stirrer,[7] reflux condenser and dropping funnel were placed 28 g. (1.2 moles) of sodium and 150 ml. of dry toluene. The sodium was powdered by heating the toluene to refluxing and stirring the solution vigorously. The flask was cooled to room temperature and 0.2 mole of the aminoacetonitrile[6] dissolved in 100 ml. of *n*-butanol (distilled from sodium) was slowly added with stirring. The solution refluxed during the addition, stirring being continued until all the sodium had reacted and the reaction mixture had cooled to room temperature. Fifty ml. of water was added and the two layers were separated. The toluene–alcohol layer was made acid to congo red with hydrochloric acid, more water was added and the solution was concentrated to remove toluene and alcohol. The solution was then chilled, neutralized with 40% potassium hydroxide solution and the diamine salted out by saturating the solution with anhydrous potassium carbonate. The diamine was extracted with benzene, the benzene solution dried over potassium carbonate, the solvent distilled and the residue distilled through a 15-cm. Vigreux column.

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[7] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

Summary

The reduction of certain N,N-dialkylaminoacetonitriles to the corresponding diamines has been effected satisfactorily by means of sodium in butanol or ethanol. The method does not appear to be satisfactory for monoalkyl derivatives.

DURHAM, N. C. RECEIVED DECEMBER 4, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Kinetics of the Thermal Decomposition of Gaseous Tetramethyltin[1]

BY CHAS. E. WARING AND WM. S. HORTON[1a]

The modern theory of reaction mechanism in the gaseous phase would undoubtedly be aided by kinetic studies of the decomposition of a series of molecules in which there is a stepwise gradation of structure and stability. It has been suggested[2] that the tetra-alkyls of the fourth group of the periodic table might be investigated to advantage because they offer the possibility of varying not only the length of the side chain, but also the size of the central atom. Such a series enables the comparison of the relative effects of various atomic forces.

Some work on these series of tetra-alkyl compounds has already been reported. Silicon tetramethyl,[3] tetraethyl[2] and tetrapropyl,[2] germanium tetraethyl,[4] and lead tetraethyl[5] have been investigated and found to thermally decompose homogeneously in accordance with a first order law.

It was with the view of adding another methyl compound to the existing data, and also of initiating parallel studies in the tin series of tetra-alkyls, that the present investigation was undertaken.

Experimental

Tetramethyltin was prepared by a Grignard method suggested by Dr. George Calingaert of the Ethyl Gasoline Corporation.[6] Essentially 6 to 8 moles of methylmagnesium iodide was prepared in a suitable amount of ether. One mole of stannic chloride dissolved in 100 ml. of toluene or xylene was slowly added to this with vigorous stirring and then the entire mixture refluxed for about five hours. Each preparation was carefully fractionated and only that product which had a constant boiling point of 76.8 ± 0.1°, corrected, was used. This compound had a refractive index of 1.4409 and a specific gravity of 1.2904 ± 0.0002. After purification, different preparations gave the same physical constants within the limit of error.

A micro-organic analysis gave the following results—calculated for $Sn(CH_3)_4$: C, 26.26; H, 6.15. Found: C, 28.00, 28.25; H, 6.85, 6.75. The difference between the calculated and observed values for the micro analysis are about as accurate as can be expected for this type of compound.

The course of the decompositions was followed in the usual manometric method using a mercury column in a 1.5-mm. capillary tube which had been previously examined and chosen for its uniformity of bore. The vapor reacted in Pyrex bulbs of 150-cc. capacity. Small bore capillary tubing was employed throughout so that the dead space was reduced to less than 2% of the total volume.

In the tests for the homogeneity of the reaction, a packed bulb was used which contained 100 small pieces of 7-mm. Pyrex tubing. The surface-to-volume ratio of the packed bulb was 8.8. That of the unpacked reaction bulb was calculated to be 0.94.

The reaction flask was placed in an electric furnace which was maintained at constant temperature within ±0.05° by a thyratron control device previously described.[7] Temperatures were measured by a platinum–platinum-rhodium thermocouple in conjunction with a type K potentiometer. This latter instrument was checked regularly by a Mueller bridge and a standard platinum resistance thermometer.

Since the normal boiling point of $Sn(CH_3)_4$ is well above room temperature, all tubing and taps were heated electrically by means of nichrome resistance wire. The temperature of the taps did not vary more than 2° over a period of several hours. A special high temperature tap grease was employed. The remainder of the apparatus consisted of the usual system for obtaining low pressures and no run was made unless the pressure of the system, as measured by a calibrated McLeod gage, was at least 10^{-5} mm.

The gaseous reaction products were analyzed in a modified Bone and Wheeler apparatus. The higher olefins were separated from ethylene by the method of Hurd and Spence.[8]

Data and Results

1. Nature of the Decomposition.—From photochemical evidence with allied organo-metallic compounds, one might reasonably expect the

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[1] Original manuscript received August 21, 1944.

