THE KINETICS OF THE THERMAL DECOMPOSI-TION OF GASEOUS SILICON TETRAETHYL AND SILICON TETRAPROPYL.*

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Received 26th August, 1940.

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. To some extent this has been done for some of the simpler hydrocarbons. It was thought that a study of a series consisting of more complicated type molecules might prove helpful. In this regard the tetra-alkals of the fourth group of the periodic table suggest themselves as interesting subjects for investigation. It might also be of interest to see what type of reaction is produced by compounds which might presumably be expected to split off alkyl radicals as a primary process.

Research on the thermal decomposition of tetra-alkyls has been confined to date to lead¹ and germanium,² tetraethyl, and silicon tetramethyl,³ but no attempt has been made to study the effect of changing the alkyl radical on the same central atom. Since a beginning has been made with silicon tetramethyl, it was felt worth while in the present investigation to extend this series to include silicon tetraethyl and silicon tetrapropyl.

Experimental.

The course of the decompositions was followed in the usual manometric method. The gas reacted in pyrex bulbs of 100 and 250 c.c. capacity, and by using small bore capillary tubing the dead space was reduced to about 2 per cent. of the total volume.

An electric furnace was maintained at constant temperature within a half degree by a special thermoregulator-mercury relay device. Tem peratures were measured by a platinum-platinum-rhodium thermocouple which was regularly checked by a standard potentiometer. Since the normal boiling-points of these compounds were 151° (Si(C₂H₅)₄) and over 200°, all tubing and taps were heated electrically. The temperature of the taps did not vary more than 3° over a three-hour period. A special aluminium stearate tap grease was employed. The rest of the apparatus consisted of the usual system for attaining low pressures.

Silicon tetraethyl and tetrapropyl were prepared by a Grignard method suggested by Dr. George Calingert of the Ethyl Gas Corporation. ‡ Each preparation was carefully fractionated under reduced pressure and only that product which had a constant boiling-point within $\pm 0.05^{\circ}$ was used. Different preparations gave the same boiling-points within this limit after purification.

- * Presented at the Detroit Meeting of the American Chemical Society. † Lalor Foundation Fellow, 1939-40, Balliol and Trinity Laboratory, Oxford. Private communication.
- ¹ Leermakers, J.A.C.S., 1933, **55**, 4508. ² Geddes and Mack, *ibid.*, 1930, **52**, 4372.
- ⁸ Helm and Mack, *ibid.*, 1937, **59**, 60.

The gaseous products were analysed on a Bone and Wheeler apparatus. The higher olefines were separated from the ethylene by the method of Hurd and Spence.4

Silicon Tetraethyl.

1. Nature of the Decomposition.

From photochemical evidence with allied organo-metallic compounds, one might reasonably expect the primary step in the thermal decomposition of silicon tetraethyl to be

or

$$\begin{array}{l} \operatorname{Si}(C_2H_5)_4 &= \operatorname{Si} + 4(C_2H_5), \\ \operatorname{Si}(C_2H_5)_4 &= \operatorname{Si}(C_2H_5)_3 + C_2H_5 \text{ (slow)}, \\ \operatorname{Si}(C_2H_5)_3 &= \operatorname{Si} + 3C_2H_5 \text{ (fast)}. \end{array}$$

In a recent paper, Moore and Taylor⁵ indicated the various possibilities of recombination and reaction that ethyl radicals may undergo. These authors considered, in the main, only the reactions of ethyl radicals produced photochemically, and at temperatures well below those employed thermally. Hence, in the present study, secondary reactions



involving ethyl radicals may not necessarily result in the same final products of reaction. Thus, if ethyl radicals are initially produced in the thermal decomposition of silicon tetraethyl 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 This procedure is straightforward enough for rate of pressure change. 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.

Silicon tetraethyl decomposes to give a total pressure increase of about two and one-half times that of the initial pressure. Fig. I shows that the ratio of the final to the initial pressure is not exactly constant

⁴ Hurd and Spence, J.A.C.S., 1929, **51**, 3353. ⁵ Moore and Taylor, J. Chem. Physics, 1940, **8**, 396.

and varies somewhat with the initial pressure. On the whole, the total pressure increase is greater at low initial pressures, and falls off asymptotically at higher pressures. The figure does indicate, however, that the end-points are not affected by temperature.

