[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CORNING GLASS WORKS AND THE DOW CHEMICAL COMPANY]

Cyclo-diphenylsiloxanes

BY J. F. HYDE,[1] L. K. FREVEL,[2] H. S. NUTTING,[2] P. S. PETRIE[2] AND M. A. PURCELL[1]

The marked tendency of di-organosiloxanes to assume cyclic structures was demonstrated by the early isolation of a hexaphenylcyclotrisiloxane, $[(C_6H_5)_2SiO]_3$,[3a,3b] melting at 188°, and an octaphenylcyclotetrasiloxane, $(C_6H_5)_2SiO]_4$,[3b] melting at 201° (for convenience these are hereafter called trimer and tetramer, respectively).

Kipping and Robison[3c] showed that the trimer crystallized in the orthorhombic system and the tetramer in the triclinic (anorthic) system. They first encountered the variations in melting points and appearance of crystals along with low molecular weight values, which have been a source of difficulty in subsequent investigations.[3]

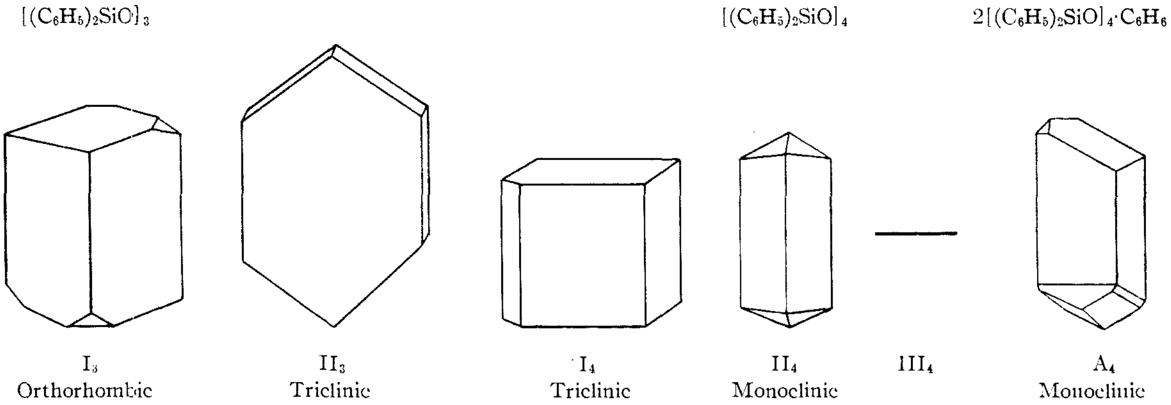

Fig. 1.—Crystal habits of trimer and tetramer.

Such variations have been observed by the authors[3h] during the past four years but it was not until X-ray methods were applied to the problem that it was fully appreciated that these variations are due to polymorphism, solvent of crystallization and eutectic formation. Burkhard[3e,f] and co-workers have also used X-ray techniques and have described one of the new tetramer polymorphs.

It has been found that certain of the polymorphs may be changed to others at will but due to their similarity and instability the procedures presented are not to be considered infallible. No attempt has been made to work out complete phase diagrams.

Polymorphism

The trimer has been found to exist in two crystalline forms. The first, I_3, is orthorhombic and is identical with that described by Kipping.[3c] The second, II_3, is triclinic. Each form melts at 187–188° and there is no lowering in melting point when they are mixed together. Diagrams of their crystalline appearance are shown in Fig. 1.

The two forms have been obtained simultaneously upon crystallization from ethyl acetate in large enough crystals so that they could be separated by hand. I_3 is converted to II_3 upon resolidification of molten I_3.

The tetramer has been found to exist as a crystalline substance, A_4, containing two moles of tetramer to one of benzene and as three solvent-free crystalline polymorphs I_4, II_4 and III_4. Diagrams of their crystalline appearance are shown in Fig. 1 and a diagram indicating their transformations from one to the other is shown in Fig. 2.

I_4 is triclinic and its crystal measurements correspond almost exactly with those given by Kipping.[3c]

II_4 is monoclinic and is the material described by Hyde and DeLong.[3d] It is also identical with the material described by Burkhard and co-workers with the exception that the crystals were clear and not opaque as described by the latter authors. This has been confirmed by X-ray examination of the original crystals erroneously described by the former as a trimer melting at 200° and by simultaneous X-ray examination of a recent sample with one which was kindly loaned by Dr. Burkhard for the purpose. I_4 and II_4 and their mixtures melt at 200–201°. They are stable at room temperature over a period of years.