[1a] Present address: The Ohio State University, Columbus, Ohio.

[2] C. E. Waring, *Trans. Faraday Soc.*, **236**, 1142 (1940).

[3] Helm and Mack, THIS JOURNAL, **59**, 60 (1937).

[4] Geddes and Mack, *ibid.*, **52**, 4372 (1930).

[5] Leermakers, *ibid.*, **55**, 4508 (1933).

[6] Private communication.

[7] Waring and Robison, *Rev. Sci. Inst.*, **14**, 143 (1943).

[8] Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

primary step in the thermal decomposition of tetramethyltin to be

$$Sn(CH_3)_4 = Sn + 4(CH_3)$$
$$\text{or } Sn(CH_3)_4 = Sn(CH_3)_3 + CH_3 \text{ (slow)}$$
$$Sn(CH_3)_3 = Sn + 3(CH_3) \text{ (fast)}$$

The methyl radicals produced photochemically have various possibilities for recombination and reaction and these occur at temperatures well below those employed thermally. Thus, in the present study, secondary reactions involving methyl radicals may not necessarily result in the same final products of reaction. Hence, if methyl radicals are initially produced in the thermal decomposition of tetramethyltin at high temperatures, these radicals may be expected to react rather rapidly and give rise to secondary reactions which may tend to mask the primary step. Moreover, the hydrocarbons produced initially from these radicals may undergo further decomposition. This means that the relation of the primary and secondary change to the actual chemical reaction must be rather carefully thought out.

The most convenient method of following this reaction is by the rate of pressure change. This procedure is straightforward enough for decompositions in which the initial products undergo no subsequent change, but may lead to erroneous conclusions in the event of complicating side reactions. Therefore, it is our plan to interpret our kinetic data in the light of analyses.

Tetramethyltin decomposes at a conveniently measurable rate between 440–493° to give a total pressure increase of about three times that of the initial pressure. Figure 1 shows that the ratio of the final to the initial pressure is reasonably constant down to about 10 mm., and thereafter varies somewhat with the initial pressure. The figure also indicates that the end-points are not affected by temperature to any great extent. The average ratio of the final to the initial pressure, P_f/P_i, for all runs carried to completion (*i. e.*, where $\Delta p = 0$) was 2.91 ± 0.05. This is in close agreement with the value of 2.95 found by Helm and Mack[3] for $Si(CH_3)_4$.

The question arises, as always, as to the best method for determining a rate constant which will give the correct order of the reaction. From what has been said, it should be apparent that a different value for the order of the reaction might be obtained, depending upon whether the rates are determined on the basis of a given fraction of the initial pressure, or from the total pressure increase. Since there is a complex series of secondary reactions in the decomposition of tetramethyltin, and since it is the primary process that is of greater importance, one should place the greater dependence upon the initial rate measurements. It will be shown, however, that the results are substantially the same, no matter whether the order of reaction is obtained from the initial rate, or from the half-time for the total pressure increase.

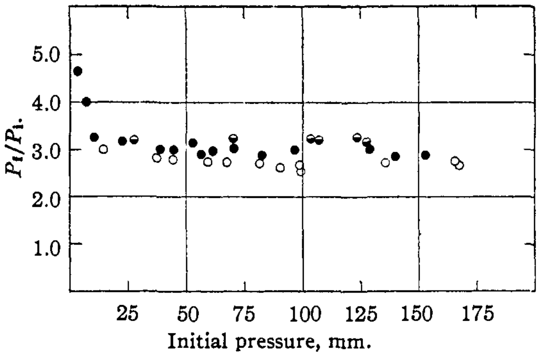

Fig. 1.—The ratio of final to initial pressure as a function of the initial pressure: ○, 467.4°; ●, 484.7°; ⊖, 493.2°.

2. **Order of Reaction.**—The decomposition of tetramethyltin was found to be of the first order by three criteria. Figure 2 shows the change of pressure with time for various initial pressures, the increase in each case being expressed as a percentage of the initial pressure. Above 80 mm. initial pressure, and over about a three-hour period, these curves almost coincide exactly. This reproducibility in the early stage indicates that the primary process, at least, is a first order reaction. Any deviations which occur in the later stages need not concern us too much, as they relate to the secondary decompositions of the primary products, and over a wide pressure range do not influence the initial rate.

Since the end-points of the decompositions at various initial pressures have been shown to be relatively reproducible, the determination of fraction-life times, based upon the final pressure increase, offers a fairly reliable method for establishing the order of the reaction. That the decomposition of tetramethyltin was of the first order is further substantiated by Fig. 3, in which the reciprocal of the half-life is plotted against the initial presssure. This curve indicates that the decomposition of tetramethyltin above 80 mm. pressure is of an order which is predominantly the first, but that the order approaches that of second at lower initial pressures. Below 80 mm. initial pressure a plot of the logarithm of the reciprocal of the half-time as a function of the initial pressure gave an order of reaction of 1.64.

