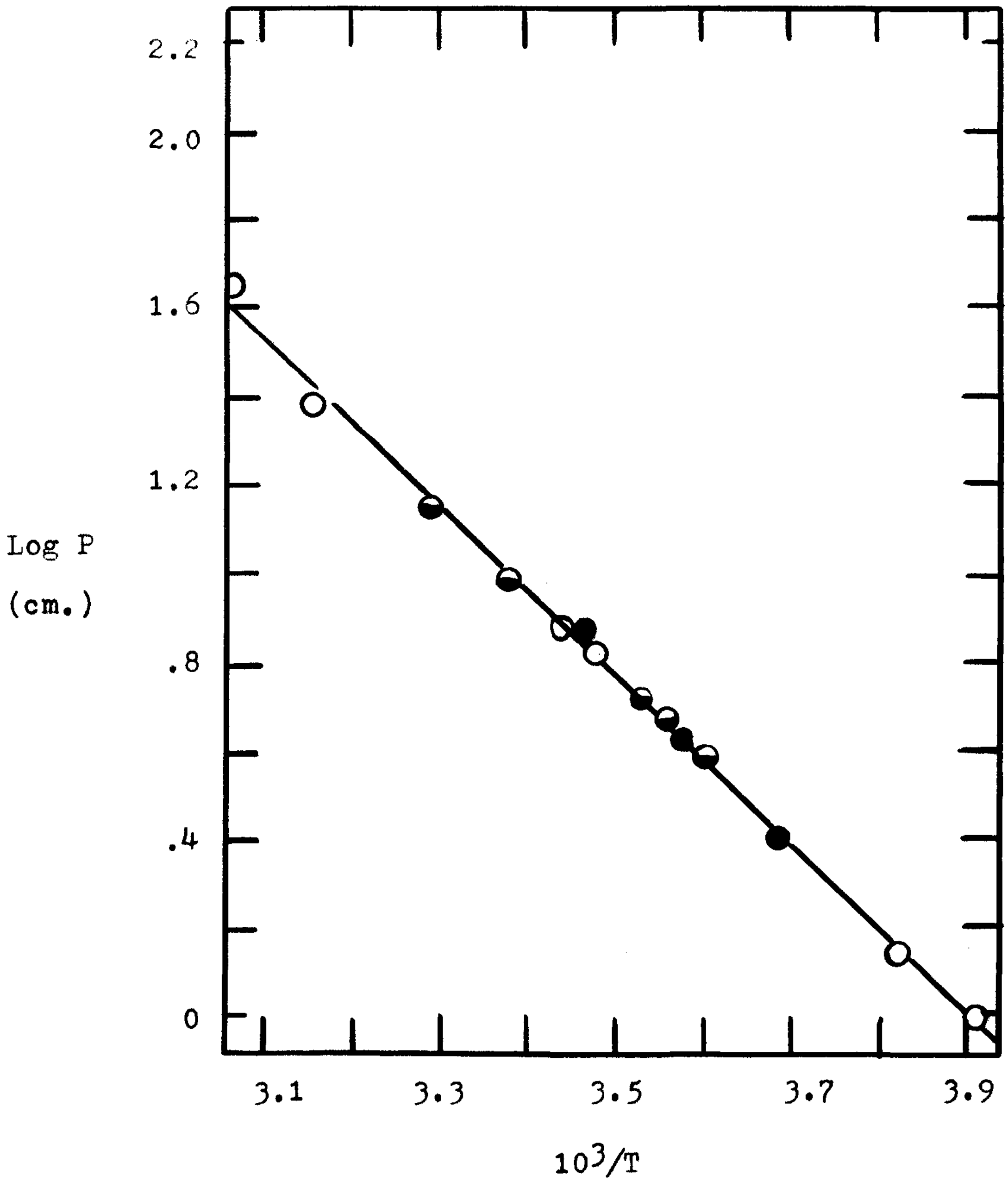

Fig. 6 : Vapour Pressure curves for Tetramethyltin

◒ Literature and observed correspond.

○ Literature value alone.

● Observed value alone.

TABLE II

VAPOUR PRESSURE OF TETRAMETHYLTIN
(literature and observed)

(°C) Temperature	Pressure observed(cm.)	Pressure literature(cm).
-21		1.00
0	2.60	
+ 3	3.95	4.00
+ 4.3	4.20	
+ 8	4.65	4,62
+11	5.60	5.57
+14		6.54
+16	7.10	
+18		7.92
+23	9.90	10.00
+28	12.35	12.42
+32		14.88
+45		25.07
+60		42.98

Literature values quoted are from (15).