III_4 melts at 188°, the same point as the trimer, and is quite unstable, changing over to I_4 at room temperature in a matter of a few hours. Conversely, I_4 is converted to III_4 by cooling its melt

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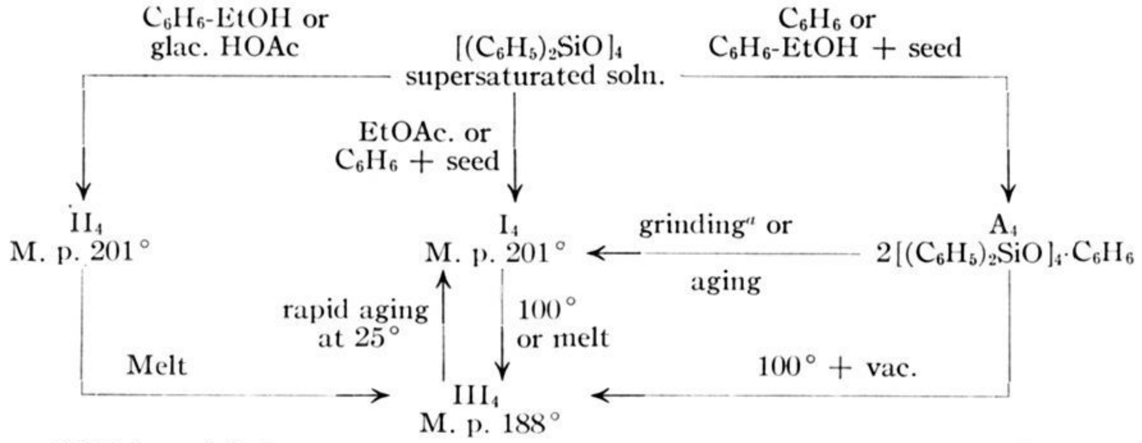
(1) Corning Glass Works.

(2) The Dow Chemical Company.

(3) (a) Dilthey, *Ber.*, **38**, 4132 (1905); (b) Kipping, *J. Chem. Soc.*, **101**, 2125 (1912); (c) Kipping and Robison, *ibid.*, **105**, 484 (1914); (d) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941); (e) Burkhard, *ibid.*, **67**, 2173 (1945); (f) Burkhard, Decker and Harker, *ibid.*, **67**, 2174 (1945); (g) Kipping, *Chem. Ind.*, 168 (1945); (h) Hyde, *ibid.*, 270 (1945).

Fig. 2.—Transformations of tetramer.



[a] With loss of C_6H_6.

slowly or by holding the crystals at 100° for about an hour. Mixtures of I_4 and III_4 sometimes melt gradually over the entire range between 188 and 201 and at other times they melt relatively sharply at some intermediate point. III_4 is also formed by cooling the molten II_4 slowly, but the corresponding change at 100° does not seem to take place.

A_4 can be obtained as large transparent monoclinic crystals which are quite stable when held in the mother liquor or in a small closed container. When these are subjected to conditions under which the benzene may escape, the crystals retain their original size and shape but become opaque and the X-ray shows that they have changed to polycrystalline I_4 (see Fig. 3). The same change takes place rapidly upon grinding to a fine powder.