The fact that certain gas reactions are unimolecular at high initial pressures but fall off in rate below the unimolecular law at low pressures is not unusual. This particular reaction, then, offers additional evidence for the theory of quasi-unimolecular processes which was originally proposed by Hinshelwood and Lindemann[9] and later expanded by Rice and Ramsperger.[10]

Finally, the specific rate constants calculated directly from fractions of the total pressure in-

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(9) Hinshelwood and Lindemann, *Proc. Roy. Soc.* (London), **A113**, 230 (1926).

(10) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); **50**, 617 (1928).

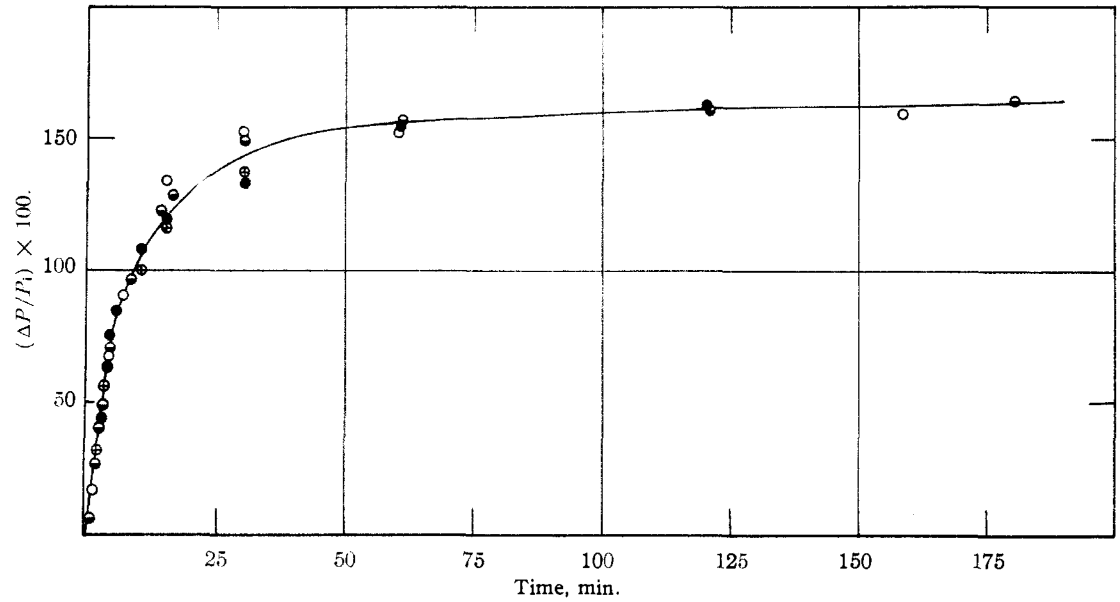

Fig. 2.—The pressure increase expressed as percentage of the initial pressure ($\Delta P/P_i$) × 100, as a function of time. Results are from four different initial pressures at 467.4°: ○, 91 mm.; ⊕, 99 mm.; ◒, 136 mm.; ●, 166 mm.

crease agreed well with those calculated indirectly from given fractions of the initial pressure. This indicated that, at least above 80 mm. initial pressure, the order of reaction was the same when evaluated by a direct and indirect method. Accidental compensation of error would be unlikely to lead to the same result by both methods.

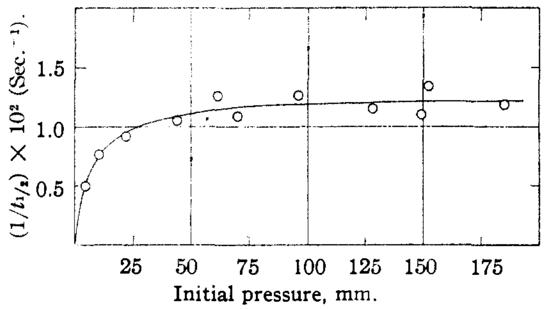

Fig. 3.—The reciprocal of half-life time as a function of the initial pressure at 467.4°.

3. **Surface Effects.**—Experiments were conducted at three different temperatures in a packed reaction vessel having a surface/volume ratio of 9 times that of the unpacked vessel. The first few runs made in a clean, packed vessel always gave abnormally high rates, but after the bulb became well coated with a deposit of tin and carbon, the rates became normal and quite reproducible and the P_f/P_i ratios remained the same as for the unpacked flask. In all cases, the increase in rate was always less than 30% and this high only at lower temperatures. Using the method employed by Geddes and Mack,[4] this amounted to 3% heterogeneity. The decomposition of tetramethyltin can therefore be said to be predominantly homogeneous in character.

4. **Effect of Nitric Oxide.**—In a previous paper,[2] it was demonstrated that small amounts of nitric oxide had no effect on the decomposition of silicon tetraethyl and tetrapropyl. On the other hand, large amounts of nitric oxide affected the total pressure increase very markedly in the secondary stages of the reaction, while the primary rate was affected only very slightly.