This lack of complete reproducibility in end-points obtained from the same initial pressures creates the problem of determining the best method of expressing the rate constant. From what has been said, it should be clear that a different value for the order of reaction might be obtained, depending 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 silicon tetraethyl, and since it is the primary process that is of greater importance, we shall depend upon the initial rate. It will, however, be shown later that the result is substantially the same, no matter whether the order of reactions is obtained from the initial rate, or from the halftime for the total pressure increase.

2. Reaction Products.

The analyses of the final reaction products gave but little indication as to the probable mechanism. In order to gain a clearer picture of



FIG. 2.—Showing the change in the decomposition products of $Si(C_2H_5)_4$ with time at 580° C. Each point is the average of five analyses.

what was occurring during the primary stage, samples were withdrawn from the reaction vessel over the whole range of the decomposition. The results are shown in Fig. 2.

The analyses indicate that the initial step in the reaction is the formation of ethyl radicals and silicon. These ethyl radicals then react to give ethylene and hydrogen and a very slight amount of higher olefines. The ethylene formed is slowly converted into methane and carbon. Although two ethyl radicals might unite to form butane, at 580° C. none was found. Since all the analyses gave a mean carbon atom value of $I \cdot O$ for the saturated hydrocarbons, it is concluded that the only one of any stability formed is methane. Undoubtedly, it is the

slow subsequent conversion of ethylene which makes the end-points difficult to interpret, and gives added reason for basing the order of reaction upon the initial rates.

At 580° C. the decomposition is practically complete within twenty-five minutes. Up to within five minutes of the end-point, the only noticeable deposit on the walls of a new flask is a white coating of silicon. After runs have gone to completion the walls show the blackish-gray deposit, which eventually assumes the shiny-black appearance of carbon particles. Even after no further change in pressure occurs the ethylene concentration continues to decrease and the methane concentration to increase. which suggests a reaction of the type

$$C_2H_4 = CH_4 + C.$$

It is now possible to postulate the following mechanism as being the most predominant :---

Primary Process,	or,	$\begin{array}{l} {\rm Si}({\rm C_2H_5})_4 = {\rm Si} + 4{\rm C_2H_5},\\ {\rm Si}({\rm C_2H_5})_4 = {\rm Si}({\rm C_2H_5})_3 + {\rm C_2H_5} \ ({\rm slow}),\\ {\rm Si}({\rm C_2H_5})_3 = {\rm Si} + 3{\rm C_2H_5} \ ({\rm fast}). \end{array}$
Secondary Process		$C_{2}H_{5} = C_{2}H_{4} + H,$ H + H = H ₂ (fast), $C_{2}H_{4} = CH_{4} + C$ (slow).

The question may arise concerning the difference between the observed pressure increase at the end of the reaction and that expected from stoichiometric considerations. It is well known that hydrogen is adsorbed on the walls of reaction vessels. On a silicon surface this process may occur to an even greater extent. This explains the initial deficiency of hydrogen and its slight decrease in concentration towards the end of the reaction.

Secondly, it is known that the pyrolysis of olefines at these temperatures can be accompanied by polymerisations which in some cases are catalytic, and condensates will be formed which do not appear in the gaseous products.

Polymerisation would be facilitated at higher rather than lower initial pressures, making the P_f/P_0 ratio greater in the latter case. Fig. 1 substantiates this and by extrapolating to zero pressure, a total pressure increase of about the right order of magnitude is obtained for the stoichiometric equation. Therefore, under the conditions of the experiments it is not surprising that the total pressure increase is somewhat smaller than that expected from a theoretical standpoint.

3. Order of Reaction.

Fig. 3 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. Between 200 and about 50 mm. the pressure-time curves almost exactly coincide over the initial stage of the decomposition, which corresponds to the splitting off of ethyl radicals from the silicon This reproducibility in the early stage indicates that the primary atom. process, at least, is a first order reaction. Deviations which occur in the later stages need not interest 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.