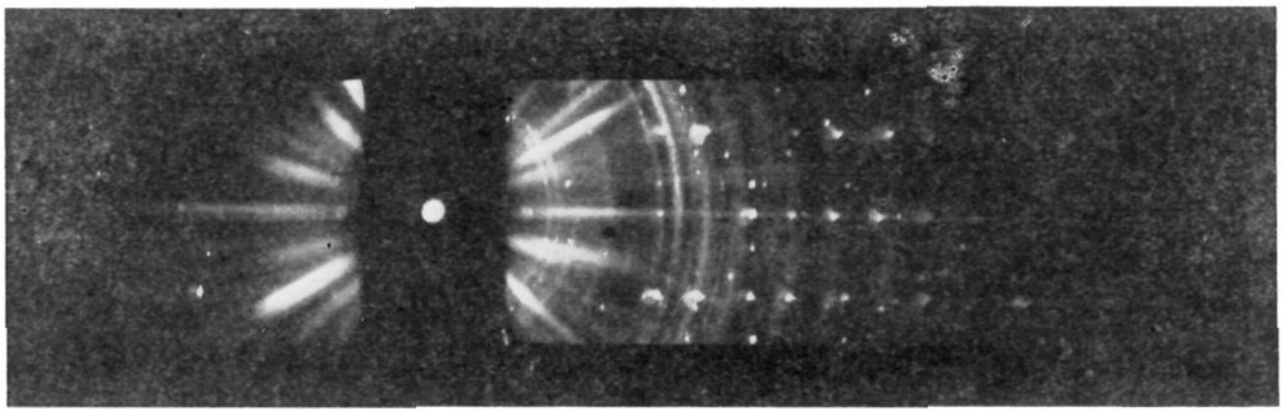


Fig. 3.—Oscillation photograph of a single crystal of $2[(C_6H_5)_2SiO]_4 \cdot C_6H_6$ partially decomposed. The layer lines correspond to the undecomposed portion of the original crystal and the Debye–Scherrer rings to the polycrystalline phase, I_4.

On the other hand, when the crystals of A_4 are held at 100° under vacuum, they become opaque and powdery and are transformed in the course of thirty minutes to III_4.

The fugitive nature of III_4 makes it very difficult to obtain at will, but there seems to be no question as to its existence and to the transformations indicated.

The I_4, II_4 and A_4 crystals can usually be formed at will by seeding from solution as indicated. They were first obtained accidentally by crystallization procedures. The conditions leading to the formation of any particular form from solutions have not been studied further.

X-Ray Investigation

In view of the fact that most of the molecular weight determinations on the trimer and tetramer (see Table IV) give indecisive values, it was decided to investigate the problem by X-ray diffraction methods. The procedure followed parallels that reported by Burkhard, Decker and Harker.[3f] Both Laue and oscillation photographs were used to determine the unit cell dimensions. The density value for II_4 of 1.198 g./cc. is believed to be quite accurate, since it was determined on a clear crystal specimen (0.5 × 1 × 5 mm.). This density gives a value of 15.83 monomer units per unit cell as compared with the value 15.52 shown by Burkhard. This value of 15.83 represents an integer which is sufficiently closer to 16 than to 15, to warrant the conclusion that 16 is the real value to be employed. Accordingly there are $(16^*/x)$ $[(C_6H_5)_2SiO]_x$ molecules in the unit cell where x and $16/x$ have to be integers. This requirement uniquely excludes the trimer formula inasmuch as 3 is not an integral factor of 16. Since cryoscopic data preclude $x = 2$ or 8, the crystalline substance II_4 can be characterized definitely as being made up of tetramer molecules. By carrying out a complete structure determination it could be shown, without recourse to supplementary physical data, that II_4 is the cyclic tetramer as was demonstrated[4] for the cyclic octamer, $[(CH_3)_2SiO]_8$. However, this proposed structure determination is beyond the scope of the present paper.

For sake of completeness the unit cell dimensions of the room-temperature stable modifications of the trimer and tetramer have been determined from Laue diagrams and 20° oscillation photographs and are compiled in Table I. The agreement of these findings with published data is shown in Table II.

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(4) Frevel and Hunter, This Journal, **67**, 2275 (1945).

TABLE I

SINGLE CRYSTAL DATA

Legend: The symbols *a*, *b*, *c*; α, β, γ refer to the lattice constants of the particular unit cell selected. *Z* is the number of stoichiometric molecules per unit cell. The absence of {*h*0*l*} reflections with *h* + *l* odd indicates a B-centered lattice for A$_4$.

Substance		Crystal class	*a*, kX	*b*, kX	*c*, kX	α°	β°	γ°	Z	Density, g./cc. Obs.	Density, g./cc. Calcd.
$[(C_6H_5)_2SiO]_3$	I	D$_2$-222	15.67 ± 0.10	20.16 ± 0.08	10.03 ± 0.10	90	90	90	4	1.22	1.24
	II	Ci-$\bar{1}$	12.89 ± 0.10	14.93 ± 0.15	16.50 ± 0.10	96	95.3	101	4	1.22	1.28
$[(C_6H_5)_2SiO]_4$	I	Ci-$\bar{1}$	10.74 ± 0.08	19.10 ± 0.10	22.00 ± 0.10	83.7	104	96.5	4	1.24	1.21
	II	C$_{2h}$-2/m	22.93 ± 0.15	10.03 ± 0.05	21.7 ± 0.05	90	120	90	4	1.20	1.21
$2[(C_6H_5)_2SiO]_4 \cdot C_6H_6$		C$_2$-2	14.46 ± 0.10	21.60 ± 0.10	14.10 ± 0.10	90	92.9	90	2	1.24	1.25