In the case of tetramethyltin, however, a comparison of the rate constants for the inhibited and uninhibited reactions indicated that nitric oxide produced no inhibition of the primary process. Instead, nitric oxide was found to have a slight catalytic effect, the initial rate being increased about 10%.

Some inhibition occurred in the secondary stages of the decomposition. The magnitude was very small, and although various runs gave a mean chain length of 1.03 ± 0.01 from 12 to 50% of the completed reaction, it is doubtful whether any real significance can be placed on this value.

The fact that nitric oxide does not inhibit the initial rate does not necessarily mean that free radicals are not formed in the decomposition of $Sn(CH_3)_4$. The possibility always exists that nitric oxide may initiate as many chains as it stops—a theory proposed by F. O. Rice, and experimentally confirmed recently by Smith and Hinshelwood.[11] However, from the results of experiments in packed reaction flasks, it appears that the reaction $Sn(CH_3)_4$ + Radical = does not occur to any great extent. Hence, while free radicals may, indeed, be formed in this decomposition, one may safely assume that a chain reaction is not the predominant mechanism.

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[11] Smith and Hinshelwood, *Proc. Roy. Soc.* (London), **A180**, 237 (1942).

TABLE I

Temperature °C. (P_i = 100 mm., approx.)

440°		450°		467.4°		484.7°		493.2°	
r	$k \times 10^3$	r	$k \times 10^3$	r	$k \times 10^3$	r	$k \times 10^3$	r	$k \times 10^3$
0.1250	0.3151	0.1250	1.191	0.1250	4.268	0.1250	10.86	0.1128	22.34
.1369	.3167	.1354	1.181	.1462	3.681	.1273	16.40	.1250	27.49
.2500	.3311	.2500	1.402	.2500	5.619	.2500	12.51	.2256	24.72
.2738	.3100	.2709	1.305	.2924	5.032	.2546	12.18	.2500	28.54
.4107	.2438	.4063	1.048	.4386	4.729	.3819	11.83	.3384	25.49
.5000	.2021	.5000	0.872	.5000	3.415	.5000	8.84	.4513	21.81
.5476	.1869	.5417	0.645	.5848	3.069	.5092	8.84	.5000	20.41

5. Rate Constants and Energy of Activation.—The eighth-, quarter-, and half-life times were determined from the pressure–time curves and the specific reaction velocity constants calculated by the equation

$$k_r = \left[\ln\left(\frac{1}{1-r}\right)\right]\Big/t_r \qquad (1)$$

Here k_r is the specific rate constant when the reaction is the fraction r complete.

From the times for a given percentage increase of the initial pressure, $t\%$, the corresponding fractional life times, t_r, were determined by dividing $t\%$ by the $\Delta P_f/P_i$ value for the reaction at a given temperature, where ΔP_f refers to the change in pressure for the completed reaction. At 450°, for example, the average value for P_f/P_i was 2.85, hence

$$\frac{\Delta P_f}{P_i} = \frac{P_f - P_i}{P_i} = \frac{P_f}{P_i} - 1 = 1.85$$

Consequently, the values of r corresponding to the percentage increase over the initial pressure are 0.25/1.85, 0.50/1.85, etc. Thus, if q is the fraction increase over the initial pressure and s the average value for $\Delta P_f/P_i$—or, one less than the average P_f/P_i value for the temperature under consideration

$$r = q/s \qquad (2)$$

By determining the values of r and substituting them in equation (1), the "indirect" specific rate constants are obtained.

In Table I are given the specific rate constants calculated by both the direct and indirect methods. The r's for the direct constants $t_{1/8}$, $t_{1/4}$ and $t_{1/2}$ are equal to 0.1250, 0.2500 and 0.5000, respectively, whereas the indirect constants are not round numbers.

The rate constants, obtained from both the fractional life times and the times for a given percentage increase over the initial pressure, represent average values based upon all the determinations made at the same initial pressure.

A plot of the logarithm of the rate constants against the reciprocal of the absolute temperatures was linear in all cases, the example shown in Fig. 4 being typical. From the data in Table I, the activation energies for the corresponding r values were determined by the method of least squares. These are listed in Table II together with the logarithm of the frequency factor, A, and the ratio E_a log A. For the indirect constants, the r listed is the average value of all r's for the same percentage increase over the initial pressure.

TABLE II

	E_a, kcal.	Log A	E_a/log A
0.1250	85.2	22.7	3.753
.1317	86.1	22.5	3.827
.2500	84.8	22.6	3.752
.2635	84.3	22.5	3.747
.3952	90.0	24.1	3.734
.5000	88.4	23.5	3.762
.5269	93.2	24.9	3.743

The above data indicate that the activation energy tends to increase as the reaction proceeds. Providing the initial products of reaction undergo no further decomposition, the activation energy should be a constant, regardless of when it was measured during the course of the reaction. It is only under these special conditions that the energy determined from half-lifes, etc., has any real significance. In the case of a complex reaction, however, the activation energies determined at various stages throughout its course are merely summations of the energies for all the many reactions which are taking place simultaneously. Consequently, such a state of affairs is not unexpected in a decomposition like that of tetramethyltin.