That the reaction is of the first order is further substantiated by Fig. 4, in which the reciprocal of the half life is plotted against the initial pressure. At one temperature, however, a plot of the logarithm of the half-time against the logarithm of the initial pressure, gave an order of reaction of 1.36. On the whole, it may be said that the decomposition

 $Si(C_2H_5)_4$.

of silicon tetraethyl is of an order which is predominately the first. although increasing slightly at lower initial pressures.

4. Effect of Nitric Oxide.

It is definitely known (Staveley and Hinshelwood,⁶ Staveley,⁷ and Hobbs and Hinshelwood ⁸) that NO will markedly inhibit the rate of

decomposition of ethane at 600° C. According to the theory of NO inhibition radicals which propagate chains are removed by reaction with

⁶ Staveley and Hinshelwood, Proc. Roy. Soc. A, 1936, 154, 335.

⁷ Staveley, *ibid.*, 1937, 162, 557.
⁸ Hobbs and Hinshelwood, *ibid.*, 1938, 167, 439.

the NO. Thus, an investigation of the decomposition of silicon tetraethyl in the presence of NO should be a test not only for the presence of ethyl radicals, but also an indication of the existence of reaction chains of any appreciable length.

It was found that small amounts of NO have no effect upon this reaction. Large amounts of NO affect the total pressure increase in a manner that is very marked in the secondary stages of the reaction, while the primary rate is affected only very slightly. A comparison between the inhibited and uninhibited reactions is given in Fig. 5.

The fact that NO does affect the initial rate—even though the effect is not great—indicates that radicals are present, which react with it. However, since the magnitude of this effect is so small it can be safely assumed that the reaction $Si(C_2H_5)_4 + Radical = is$ not occurring to any

FIG. 5.—Inhibition by nitric oxide of the thermal decomposition of $Si(C_2H_5)_4$ at 560° C.; $\bigcirc P_0 = 97$ mm. unhibited; $\oplus P_0 = 66$ mm. + 2 mm. NO; $\bigcirc P_0 = 103$ mm. + 10 mm. NO'; $\oslash P_0 = 109$ mm. + 30 mm. NO; $\odot P_0 = 127$ mm. + 25 mm. NO.

great extent. Hence, the decomposition of silicon tetraethyl does not proceed by a chain mechanism.

Since, however, ethyl radicals are formed in the primary process, the question arises as to their ultimate fate. They might recombine by simple binary collisions to form butane. However, at no stage of the reaction does analysis give evidence for this product. Although the possibility exists, on general grounds the removal of an ethyl radical by a hydrogen atom, in a simple binary process, is less likely. Since little or no ethane is formed this process cannot occur to any measurable extent.

It would appear, then, that the ethyl radicals formed in the initial break-up of $Si(C_2H_5)_4$ must disappear by reactions of which

$$C_2H_5 = C_2H_4 + H$$

becomes the predominant one. The hydrogen atoms so produced are converted into hydrogen molecules by homogeneous ternary collisions

and/or reaction at the walls. In either case, this rate is fast, and has no effect upon the kinetics of the reaction as a whole. The possibility of reactions between hydrogen atoms and unsaturated hydrocarbons are not excluded but do not assume an important rôle in this particular reaction.

5. Surface Effects.

Experiments in a packed reaction vessel having a surface/volume ratio of 10 times over that of the unpacked bulb showed that at three different temperatures the initial rate remained unchanged. The secondary stages of the reaction were found always to be depressed slightly. The ratio of P_f/P_0 remained essentially the same. The first half-dozen runs made in the clean, packed reaction vessel gave very heterogeneous results, but after the bulb became well coated with a deposit of silicon the results were quite reproducible.

From these experiments it is concluded that the decomposition of silicon tetraethyl is predominately homogeneous in nature. The secondary stages of this reaction involving mainly the decomposition of hydrocarbons seem to be slightly heterogeneous in character. It may well be that the lack of exact reproducibility manifested in the later stages of this reaction is due to the slight changes which take place on the surface of the bulb from run to run.

Nitric oxide has essentially the same effect in the packed as in the

FIG. 6.—White circles, $Si(C_2H_5)_4$, $E_a = 51,000$ cal. Black circles, $Si(C_3H_7)_4$, $E_a = 46,000$ cal.

unpacked vessel, except that in the secondary stages the reaction appears to be inhibited to a slightly greater extent.