TABLE II

COMPARISON OF CRYSTALLOGRAPHIC DATA

Source		Form	*a*:*b*:*c*	α	β	γ
$[(C_6H_5)_2SiO]_3$	Kipping and Robison[3c]	I	0.775:1:0.4993	90°	90°	90°
	This paper	I	0.777:1:0.498	90°	90°	90°
$[(C_6H_5)_2SiO]_4$	Kipping and Robison[3c]	I	0.5614:1:0.5770	83.93°	103.87°	96.73°
	This paper	I	0.562:1:0.576 × 2	83.7°	104°	96.5°
Burkhard, Decker and Harker[3f]		II	23.11:10.07:21.58	90°	121.32°	90°
This paper		II	22.93:10.03:21.7	90°	120°	90°

The crystal class designation of Table I is based primarily on face development and should not be considered as final. The densities recorded in Table I were determined indirectly by suspending a clear crystal specimen in aqueous calcium chloride solution of matched density.

For rapid identification work it was found expedient to use powder diffraction data. To that end accurate patterns were prepared with CuKα radiation (Table III). The pattern for the metastable III$_4$ was difficult to obtain and does not carry the same reliability as do the others in view of the fact that the rate of transformation of III$_4$ to I$_4$ is rather rapid.

Eutectic

Another complication in this field is the fact that the trimer and tetramer form a eutectic at approximately 40 mole per cent. melting at 164–165° as shown in Fig. 4. These mixtures were prepared by melting and stirring at 195° in order to obtain uniform samples. The open blocks indicate the melting point range of such mixtures taken in the usual manner. The solid blocks indi-

TABLE III

X-RAY POWDER PATTERN DATA[a]

$[(C_6H_5)_2SiO]_3$				$[(C_6H_5)_2SiO]_4$						$2[(C_6H_5)_2SiO]_4 \cdot C_6H_6$	
I		II		I		II		III			
d, kX	I/I_1	*d*, kX	I/I_1	*d*, kX	I/I_1	*d*, kX	I/I_1	*d*, kX	I/I_1	*d*, kX	I/I_1
12.45	0.15	9.68	1.00	10.4	1.00	10.8	0.36	10.7	0.60	12.1	0.12
10.05	.20	8.49	0.07 B	9.50	1.00	9.87	.30	8.6	1.00	10.2	.58 B
8.49	.09	7.81	.45	8.37	0.17	8.96	1.00	5.1	0.24 B	8.64	1.00
7.81	1.00	7.41	.07	7.35	.02	7.62	0.50	4.41	.32	7.39	0.22
7.25	0.15	6.98	.20 B	6.73	.50	7.06	.16	4.30	.20	6.71	.10
7.15	.15	6.30	.25	5.85	.06	5.87	.08	4.06	.28 B	5.90	.12
6.20	.06	5.80	.03	5.40	.02	5.32	.12	3.79	.40 B	5.48	.03
5.92	.03	5.50	.12	5.16	.55	4.94	.30	3.39	.24 B	5.07	.33
5.25	.06	5.22	.07	4.75	.85	4.59	.80			4.74	.50
5.04	.55	4.94	.65	4.49	.60	4.46	.80			4.43	.22
4.80	.06	4.66	1.00	4.36	.10	4.31	.10			4.11	.46
4.63	.15	4.41	0.07	4.27	.65	4.18	.10			3.95	.46
4.52	.23	4.25	.48	4.04	.06	4.02	.08			3.65	.08 B
4.33	.09	4.08	.25	3.87	.20	3.80	.03 B			3.44	.40
4.23	.88	3.92	.19	3.74	.20	3.63	.08			3.25	.08
3.92	.36	3.58	.10	3.53	.20	3.54	.20			3.11	.15
3.62	.39	3.49	.27	3.44	.20	3.30	.40				
3.41	.09	3.30	.05	3.37	.22						
3.23	.18	3.22	.05	3.26	.22						

[a] Filtered CuKα radiation was used to obtain the powder diffraction data. B = broad; *d* = interplanar spacing; I/I_1 = relative intensity.

cate the melting point range on the identical samples which were held at 220° for five minutes before resolidifying for the second determination.

It will be noticed that the tetramer appears as the III_4 polymorph under these conditions. It is possible that when the trimer and tetramer co-crystallize from solution, a different tetramer polymorph may be present and that the melting point of such crystals may not conform to this curve.