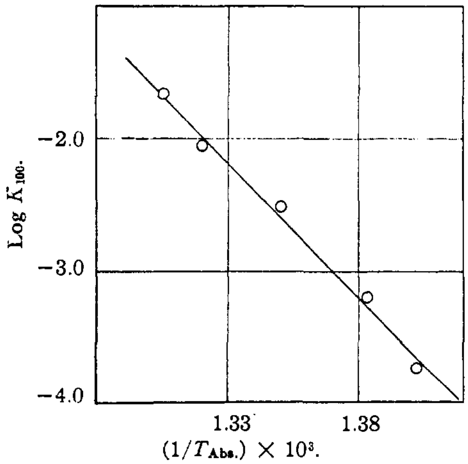

Fig. 4.—Logarithm of the rate constant from experimental values of t_{100} *versus* the reciprocal of the absolute temperature.

To evaluate the energy of activation for the initial split-up of tetramethyltin the rate con-

TABLE III

ANALYSIS OF GASEOUS PRODUCTS (T = 484.70°)

Products, %	Time, minutes 0.5	1.25	1.50	2.0	5	15	60	660	2880
Higher olefins	0.41	2.25	1.83	0.66	0.0	2.01	0.93	0.90	0.0
Ethylene	9.68	9.15	8.26	7.90	6.91	5.37	4.19	4.50	4.20
Hydrogen	7.31	10.05	7.34	4.21	3.62	5.37	4.65	6.31	6.59
Hydrocarbons (CH_4)	82.55	78.56	82.56	87.23	89.48	87.25	90.23	88.29	88.23
Carbon atom no.	1.00	1.04	0.97	0.96	1.05	1.00	0.98	1.01	1.03

stants were determined at zero time by plotting the values of E_a as a function of r and extrapolating to $r = 0$ by the method of least squares. An empirical equation for the activation energy of the primary process, E_0, was derived

$$E_a = E_0 + \alpha r + \beta r_2 \qquad (3)$$

where E_a is the composite activation energy and α and β are constants for a given reaction. Within the experimental error the squared term has no significance and the best straight line is given by

$$E_a = 82.40 + 16.03r \qquad (4)$$

E_a being expressed in kcal. per mole.

Table II also indicates that the ratio of E_a to log A is sensibly a constant, having a mean value of 3.760 ± 0.061. Thus, the universal frequency constant may be represented by the equation

$$\log A = 21.92 + 4.263r \qquad (5)$$

The initial rate of reaction may now be expressed in terms of the Arrhenius equation as

$$\text{Log } k_0 = 21.92 - (82{,}400/2.303RT) \qquad (6)$$

The value of the above activation energy is probably correct to within 1200 calories, which is slightly under 1.5% error. The average error of each of the E's in Table II, calculated by the least squares method, is 4–5%. The unusually high value for the activation energy suggests that tetramethyltin decomposes by a rearrangement rather than a chain mechanism. It is worth while to note that the value of 82,400 cal. is in accord with the equally high value of 79,000 cal. reported by Helm and Mack[3] for the decomposition of $Si(CH_3)_4$.

6. Analyses of Gaseous Products.—The analyses of the final products of reaction gave but little indication as to the probable reaction mechanism. In order to gain a clear picture of what was occurring during the primary stage, samples were withdrawn from the reaction vessel at various time intervals throughout the course of the reaction at 485°. The results are presented in Table III.

The above data show that tetramethyltin decomposes to give predominantly methane, together with some hydrogen and ethylene. As is usually the case in decompositions where large numbers of molecules are formed, the activation energy is high, since more bonds must be broken and fewer formed. The large amount of methane present at the beginning, and its relative constancy throughout the entire course of the reaction, argues for its formation in the initial breakup of tetramethyltin. This, in turn, is additional strong evidence for the decomposition proceeding through a rearrangement rather than a free radical mechanism.

Table III also indicates that after two minutes reaction time the percentage of methane increases slightly while the ethylene concentration decreases in a somewhat parallel manner. The only noticeable deposit on the walls of a new reaction flask, after runs of up to five minutes duration, was a whitish-gray coating presumably of tin. After runs of fifteen and sixty minutes duration, this coating became a blackish-gray. After runs had gone to completion, the walls assumed the shiny-black appearance of carbon particles. This evidence suggests a slow reaction of the type

$$C_2H_4 = CH_4 + C$$

Undoubtedly, it is this slow conversion of ethylene to methane that sometimes makes the end-points difficult to interpret, and gives added reason for basing activation energy and order of reaction upon the initial rates. The above reaction also explains why, at 689°, Helm and Mack[3] found no ethylene from the pyrolysis of $Si(CH_3)_4$.

