

ane or decahydronaphthalene in the presence of aluminum chloride catalyst, the alkyl groups are split off to yield the corresponding paraffins.

The relative stability of different alkylbenzenes

is reported.

Various applications of this reaction are proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Thermal Decomposition of Gaseous Silicon Tetramethyl

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In a previous paper¹ a study was made of the thermal decomposition of gaseous germanium tetraethyl. In the present paper the same type of study has been made of silicon tetramethyl. We have found that silicon tetramethyl gives a homogeneous decomposition which is unimolecular down to pressures of about 10 cm. In the case of germanium tetraethyl, over the temperature range employed, 420–450°, the products of the decomposition were a bright mirror-like deposit of germanium on the walls of the reaction vessel and a gas phase of essentially the same composition as the products obtained from the pyrolysis of *butane* at these temperatures. Whereas in the case of the more stable silicon tetramethyl it was necessary, to obtain a conveniently measurable rate of decomposition, to work at a much higher temperature, 660–720°, a sooty deposit was formed, consisting of silicon and carbon, and the gaseous products resembled closely those obtained from the pyrolysis of *ethane* at these temperatures.

Experimental

Silicon tetramethyl was prepared with the Grignard reaction by a method analogous to that employed² by Dennis and Hance for making germanium tetramethyl. The fraction of the purified product saved for use had a boiling point of 26.30 ± 0.05°.

The course of the decomposition was followed by three different manometer techniques, all of which gave substantially the same results. These included (1) a direct manometric method which was later abandoned in favor of (2) pointer membrane manometers and (3) clicker type null pressure gages. The pointer manometers were used in the same way as those described by Geddes¹ and Mack. Clicker gages were mounted outside the furnace and connected to the reaction vessel and the manometer line in the usual manner.

(1) Geddes and Mack, *This Journal*, **52**, 4372 (1930).

(2) Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

In the fairly high temperature range, 660–720°, it was necessary that fused quartz reaction chambers be used rather than Pyrex. Constant temperature inside a heavily lagged electric furnace was maintained within 0.3° with a platinum resistance thermometer wound near the heating coils and with an automatic controlling mechanism similar to that described by Scott and Brickwedde.³

Treatment of Data

The data for a typical run (No. 33) are given in Table I. This decomposition was carried

TABLE I
DATA FOR VELOCITY CONSTANT AT 678.7°

Time, min.	Pressure (P), cm.	$P_{\infty} - P$	k , sec. ⁻¹
Before	10.35		
0	33.00 = P_0		
3.62	38.35	58.45	
4.55	42.30	54.50	0.00126
5.28	45.70	51.10	.00147
6.00	48.64	48.16	.00137
7.03	52.60	44.20	.00139
7.92	55.70	41.10	.00137
9.07	59.35	37.45	.00135
10.02	62.13	34.67	.00135
11.25	65.45	31.35	.00136
12.48	68.37	28.43	.00132
13.75	71.10	25.70	.00133
14.92	73.35	23.45	.00131
16.07	75.45	21.35	.00136
17.50	77.73	19.07	.00131
19.35	80.32	16.48	.00132
20.65	81.91	14.89	.00130
22.08	83.50	13.30	.00132
23.55	84.95	11.85	.00131
25.17	86.40	10.40	.00134
27.20	87.90	8.90	.00128
28.62	88.85	7.95	.00132
31.05	90.22	6.58	.00130
33.12	91.20	5.60	.00129
37.08	92.66	4.14	.00127
42.06	94.05	2.75	
92.00	96.80 = P_{∞}		
After run	31.15	$P_{\infty}/P_0 = 2.95$	

Av.
0.00133

0.4 to 0.8 completed

(3) Scott and Brickwedde, *Bur. Standards J. Research*, **6**, 407 (1931).

through at 678.7° with a membrane manometer. Inspection of the velocity constants computed from the time intervals shows that, after temperature equilibrium had been established, deviations are reasonably small. There is a small but definite drift downward in the value of the velocity constant toward the end, as is usually observed in such reactions. It is probably to be ascribed, at least in part, to the effect of the relatively large proportion of products on the small fraction of remaining silicon tetramethyl.