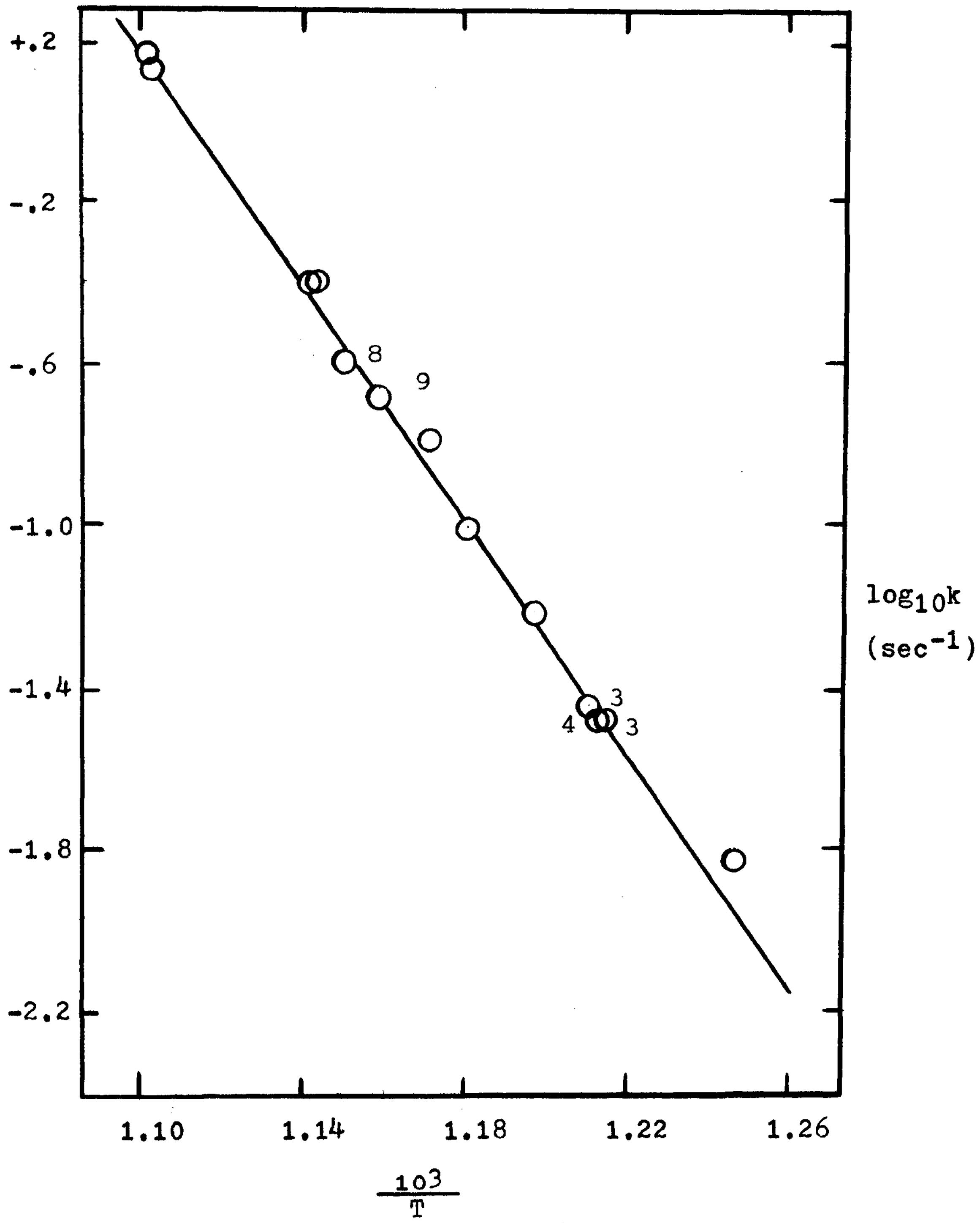

Fig.7: Arrhenius plot for decomposition of tetramethyltin. UNPACKED VESSEL and based on gas and liquid products.

Numbers indicate no. of runs averaged to obtain point.