The complexity of this reaction may be further emphasized in a somewhat different manner. Tetramethyltin decomposes predominantly in accordance with a first order law and, in the present case, under conditions of nearly constant volume. Using an average value of k = 0.0116 for the rate at T = 484.7°, the mole fraction of undecomposed $Sn(CH_3)_4$ may be found using the expression

$$x = x_0 e^{-kt}$$
$$\therefore \quad N = x/x_0 = e^{-kt}$$

where t is the reaction time in seconds.

The values for t may be obtained from Table III. Multiplying these by k = 0.0116, the corresponding values of e^{-kt} and $(1 - e^{-kt})$ may be calculated. The quantity $(1 - e^{-kt})$ is the mole fraction of all the product molecules, since the mole fraction of tetramethyltin, e^{-kt}, and its products must equal 1. The mole fraction of each individual constituent may be obtained by multiplying its per cent. by volume values in Table III, corresponding to various reaction times, by $(1 - e^{-kt})$.

In Fig. 5 the variations of the mole fraction of several constituents with the reaction times are shown. The calculations for these data are carried no further than fifteen minutes since the

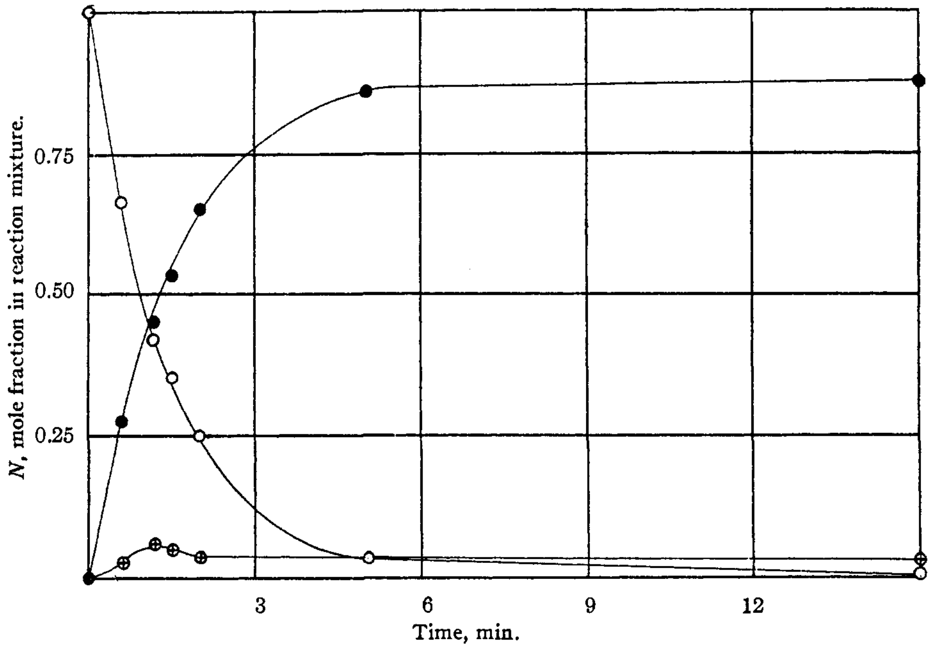

Fig. 5.—The mole fraction of the various gases in the reaction mixture at various times for a temperature of 484.7°. Ethylene has not been shown since its curve would almost coincide with that for hydrogen, except there would be no maximum. The figure is based on data shown in Table III and an average rate constant of 0.0116: ○, tetramethyltin; ●, methane; ⊕, hydrogen.

values of the factors e^{-kt} and $(1 - e^{-kt})$ become practically 0 and 1.00, within the experimental error, at this and subsequent reaction times.

The curve for hydrogen is typical of the type of maxima which are usually found in reactions where the molecules are involved in an intermediate process. That such a state of affairs may readily exist in the present decomposition will be discussed later. Since the data for ethylene nearly parallel those of hydrogen (with the exception of the maximum) this plot was not included.

Discussion

It is well known that rearrangement processes require much higher activation energies than reactions proceeding by a free radical mechanism. The high value of 82,400 cal. for tetramethyltin, therefore, argues in favor of a rearrangement mechanism for the decomposition. Likewise, the lack of inhibition by nitric oxide and the initially high concentration of methane also tend to confirm this hypothesis.

While the evidence from the nitric oxide and packed bulb experiments indicate the absence of reaction chains, Rice and Polly[12] have pointed out that such evidence does not definitely exclude the possibility of free radical formation. If methyl radicals are produced in the primary process of the present reaction, the question immediately arises as to their ultimate fate if they do not initiate chains. Two methyl radicals might unite to form ethane, which at 485° would be relatively stable. There appears to be good evidence that such a combination must occur, in the gas phase, as a three-body process. Consequently, the presence of hydrogen in the reaction products, together with the walls, should provide ample opportunity for a propitious three-body collision, since both are efficient removers of energy. However, at no stage of the reaction does the analysis give evidence for ethane. Since all analyses gave a mean carbon atom value of 1.0 for the saturated hydrocarbons, it is concluded that the only one of any stability formed is methane.