A series of runs were carried out to determine the effect of various reaction products, which proved to be negligible.

6. Energy of Activation.

A plot of the logarithm of the initial rate against the reciprocal of the absolute temperature (Fig. 6) gave a sensibly straight line. From data at eight different temperatures over a range of 80° C., the activation energy of Si(C₂H₅)₄, determined by the

method of least squares, was 50,500 cal. Since this value is based upon data obtained over the initial stage of the decomposition, namely $Si(C_2H_5)_4 = Si + 4C_2H_5$, or $Si(C_2H_5)_4 = Si(C_2H_5)_3 + C_2H_5$, this activation energy should give some information as to the strength of the carbon-silicon bond.

Silicon Tetrapropyl.

1. Nature of the Decomposition.

We might expect the decomposition of $Si(C_3H_7)_4$ to follow along the same lines as that of the ethyl compound. In general, this expectation is borne out. The procedure in studying this reaction was the same as that previously employed.

Silicon tetrapropyl decomposes to give a total pressure increase, on the average, of about 3.5 times that of the initial pressure. The ratio of the final to the initial pressure is less reproducible than that of silicon tetraethyl, and varies between 3.0 and 4.0. However, the same type curve as that for $Si(C_2H_5)_4$ (Fig. 1) is followed. Temperature changes appeared to have no effect. At all temperatures the reaction approached the end-point very slowly. For example, at 560° C.—within 10° of the highest temperature investigated—the end-point had not been reached after four and one-half hours.

Hence, we are again confronted with the problem of the best method for determining a rate constant which will give the correct order of the reaction. In some respects, the decomposition of $\operatorname{Si}(C_3H_7)_4$ is analogous to that of propane (Hobbs and Hinshelwood⁸) where the great complexity of the secondary reactions made it advisable to base measurements upon the initial rate. Since $\operatorname{Si}(C_3H_7)_4$ gives even more complex reactions we have decided to adopt the same procedure, as again we are mainly interested in the primary process.

2. Reaction Products.

Samples were withdrawn from the reaction vessel at various time intervals throughout the course of the reaction at 550° C., where the initial rate of reaction of $Si(C_3H_7)_4$ was approximately the same as that of $Si(C_2H_5)_4$ at 580° C. These results are presented graphically in Fig. 7.

FIG. 7.—Showing the change in reaction products during the course of the decomposition of Si(C₃H₇)₄ at 550° C.
Q—C₃H₆; Q—C₂H₄; ●—H₂; O—CH₄.

By way of variation, the percentage of reaction products at various pressure differences rather than the various times are recorded in this case. By extrapolation to zero pressure it can be seen that the primary product is predominantly a higher olefine, most probably propylene, which suggests as the primary step

$$\begin{array}{l} {\rm Si}({\rm C_3H_7})_4 = {\rm Si} + 4{\rm C_3H_7},\\ {\rm or} \quad {\rm Si}({\rm C_3H_7})_4 = {\rm Si}({\rm C_3H_7})_3 + {\rm C_3H_7} \ ({\rm slow}),\\ {\rm Si}({\rm C_3H_7})_3 = {\rm Si} + 3{\rm C_3H_7} \ ({\rm fast}). \end{array}$$

The amount of hydrogen is about half that found in the case of $Si(C_2H_5)_4$. On the basis of the proposed primary processes, there is little reason for the amounts of hydrogen to differ appreciably, unless, in one case, some of the hydrogen atoms react in some manner other than a simple recombination process. Since the hydrogen concentration remains constant after the early stage of the reaction, and since the ethylene concentration remains sensibly unchanged until the end-point is approached, it may be inferred that the secondary reactions are

$$\begin{array}{c} C_{3}H_{7}=C_{3}H_{6}+H,\\ 2H=H_{2}\ (fast),\\ C_{3}H_{6}+2H=C_{2}H_{4}+CH_{4}\ (fast). \end{array}$$

Total pressure increases are affected to a greater extent by the same factors as discussed with the previous compound.