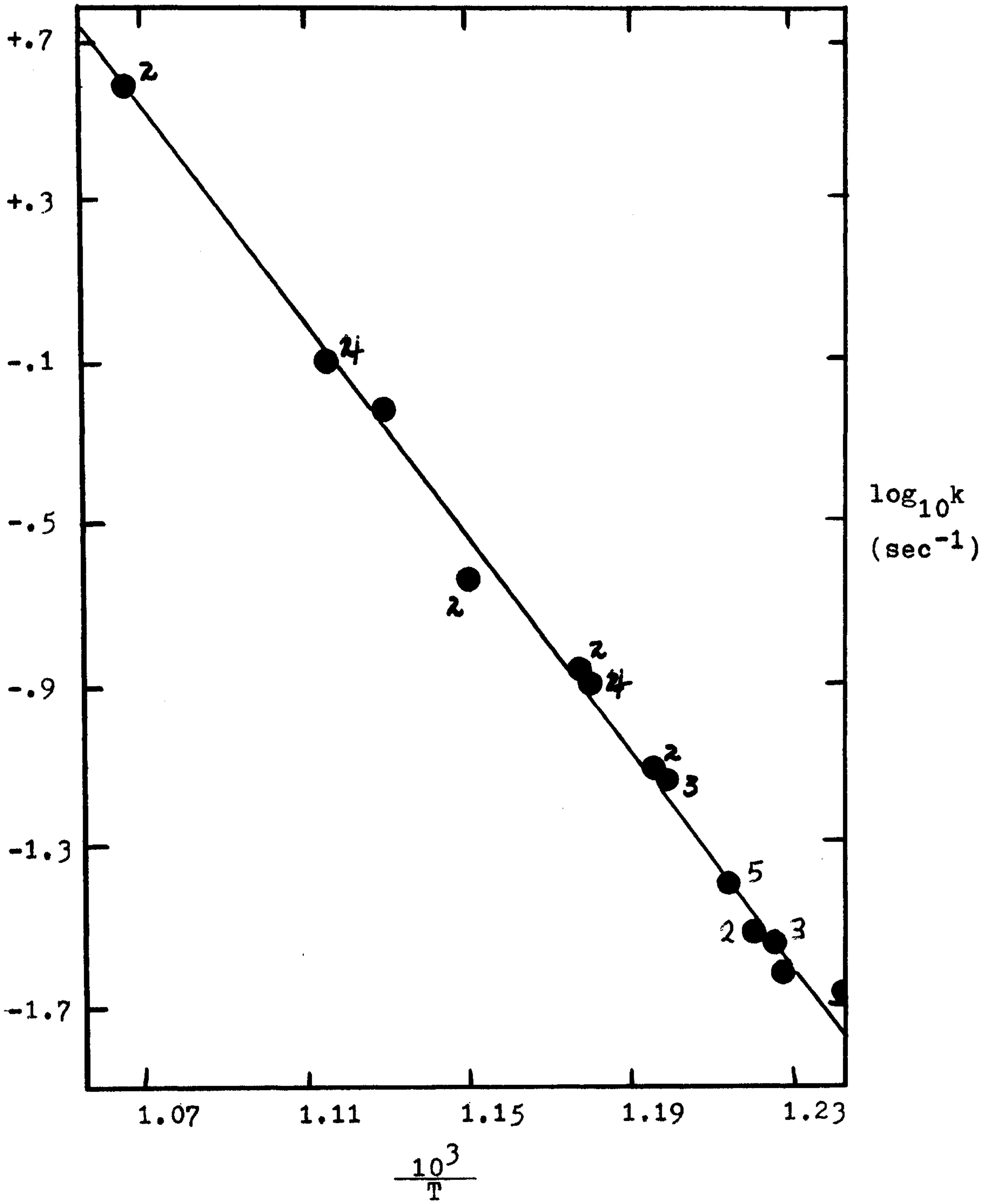

Fig.8: Arrhenius plot for decomposition of tetramethyltin. PACKED VESSEL and based on gas and liquid products.

Number indicated no. of runs averaged to obtain point.

the experiment, production of methyl radicals at a constant rate is obtained. However the uniform release of radicals throughout the reaction zone cannot be attained. This condition is approached at lower percentage decompositions. At higher percentage decompositions, the concentration of methyl radicals will be high at the beginning of the reaction zone favouring the recombination reaction and low at the end favouring abstraction. These factors are believed to be somewhat self compensating. (26,27)

A. Ratio Effect (Initial Concentration Effect)

In order to ensure that the decomposition is 1st order, the effect of varying the initial concentration upon the rate constant was studied. Since the toluene and alkyl pressures can be easily altered, this study was accomplished by keeping the total pressure constant ie. essentially the toluene pressure constant and varying the alkyl pressure. (the concentraion of alkyl in the carrier stream is determined by the extent of the alkyl pressure being larger than the toluene pressure.) At constant pressure, the ratio is inversely proportional to the initial concentration.

In Fig. 9, it can be easily seen that the ratio has no effect on the rate constant for this series of runs. The temperatures, pressures, contact times for the unpacked vessel runs were selected at random. The ratios selected vary from 53/1 to 977/1. Over this wide range of ratios, the rate constants at the extreme values only varied by 2%. Therefore if the initial alkyl concentration has no effect on k, we can say that the process is 1st order within the experimental error. These findings are consistant with those found for $Pb(CH_3)_4$. (2)

In work done on $Ga(Me)_3$ and $In(Me)_3$, it was found that the toluene to alkyl ratio of not less than 45 and 150 respectively were essential for consistant rate