In systems containing hydrogen and methyl radicals, it has always been observed that the major product formed is methane. On the other hand, in the absence of hydrogen, there is a markedly decreased methane and increased ethane formation. As a consequence, Taylor and Burton[13] have shown that the combination of two methyl radicals, with hydrogen as a third body, would result in the splitting of the hydrogen molecules and the production of two molecules of methane. Thus, if methyl radicals are produced initially in the decomposition of tetramethyltin, we might reasonably expect them to disappear in accordance with the reaction

$$2CH_3 + H_2 = 2CH_4$$

providing, of course, hydrogen molecules are initially present.

There also exists the possibility that methyl radicals might also react according to

$$CH_3 + CH_3 = C_2H_4 + H_2$$

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[12] Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938).

[13] Taylor and Burton, *ibid.*, **7**, 675 (1939).

From the work of Spence and Wild[14] on acetone, however, it appears doubtful whether the above process occurs to any great extent in the absence of free H-atoms.

In the present reaction, the kinetic evidence suggests the process to be mainly a rearrangement. While there are good indications that chains of appreciable length are not formed, kinetic information does not deny, and analyses tend to support, the possibility that some small percentage of free radicals are also produced. This would mean that two types of primary processes occur in the decomposition of tetramethyltin—a not unlikely assumption. Based on this, the following probable mechanism is postulated as being the most predominant

Primary process

1. Rearrangement

$$Sn(CH_3)_4 \longrightarrow \begin{cases} Sn + 2C_2H_4 + 2H_2 \\ Sn + C_2H_4 + 2CH_4 \\ Sn + C + 3CH_4 \end{cases}$$

2. Free Radical

$$Sn(CH_3)_4 \begin{cases} \nearrow Sn + C_2H_4 + H_2 + 2CH_3 \\ \searrow Sn + 4CH_3 \end{cases}$$

Secondary Process

$$2CH_3 + H_2 = 2CH_4 \quad \text{(fast)}$$
$$C_2H_4 = CH_4 + C \quad \text{(slow)}$$

It should be emphasized that in complicated decompositions it is difficult to say with any degree of assurance whether or not all, or indeed, any, of the postulated reactions are taking place, and if so, to what extent. Consequently we have simply formulated here a mechanism which conforms, in a logical fashion, with both the available experimental data and the existing knowledge on reaction energetics.

The question may now arise concerning the difference between the ratio of the final to the initial pressure at low and high pressures of tetramethyltin. Figure 1 indicates that for initial pressures greater than about 10 mm. this ratio was close to 3. The value of 3 is the expected one if the principal stoichiometric reaction is

$$Sn(CH_3)_4 \longrightarrow Sn + C + 3CH_4$$

It is significant to point out here that the results of analyses and the P_f/P_i ratio both may be fairly reproduced by assuming that for every 29 molecules decomposing according to the last equation, 3 more decompose stoichiometrically according to

$$Sn(CH_3)_4 \longrightarrow Sn + 2C_2H_4 + 2H_2$$

This would yield concentrations of gaseous products by volume of approximately 88% CH_4, 6% C_2H_4 and 6% H_2. It would also result in a P_f/P_i value of about 3.1. Thus it is plausible to assume that stoichiometrically the reaction is about 90% of the former equation and 10% of the latter.

In the case of low initial pressures the results show sensibly higher values which extrapolate to about 5. This difference between the low and high pressure P_f/P_i ratio can be explained, at present, only in the following general terms. It is known that the pyrolysis of olefins at these temperatures can be accompanied by polymerizations which in some cases are catalytic. Thus, condensates may be formed which will not appear in the gaseous products. These polymerizations would be facilitated by higher rather than lower initial pressures, making the P_f/P_i ratio greater in the latter case. Figure 1 substantiates the possibility of some such set of conditions existing in this reaction.

One final point should be discussed, namely, the differences in the activation energies of the various tetra-alkyls thus far investigated. Table IV lists these compounds together with their energies of activation given to the nearest whole number.

TABLE IV

Compound	E, cal.
$Si(CH_3)_4$	79,000
$Sn(CH_3)_4$	82,000
$Si(C_2H_5)_4$	51,000
$Ge(C_2H_5)_4$	51,000
$Pb(C_2H_5)_4$	37,000
$Si(C_3H_7)_4$	46,000

It is not surprising that the methyl compounds possess comparable activation energies since the alkyl groups are identical and the size of the central atoms not too different. In spite of these similarities, if one compound decomposed through a rearrangement process and the other by a chain mechanism, widely different values for the respective energies would be obtained. We may presume, therefore, that silicon and tin tetramethyl decompose by the same predominant mechanism, *i. e.*, a rearrangement process.

For the same reasons, the activation energies of silicon and germanium tetraethyl are also in close agreement with each other. They differ markedly, however, from the values of the methyl compounds.