Before any end-point run had been made the only deposit in the reaction vessel was silicon, but afterwards carbon was also found, suggesting the reaction

$$C_2H_4 = CH_4 + C,$$

as found with the silicon tetraethyl. A further indication that the decomposition of $Si(C_{3}H_{7})_{4}$ proceeds by a mechanism which is essentially the same as that of $Si(C_{2}H_{5})_{4}$ is the fact that no saturated hydrocarbon other than methane could be found in the gaseous products. In all analyses the mean number of carbon atoms was 1.0.

The results confirm suspicions as to the complexity of this reaction. Surface influences explain the somewhat irregular results obtained in the secondary stages and at the end-point. However, the analyses seem to justify our method of determining the rate constant.

3. Order of Reaction.

As in the case of silicon tetraethyl the *p*-t curves for various initial pressures are almost exactly coincident in their initial stages when Δp

FIG. 8.—Variation of the reciprocal of percentage pressure increase with initial pressure at 530° C. for Si(C₃H₇)₄.

is plotted as a percentage of initial pressure. Apart from some deviation at lower pressures, these curves indicate that over a wide pressure range the primary reaction is of the first order. The secondary reactions, while more complex than those of silicon tetraethyl, are found not to influence the initial rates over the pressure range investigated.

The curves in Fig. 8 show the reciprocals of a 25 and 50 per cent. pressure increase plotted as a function of the initial pressure. Even though

there is a tendency for the rate to fall off at low initial pressures, the reaction is clearly of the first order over a wide pressure range. We conclude, then, from measurements based upon initial rates and times for a given fractional increase of the initial pressure that the decomposition of $Si(C_3H_7)_4$, like that of $Si(C_2H_5)_4$, is predominantly of the first order. Accidental compensation of error would be unlikely to lead to the same result by both methods.

4. Effect of Nitric Oxide.

As with the tetraethyl compound, small quantities of NO had no effect. With 25-35 mm. NO, however, the secondary processes were noticeably inhibited though the primary process was affected to only a very slight degree. The substantial effect on the total pressure increase with larger amounts of NO indicates that radicals have, in fact, been present during the reaction; the absence of any marked inhibition in the initial rate shows that these radicals have not propagated chains with the primary reactants.

By the arguments previously used, the propyl radicals formed in the primary process disappear according to reactions of which the principal one is

$$C_3H_7 = C_3H_6 + H.$$

Here, however, only half the hydrogen atoms are removed by simple recombination, the other half reacting with the secondary products, probably in the manner

$$C_{3}H_{6} + 2H = C_{2}H_{4} + CH_{4}$$

5. Surface Effects.

A new reaction vessel packed with uniform bits of pyrex tubing had a surface/volume ratio 10 times greater than that of the unpacked bulb. The first half-dozen or so runs gave an abnormally fast initial rate over the first two minutes after which they slowed down abruptly. With each subsequent run the initial rate became slower until finally reproducible p-t curves were obtained. The initial rates of these runs correspond to those in the unpacked vessel. Check runs made in the packed vessel after it had been in use over a three-month period showed that the rates had not varied. This indicates that a certain minimum coating of silicon on the walls is necessary for reproducibility, but that after a lower limit is attained subsequent layers of silicon have no effect upon the initial process.

With a new 250 c.c. unpacked bulb the results were essentially the same. The only exception was that the "conditioning period" necessary for reproducibility was much shorter.

These results seem to indicate that we are dealing with a reaction which borders on heterogeneity.

6. Activation Energy.

From the initial rates at six different temperatures (cf. Fig. 6) the activation energy was determined by the method of least squares. Its value was 46,000 cal., which is about 4,500 cal. less than that of the ethyl compound. One does not know, exactly, whether to attribute this difference to the negative influence of the additional CH_3 substituent which tends to weaken the Si—C bond, or to slight differences in the reaction mechanisms (vide supra).

Data available showed that the final gaseous decomposition products of silicon tetramethyl are mainly methane and hydrogen, carbon and silicon being deposited on the walls. No ethane was found. The amount of hydrogen formed is about 40 per cent., a somewhat higher value than that for the tetraethyl which itself is 50 per cent. higher than

that of the propyl. Based on these facts, the probable mechanism that suggests itself for the methyl compound is

$$Si(CH_3)_4 = Si + 4CH_3,$$

or $Si(CH_3)_4 = Si(CH_3)_3 + CH_3$ (fast),

followed by

$$2CH_3 = C_2H_4 + 2H \text{ (practically complete)},\\ 2H = H_2 \text{ (fast)},\\ C_2H_4 = CH_4 + C.$$

The published results for the activation energy (Helm and Mack³) is 79,000, but since this was determined for a range of 20-80 per cent. pressure change, it is by no means strictly comparable with the present results.