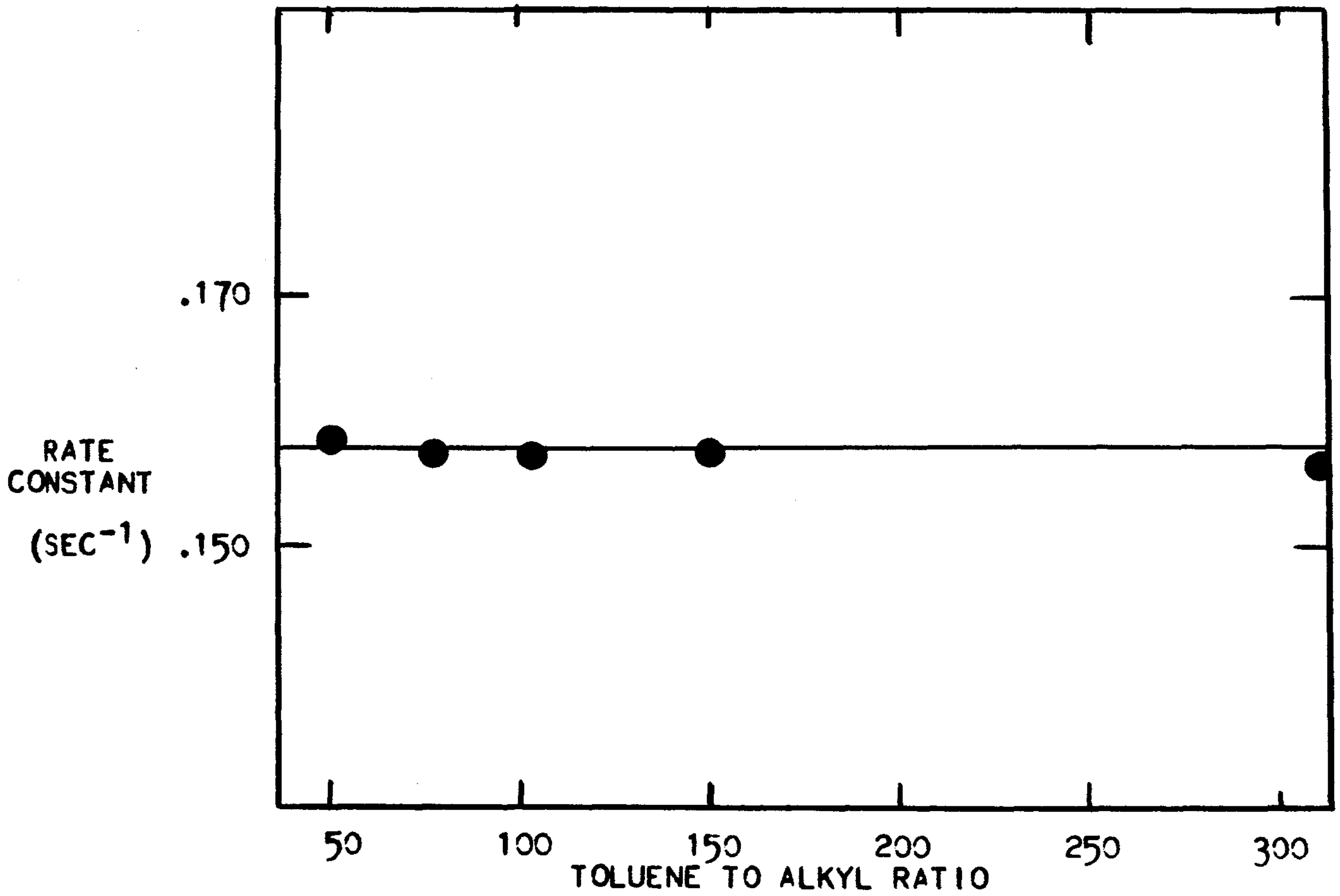

FIG. 9: RATE CONSTANT VERSES TOLUENE TO ALKYL RATIO

constants. (21,22). For $Sn(CH_3)_4$, ratios smaller than the 53/1 of Run Sn 84 were used. For example Runs Sn 7, Sn 9, Sn 14, and Sn 18 had ratios in the twenties to one area, and these rate constants agreed favourably with runs done under exactly the same conditions but with higher ratios. The runs plotted were selected because they were part of the series of runs exactly controlled to study ratio effect. The runs mentioned above were only verifed with one or two verifying runs and were not part of a series. Considering the series of runs and the others done at lower ratios, it may be said the ratio does not play a part in the rate constant determinations from very small ratio runs (high alkyl concentraions) to very high ratio runs. (very dilute alkyl concentrations)

The fall offs noted in the gallium and indium work, were due to secondary reactions of the radicals produced to form alternate products. As the toluene concentration is increased these secondary reactions occur less and less frequently.

TABLE IV

EFFECT OF TOLUENE TO ALKYL RATIO ON THE RATE CONSTANTS

Temperature 861.0°K, Pressure = 1.54cm., t_c = 1.866sec.
UNPACKED

Run #	% Decomp. (gas)	% Decomp. (alkyl)	Toluene to Alkyl Ratio	Rate Constant (gas) sec^{-1}
Sn 82*	38.4%	39.4%	156/1	+ .1587
Sn 83	25.5%	24.9%	78/1	.1581
Sn 84	26.8%	26.2%	53/1	.1598
Sn 85	25.7%	23.4%	107/1	.1583
Sn 87	25.8%	18.9%	977/1	.1567

* run Sn 82 done with a slightly longer contact time.

B. Contact Time Effect

From Fig. 10, it can be easily seen that contact time has little bearing on the rate constant for the dissociation of tetramethyltin. The pressures for all these runs were keep at 2.0cm. and the contact times were altered by changing the settings on the Edward's valve.

Run Sn 90 merits some discussion. Mulcahy and Pethard (23) stated that to have the measured value of the rate constant accurate within 10%, the ratio of contact time to pressure expressed in cm. should be greater than .5 to attain thermal equilibrium. To avoid errors due to diffusion, this ratio should be less than 3 at 50% decomposition and less than 10 at 25%. Since Run Sn 90 would have a ratio of 5.478 over 2.02 equals 2.74 and our decomposition is 84%, problems due to diffusion are very possibly and thus the deviation from the line.

The values of $k_a/k_r^{\frac{1}{2}}$ for the same runs again show little dependence on contact time, except for Run Sn 90. Here, as stated above , back diffusion and flow difficulties were present. This was noted by Mulcahy (23) and Batten (24) also under similiar conditions. With high decomposition as in Run Sn 90, a high concentration of methyl radicals would be present at the start of the reaction zone. Both these conditions would create a situation favouring recombination. Thus, the rate constant ratio $k_a/k_r^{\frac{1}{2}}$ would decrease.

For the other runs, the per cent decompositions can be said to be in the medium per cent decomposition range. Under these decompositions, there will not be a very large concentration of methyl radicals at the front of the hot zone and even if the contact time is fairly long and therefore the accompanying slower flow, the recombination would not be as highly favoured as in the case of the high decompositions.