Neglecting lead tetraethyl for the moment, silicon tetrapropyl has an energy lower than either the methyl or ethyl compounds. The difference in the activation energies between the methyl, ethyl and propyl tetra-alkyls may be attributed to the negative influence of the additional CH_3 substituents which tend to weaken the metal-to-carbon bonds. Differences in reaction mechanisms could also lead to an increased or decreased activation energy in going from methyl to ethyl, etc., alkyls. However, those differences in mechanism that are known to exist in the case of the silicon compounds appear to be slight.

The E_a value for lead tetraethyl presents somewhat of an enigma. One does not know whether this difference in energy between $Pb(C_2H_5)_4$ and the other ethyl compounds is due to the difference

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[14] Spence and Wild, *Nature*, **138**, 206 (1936); *J. Chem. Soc.*, **60**, 10 (1938).

in size of the central atom or to radical differences in the reaction mechanism. The first possibility can be better evaluated only when more data are available on additional members of the tetra-alkyl groups. As for the second alternative, a more thorough examination of the decomposition of tetraethyl lead would undoubtedly yield valuable information concerning its mechanism and energy of activation.

Summary

The thermal decomposition of tetramethyltin has been investigated between 440 and 493° over a range between 5 and 185 mm. initial pressure.

By the criteria of half-life periods, times for a given fractional pressure increase and initial rates, the reaction was found to be predominantly of the first order above 80 mm. initial pressure. At lower initial pressures the order increases, approaching that of second.

The specific velocity constant of the primary process was found to be $k_0 = 8.32 \times 10^{21} e^{-82,400/RT}$. Rate constants calculated by an indirect method agreed well with those obtained directly.

The reaction was found to be homogeneous once the reaction vessel was thoroughly coated with a deposit of tin and carbon.

Nitric oxide produced no inhibition but instead caused a slight catalytic acceleration of the primary process.

Chemical analyses made over the entire range of decomposition revealed the predominant gaseous product to be methane, together with some hydrogen and ethylene. Tin and carbon were also found as a deposit on the walls.

Based upon the kinetic data and the chemical analyses, a probable reaction mechanism was proposed.

An explanation is offered for the changes in activation energy observed in going from the methyl to ethyl to propyl tetra-alkyls thus far investigated.

BROOKLYN, N. Y. RECEIVED JANUARY 18, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

The Polarographic Reduction of the Platinum Metals

BY J. B. WILLIS

In a previous communication[1] the polarographic reduction of rhodium compounds was discussed in detail. In the present paper similar work is extended to the other platinum metals. With the exception of a recent paper on the polarographic reduction of osmium tetroxide,[2] the only published work in this field seems to be that dealing with catalytic hydrogen waves produced in acid solutions containing small amounts of the platinum metal chlorides.[3,4]

Theory

It was shown in the previous paper[1] that although rhodium trichloride itself was rapidly decomposed by mercury, complex salts of rhodium could be obtained which were stable toward mercury, and which were reducible at the dropping electrode. In the present work it is shown that the other platinum metals also form stable complexes, which in some cases give polarographic steps.

In order to calculate *n*, the number of electrons involved in each reduction step, the Ilkovič equation was applied and the log plot calculated in the previously described way. As explained before, in the calculation of the diffusion coefficient of a complex metal ion conductivity data for similar ions of other metals can be used without any serious error.

Experimental

A manual instrument was used, similar to the previously described one. All measurements were carried out at 25°, air being displaced from the solutions by purified nitrogen. The half-wave potentials ($E_{1/2}$) are expressed relative to the saturated calomel electrode, and are considered to be in error by not more than ±10 mv.

The solutions used were prepared by adding 1 ml. of an analyzed stock solution of a salt of the metal to an excess of the complex-forming substance, which also acted as supporting electrolyte, warming to complete the reaction, and making up to 50 ml. The solutions were 0.001 *M* with regard to the metal to be studied, unless otherwise stated.

Results

Chloro-complexes of the Platinum Metals.—All the chlorosalts used as stock solutions in this work were spontaneously decomposed by mercury, though in the case of the hexachlororuthenate and aquopentachlororuthenate the decomposition was very slow. No polarographic steps could be obtained from any of the chlorosalts. With the exception of di-ethylenediamine platinous chloride, however, none of the complexes studied polarographically were decomposed even by long standing over mercury.

Ruthenium.—Potassium hexachlororuthenate $K_2[RuCl_6]$ was used for Ru^{IV}, and potassium

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[1] Willis, THIS JOURNAL, **66**, 1067 (1944).

[2] Crowell, Heyrovsky, and Engelkemeir, *ibid.*, **63**, 2888 (1941).

[3] Herasymenko and Slendyk, *Coll. Czech. Chem. Comm.*, **5**, 479 (1933).

[4] Herasymenko and Slendyk, *Z. physik. Chem.*, **162**, 223 (1932).