Table I gives a comparison between the results obtained in the kinetic studies on silicon tetraethyl and silicon tetrapropyl.

TABLE	IComparison	Between	SI(C,H)	AND	$SI(C_H_{2})_{4}$
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	Si(C ₂ H ₅) ₄ .	Si(C ₃ H ₇) ₄ .	Ratio
<i>T</i> ° C,	Approx. $k_1 \times 10^{-3}$ sec. ⁻¹ .	$\begin{array}{c} \text{Approx.} \\ k_1 \times 10^{-3} \text{ sec.}^{-1}. \end{array}$	kPr/kEt.
520		1.43	
530	0.875	1.85	2.12
540	1.08	3.00	2.77
550	1.83	3.83	2.09
560	2.53	5.85	2.31
570	3.26	7.68	2.36
580	5.28	—	_
590	7.75		_
600	10.35		

Ratio of PtPo.

Activation Energy.

Si(C ₂ H ₅) ₄ .	Si(C ₃ H ₇) _€ .	Si(C ₂ H ₃) ₄ .	Si(C ₈ H ₇) ₄ .	
From 2—3 Av. 2·5	3—4 3`5	50,500	46,000	

Summary.

The thermal decomposition of silicon tetraethyl and silicon tetrapropyl is kinetically complex. By the criteria of initial rates, half-life periods and times for a given fractional pressure increase, the primary process, in both cases, is found to be predominantly of the first order. At lower initial pressures the order increases slightly.

Both reactions are homogeneous over the primary stage but show some tendency toward heterogeneity in the secondary processes, this effect being greater in the case of the propyl compound.

Small amounts of NO have no effect. Large quantities of NO inhibit the primary process of both reactions only slightly, indicating that radicals

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are formed initially but that long chains are not propagated with the primary reactant. The secondary processes of both reactions are markedly inhibited by large amounts of NO. Chemical analyses made on the gaseous products over the entire decomposition range together with the kinetic data indicate that the predominant reaction mechanisms are :

Silicon Tetraethyl

Primary Process or,	$\begin{array}{l} {\rm Si}({\rm C_2H_5})_4 = {\rm Si} + 4{\rm C_2H_5}, \\ {\rm Si}({\rm C_2H_5})_4 = {\rm Si}({\rm C_2H_5})_3 + {\rm C_2H_5} \ ({\rm slow}), \\ {\rm Si}({\rm C_2H_5})_3 = {\rm Si} + 3{\rm C_2H_5} \ ({\rm fast}). \end{array}$
Secondary Process	$C_{2}H_{5} = C_{2}H_{4} + H,$ $2H = H_{2} \text{ (fast)},$ $C_{2}H_{4} = CH_{4} + C \text{ (slow)}.$
Silicon Tetrapropyl	
Primary Process or,	$\begin{array}{l} {\rm Si}({\rm C_3H_7})_4 = {\rm Si} + 4{\rm C_8H_7}, \\ {\rm Si}({\rm C_3H_7})_4 = {\rm Si}({\rm C_3H_7})_8 + {\rm C_3H_7} \ ({\rm slow}), \\ {\rm Si}({\rm C_3H_7})_5 = {\rm Si} + 3{\rm C_3H_7} \ ({\rm fast}). \end{array}$
Secondary Process	$C_{3}H_{7} = C_{3}H_{6} + H,$ $2H = H_{2} \text{ (fast)},$
C_3H_6	$+ 2H = C_2H_4 + CH_4,$
	$C_2H_4 = CH_4 + C \text{ (slow)}.$

The author wishes to express his thanks to the Lalor Foundation, whose grant of a Fellowship has made possible these investigations.

The author is also deeply grateful to Professor C. N. Hinshelwood for his continual guidance, interest and advice throughout the course of this research.