TABLE V

Effect of Contact Time on Rate Constant and $k_a/k_r^{\frac{1}{2}}$

Run #	t_c (sec.)	%Decomp. (gas)	%Decomp. (alkyl)	Log k	$k_a/k_r^{\frac{1}{2}}$
Sn 92	.566	13.4	14.3	-.5946	655.2
Sn 91	.937	19.5	22.7	-.6357	660.5
Sn 88	1.849	35.4	34.2	-.6263	670.6
Sn 89	2.598	48.0	50.6	-.5991	662.6
Sn 90	5.478	83.2	86.3	-.4870	481.8

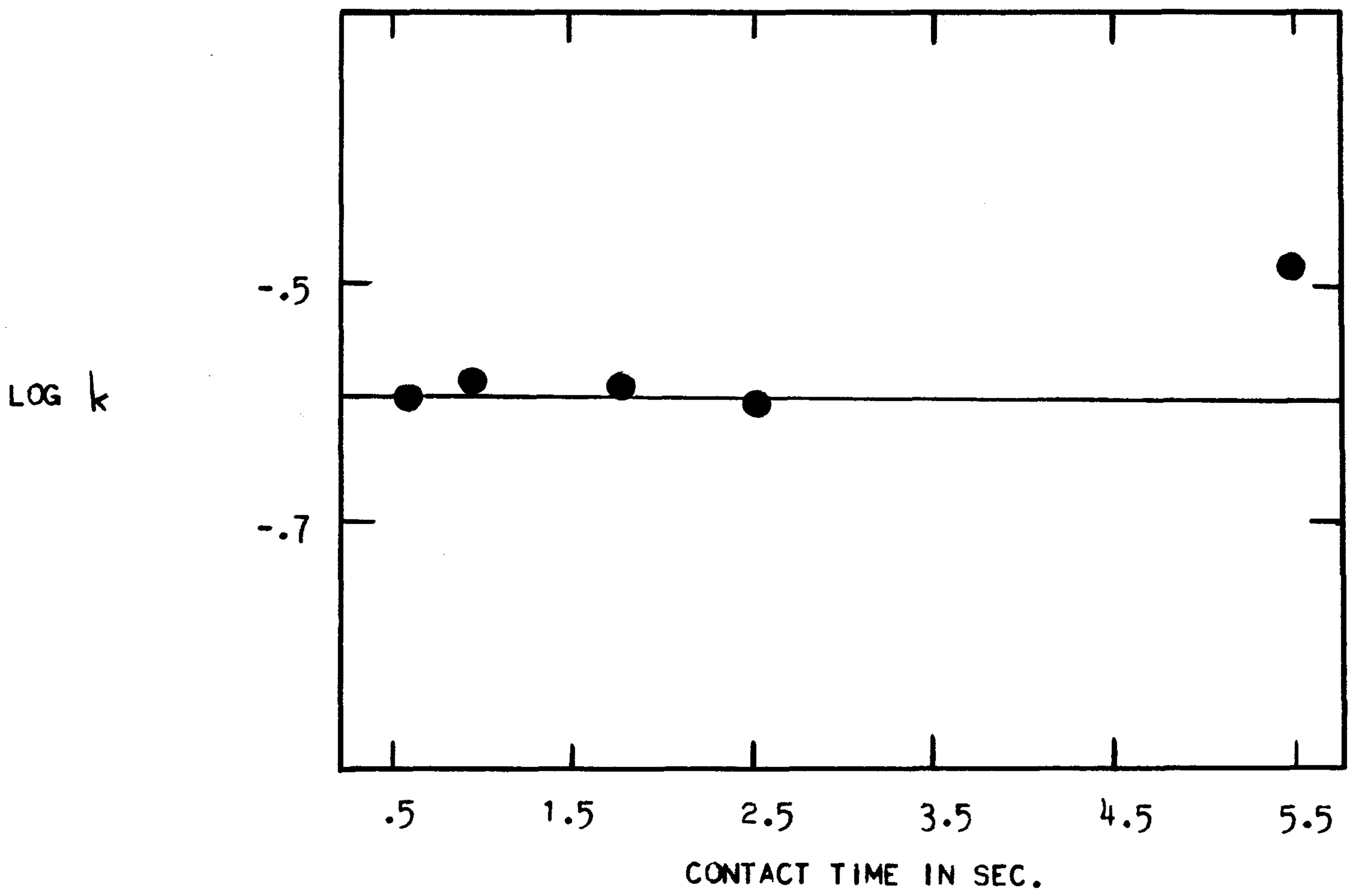

FIG.10: LOG OF RATE CONSTANT VERSES CONTACT TIME.

C. Pressure Effect

As previously discussed in the theory section of Bond Dissociation Energies by the Kinetic Method, it is necessary that the rate constants should be determined in a pressure "independent" region. In this series of runs, the total pressure of the system was changed from 10.64 mm. to 52.41 mm. and very little effect was noted in the rate constant. Studies involving $Hg(Me)_2$ and $Cd(Me)_2$ (25) did show a pressure effect. Increased pressure yielded an increase in 'k', but a maximum 'k' was reached on increasing pressure.

TABLE VI

EFFECT OF PRESSURE ON THE RATE CONSTANT

Run #	Temp °C	Pressure(cm.)	$k_g(sec^{-1})$
Sn 94	867	10.64	.21014
Sn 93	867	14.87	.21122
Sn 95	865	23.93	.22063
Sn 96	864	35.56	.20323
Sn 98	866	40.62	.20062
Sn 97	866	52.41	.21408