It was our uniform practice to compute the velocity constant for the interval from 0.4 to 0.8 completed and to consider this the constant for the run. The velocity constant for run No. 33 in Table I consequently is taken as 0.00133 sec.⁻¹. The ratio of the pressures (room temperature) before and after the decomposition was found to be 3.01; its close equivalent, P_{∞}/P_0 , was 2.95.

Table II gives data for decompositions, at various pressures, all carried out at 689°. The method employed is given as (P) for pointer membrane and (C) for clicker system.

TABLE II
DATA FOR DECOMPOSITIONS AT 689°

Run	Method	P_0 , cm.	P_{∞}/P_0	k , sec. ⁻¹
2	P	43.8	2.98	0.00188
4	P	27.0	2.61	.00203
8	P	25.1	3.00	.00210
9	P	36.8	2.87	.00180
10	P	32.5	2.92	.00193
11	P	34.6	2.87	.00193
16	P	23.1	3.03	.00202
52	P	35.5	2.90	.00188
51	P	15.3	3.20	.00212
47	P	13.5	2.98	.00220
75	C	12.6	..	.00182
46	P	7.8	3.45	.00215
76	C	7.7	..	.00188
77	C	7.5	..	.00193
45	P	7.4	3.25	.00222
78	C	6.9	..	.00205
50	P	5.8	2.79	.00217
44	P	4.0	3.89	.00232
79	C	3.68	..	.00200
42	P	3.58	3.95	.00245
80	C	3.3	..	.00198
43	P	3.12	3.39	.00233
81	C	1.48	..	.00210
82	C	1.22	..	.00215
49	P	0.85	..	.00225
83	C	.44	..	.00207
13	P	27.3	2.93	.00195
14	P	25.7	3.46	.00212
15	P	33.8	3.42	.00205

Av. 0.00198

Av. 0.00204
(Surface increased 40-50 times)

The separate velocity constants calculated over short time intervals during any one decomposition are in fairly good agreement if the initial pressure, P_0 , is high, and show a falling off only in the last quarter of the run. When the initial pressure is low the constants show a rapid falling off during the run, indicating that a unimolecular reaction is not being followed strictly. This second type of behavior begins to be apparent in the vicinity of 10 cm. initial pressure. A final average for the unimolecular constant is taken for P greater than 13 cm. (Below 10 cm. initial pressure the average k for a run was close to that for higher pressures but it was the mean of a rapidly descending series of values.) No critical pressure could be found below which the specific reaction rate was even reasonably constant throughout the run and lower than that secured at high pressures. The break predicted by the Lindemann theory seems lost as the unimolecular rate fades gradually into a higher order reaction with decreasing pressure.

At the bottom of Table II, the complete homogeneity of the reaction is shown by the results of Runs 13, 14, 15, in which the exposed surface area in the reaction vessel was increased 40-50 times by addition of quartz fibers, without a significant change in the velocity constant. A wall reaction may well play a significant role at low pressures, however.

The data for a typical low pressure run are

TABLE III
TYPICAL DECOMPOSITION AT LOW PRESSURE (689°)

Time, min.	Pressure, P	$P_{\infty} - P$	k , sec. ⁻¹ Uni-molecular	k' , sec. ⁻¹ Bi-molecular
0	14.9 = P_0			
3.25	26.60	18.00		
4.12	29.05	15.55	0.0028	0.00017
5.33	31.70	12.90	.0026	.00018
6.35	33.45	11.15	.0024	.00019
7.60	35.30	9.30	.0024	.00023
8.78	36.50	8.10	.0020	.00027
10.27	37.80	6.80	.0020	.00026
11.78	38.75	5.85	.0017	.00026
14.33	40.05	4.55	.0015	.00032
16.78	40.83	3.77	.0013	.00031
19.08	41.45	3.15	.0013	.00038
22.43	41.98	2.62	.0009	
26.42	42.58	2.02	.0011	
31.10	42.87	1.73	.0006	
39.30	43.45	1.15		
43.50	43.60			
54.00	43.97			
74.42	44.35			
97.0	44.60 = P_{∞}			

given in Table III. The data were secured with a clicker system and a heavy walled quartz reaction vessel to avoid appreciable loss of hydrogen by diffusion. Pressures were measured in cm. of ethyl phthalate and the initial pressure (P_0) is taken as $\frac{1}{3} P_\infty$ or 14.9 cm. ethyl phthalate or 1.22 cm. of mercury.