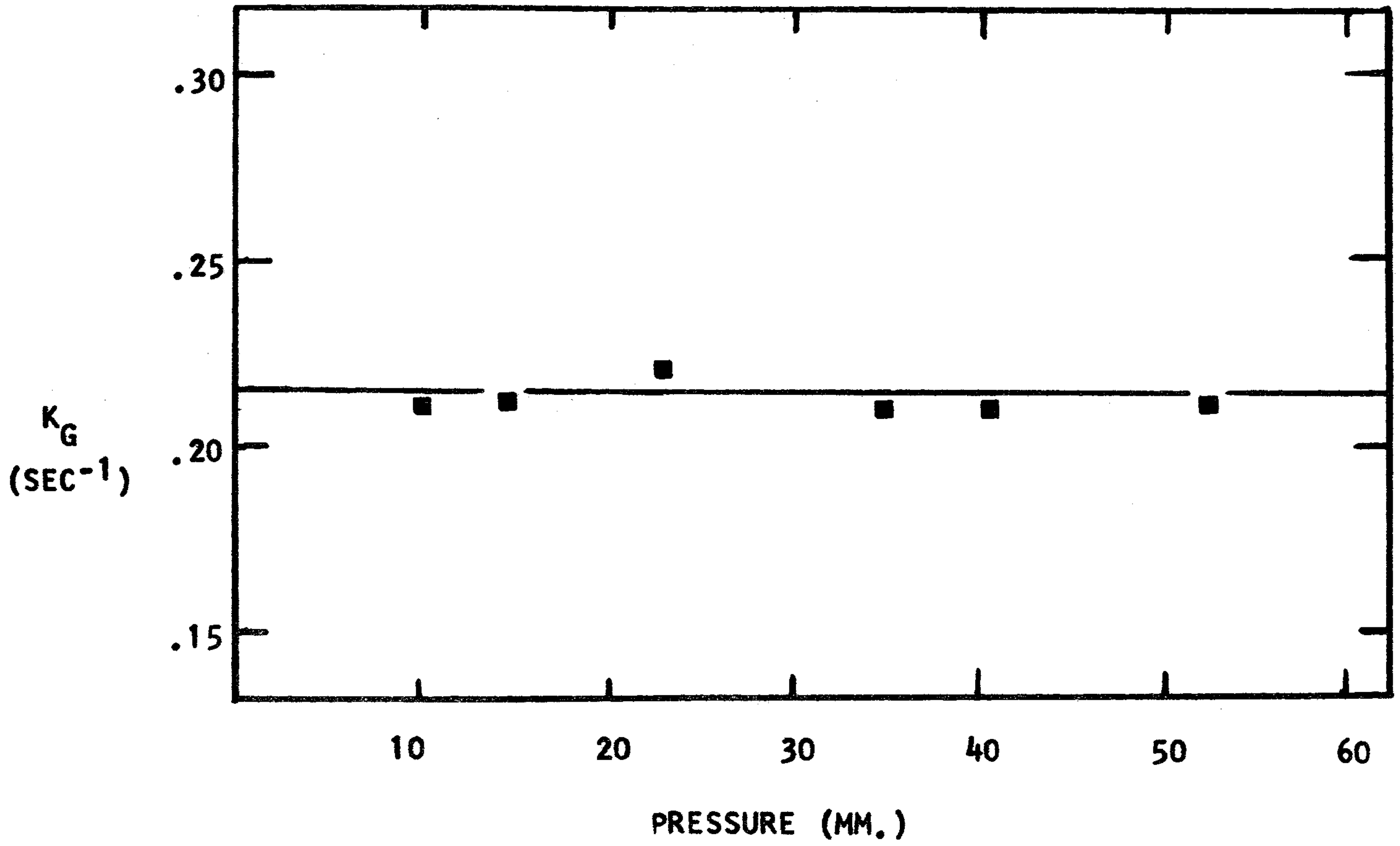

FIG.11: RATE CONSTANT VERSES PRESSURE OF TOLUENE.

D. Surface Effect

Runs Sn 1-12,Sn 22 and 23, and Sn 63-98 were run in the ordinary unpacked reaction vessel with a volume of 170.9 cc. The remaining runs were run in a packed vessel (quartz rod) which decreased the volume to 117 cc. This increased the surface to volume ratio from 2.0 cm.^{2}/ cc. to 21.2 cm.^{2}/cc. Prior to fitting the reaction vessel into the vacuum system, it was acid washed as inactive as possible with concentrated nitric acid. Water has been found to activate the surface. The unpacked vessel was treated similiarly. A small surface effect was noted in the first runs in each vessel (Sn 1 and Sn 13) after preparation but nothing was noted from then on. From the Arrhenius plot comparison, it is seen that a surface effect if any is limited to less than 2%, and therefore the reaction must be considered homogeneous. One must also consider the different flow pattern through the unpacked and packed vessels. This could easily account for the difference in the two vessels.(26)

E. Suggested Mechanism.

All these experimental observations suggest the following mechanism:

$$
\begin{array}{lllllr}
 & & Sn(CH_3)_4 \longrightarrow & Sn(CH_3)_3 & + \; CH_3 & (1) \\
 & & Sn(CH_3)_3 \longrightarrow & Sn(CH_3)_2 & + \; CH_3 & (2) \\
 & & Sn(CH_3)_2 \longrightarrow & Sn(CH_3) & + \; CH_3 & (3) \\
 & & Sn(CH_3) \longrightarrow & Sn & + \; CH_3 & (4) \\
CH_3 & + & C_6H_5CH_3 \longrightarrow & C_6H_5CH_2 & + \; CH_4 & (5) \\
CH_3 & + & C_6H_5CH_2 \longrightarrow & C_6H_5C_2H_5 & & (6) \\
 & & 2\ CH_3 \longrightarrow & C_2H_6 & & (7) \\
 & & 2\ C_6H_5CH_2 \longrightarrow & (C_6H_5CH_2)_2 & & (8)
\end{array}
$$

MINOR REACTIONS:

$$
\begin{array}{lllllr}
CH_3 & + & C_2H_6 \longrightarrow & C_2H_5 & + \; CH_4 & (9) \\
 & & C_2H_5 \longrightarrow & C_2H_4 & + \; H & (10) \\
H & + & C_6H_5CH_3 \longrightarrow & H_2 & + \; C_6H_5CH_2 & (11) \\
CH_3 & + & C_6H_5CH_2 \longrightarrow & C_6H_5C_2H_5 & & (12)
\end{array}
$$

This mechanism is proposed on the basis of the observed products and the fact there is no break in the Arrhenius plot (Fig.12) for log $k_a/k_r^{\frac{1}{2}}$ verses $10^3/T$. This line is seen to be straight and continuous indicating the 4 Tin —carbon bonds break consecutively. The fact that the gas analysis per cent decompositions agree well with

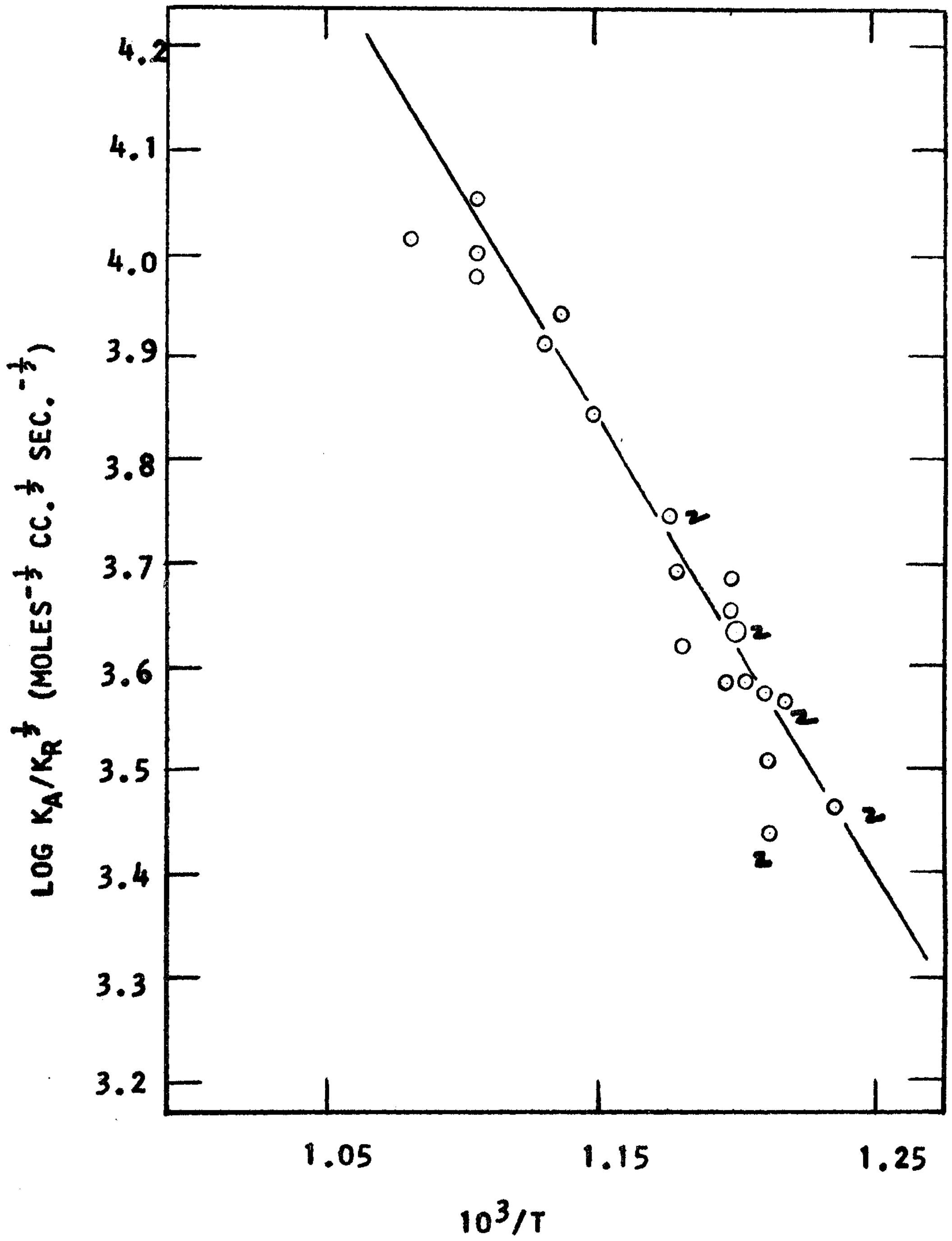

FIG.12: ARRHENIUS PLOT OF $K_A/K_R^{\frac{1}{3}}$ AT 2.0 cm. PRESSURE
(approx.)
PACKED VESSEL