Velocity constants when computed on both a uni- and a bimolecular basis are about equally unsatisfactory, and indicate an order of reaction between the two.

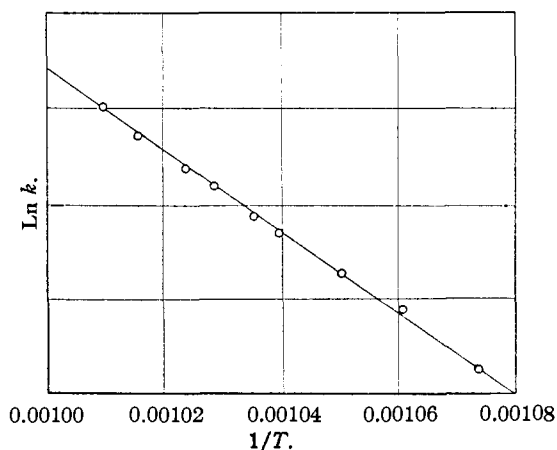


Fig. 1.

The variation of the velocity constant with temperature is shown in Table IV, and the plot of $\ln k$ against $1/T$ is given in Fig. 1.

No. of runs	Temp., °C.	Av. k , sec. ⁻¹
3	717	0.00672
3	711	.00520
3	704.6	.00380
10	700	.00320
13	693	.00233
10	689	.00198
6	679	.00134
5	669.2	.000847
3	659	.000527

The velocity constant as a function of temperature is given by the equation

$$\ln k = 35.03 - 78,800/RT$$

The energy of activation for the reaction is hence 79,000 cal. with a possible error of several thousand calories.

Analysis of Gaseous Products

In three cases after decomposition had been completed the vapor phase was pumped off and analyzed in a modified Bone-Wheeler apparatus. The results are given in Table V.

TABLE V

Compound	Temp., of decp., °C.	Acetylenes	Olefins	Hydrogen	Methane	Ethane	Time, min.
Si(Me) ₄	659	0.75	1.5	39.2	58.4	0.0	180
Si(Me) ₄	689	.13	1.0	40.0	58.8	.0	70
Si(Me) ₄	689	.52	0.0	39.1	60.4	.0	70
Ethane	675	1.9	.7	40.9	54.5	2.0	360
Ethane	810	0.5	.75	34.10	65.65	0.0	15

For comparison the table includes the analyses of Bone and Coward⁴ on the products resulting from the pyrolysis of ethane. If Si(Me)₄ decomposes through the agency of free methyl radicals, these short-lived molecules would come out of the reaction energy-loaded and in a highly reactive condition. It appears plausible that they might unite to form ethane but only momentarily, for ethane is known to decompose rapidly at these temperatures. The similarity of the products from ethane and Si(Me)₄ suggests that such a mechanism may be possible.

Summary

The thermal decomposition of silicon tetramethyl has been studied in the temperature range 659–717° and found to be homogeneous and unimolecular at pressures above 10 cm., and to fade into a higher order reaction at lower pressures.

The energy of activation is about 79,000 cal. and the velocity constant is given by the equation

$$\ln k = 35.03 - 78,800/RT$$

(In the case of germanium tetraethyl, the equation is $\ln k = 28.79 - 51,000/RT$, when k is expressed in reciprocal seconds.)

The decomposition produces a deposit of carbon and silicon and a gas phase essentially that secured upon pyrolysis of ethane.

No Lindemann critical pressure between uni- and bi-molecular rates could be located.

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(4) Bone and Coward, *J. Chem. Soc.*, **93**, 1206 (1908).