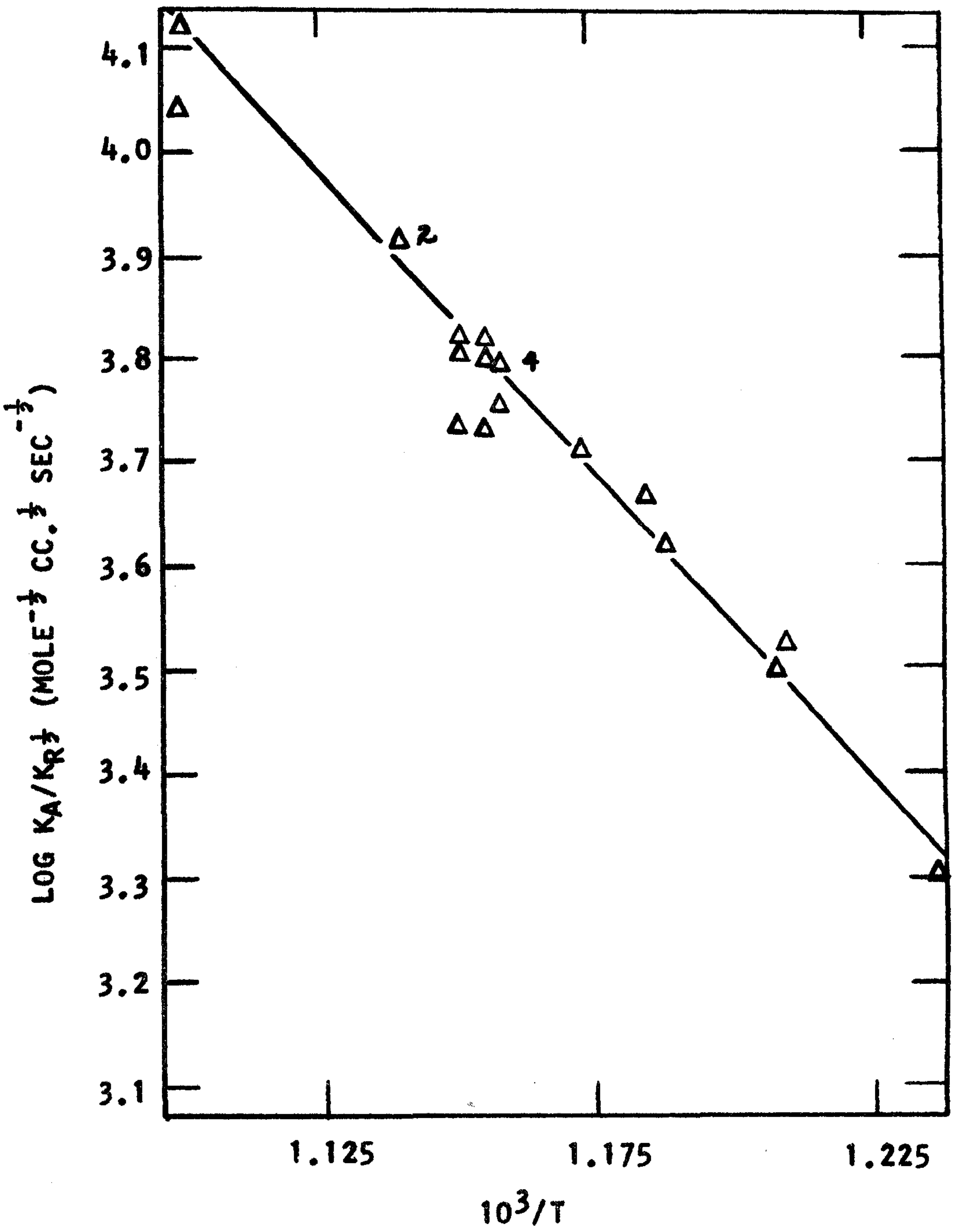

FIG.13: ARRHENIUS PLOT OF $K_A/K_R^{\frac{1}{2}}$ AT 2.0 cm. PRESSURE (approx.) UNPACKED VESSEL

those per cents determined through residual alkyl analysis, suggests that all 4 bonds are broken and that no methyl radicals are left unaccounted for. This mechanism also agrees with the mechanism proposed by Webster (2) for $Pb(Me)_4$. A few liquid samples from runs were analyzed on the electron capture (Varian 1200) and no other volatile tin product peaks of any consequence were noted. All products detected in this research are accountable for in this mechanism.

A quick check is done on the data obtained to see if the mechanism fits with respect to energy and A factors. From previous studies of tri- and di- methyl alkyls, we can assume for reactions 2, 3, and 4 of the mechanism should have A factors $A_2 = 10^{15}$

$A_3 = 10^{14}$

and the rates of these reactions are 5, 25, 125 times respectively faster than reaction 1 in order that reaction 1 is rate controlling. $\therefore$ $k_4 = 5k_3 = 25k_2 = 125k_1$. From our data, $A_1 = 10^{15.67}$ and $E_1 = 64{,}500$ cals.; $\therefore$ by substituting in the Arrhenius equation at a middle range temperature of 850°K, we get:

$$\log k_1 = \log A - 64{,}500/4.58 \times 850 = -.9000$$

Now to solve for E_2 max.,

$$\log k_2 = \log 5k_1 = 15.00 - E_2 \text{ max.}/\ 3893$$

$$\therefore\ E_2 \text{ max.} = 59{,}177 \text{ cals.}$$

Similiarly:

$$\log k_3 = \log 25k_1 = 14.00 - E_3 \max/3893$$

$$\therefore E_3 \max = 53{,}564 \text{ cals.}$$

From calorometric measurements $\bar{\bar{E}}$ for tetramethyltin is 53.5 kclas. $\therefore$ E_4 max is then given a value of 37,759 cals. for a maximum value. Substituting this value back into the Arrhenius equation,

$$\log k_4 = \log 125\ k_1 = \log A_4 - 37{,}759/3893$$

which gives us a value of $\log A_4 = 8.493$. From previous studies on $InMe_3$ and $ZnMe_2$, an acceptable value for $\log A_4$ would be equal to or less than 10.00. Therefore by this check, the mechanism again seems possible.

F. Bond Dissociation Energy

As discussed earlier, the activation energy for a unimolecular decomposition should be a good approximation to the bond dissociation energy. Thus D $(CH_3)_3Sn—CH_3$ is equal to 64.5 kcals.

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