Kipping,[3c] as well as Hyde and DeLong,[3d] described mixtures melting in the range of 160–170°.

Molecular Weight Behavior

In establishing the identity of such isomeric materials, a determination of molecular weights becomes essential. Attempts to apply conventional methods have given variable results as the data in Table IV indicate.

Dilthey,[3a] who first isolated the trimer, appears to have encountered no difficulty in determining the molecular weight of the crystalline product. On the basis of his description the purity of his materials might well be questioned.[3b] In more extensive studies by Kipping,[3b] not only the trimer but a tetramer was isolated and studied. The molecular weights which he obtained were 20% lower than the theory and he depended primarily upon chemical relationships in deducing their structures.

Hyde and DeLong[3d] obtained an apparently pure material melting at 199.5–200°. It was erroneously designated as trimer instead of tetramer on the basis of the molecular weight obtained.

Burkhard[3e,f] and co-workers appear to have encountered some difficulties in their determination of molecular weights, although the agreement with theory in the case of the tetramer is good.

TABLE IV

MOLECULAR WEIGHT DATA

Ref.		M. p., °C.	Solvent	Mol. wt.
Trimer (calcd.)				594.4
	(3a)	188	C_6H_6	601–609[a]
	(3b)	188	C_6H_6	477–490[a]
	(3e)	190	C_6H_6	567
			$C_2H_4Br_2$	540
This paper		188	C_6H_6	515–534[a,b]
			C_6H_6 (b. p.)	581
			s-Camphor[e]	482–498[a,b]
			l-Camphor	470–590[a,b]
Tetramer (calcd.)				792.6
	(3b)	200–201	C_6H_6	669–685[a]
	5		Camphor	759 (av. of 6)
	(3d)	199.5-200	C_6H_6	589[c]
	(3e)	201–202	C_6H_6	810
			$C_2H_4Br_2$	802
This paper		199–200	C_6H_6	702[c]
			l-Camphor	673–705[a,d]

The freezing point method was used except where indicated otherwise. [a] Spread of two or more measurements. [b] Polymorph I_3 was used. [c] Polymorph II_4 was used. [d] Polymorph form uncertain. [e] s indicates a small tube, and l a large tube.

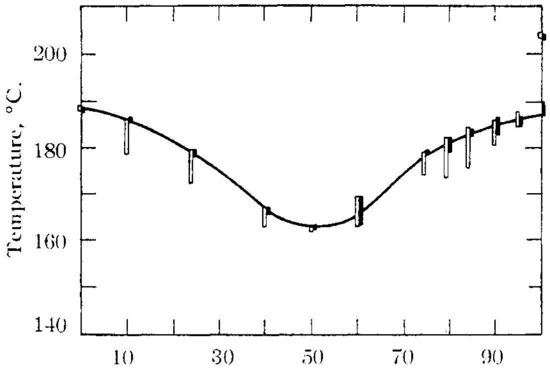

Fig. 4.

Further work by the authors using various methods on I_3, I_4 and II_4 have given the variable results shown in Table IV.

It is interesting to note that when an experimental freezing point constant for benzene was determined using $[(C_6H_5)_2(CH_3)Si]_2O$, m. p. 51–52°, as a standard, a value of 58.4 was obtained instead of the generally recognized constant of 51.2. The use of the constant 58.4 instead of 51.2 in one set of experiments raises the molecular weight value for the trimer from 526 to 600, and that for the tetramer from 702 to 801—thus giving values in good agreement with theory.

Experimental

Preparation.—The trimer and tetramer were prepared and purified by methods which have been reported previously.[3c,d] The materials were recrystallized from benzene–alcohol solution until their melting points, taken in the conventional manner, were constant and agreed with the values commonly found for these compounds, 187–188° and 199–201°, respectively. The analytical data for these compounds are as follows:

	% Si		% OH (Zerewitinoff)	
	Calcd.	Found	Calcd.	Found
$[(C_6H_5)_2SiO]_3$	14.16	14.1- .4	0.00	0.00
$[(C_6H_5)_2SiO]_4$	14.16	14.22–14.35	.00	.00

Preparation of $2[(C_6H_5)_2SiO]_4 \cdot C_6H_6$.—A slightly supersaturated solution of the cyclic tetramer in benzene–alcohol (3–1) was allowed to crystallize very slowly over a period of three days without seeding. Large crystals of the product were formed. Further quantities of this compound were prepared readily by using this material for the seeding of more concentrated solutions.

Weighed samples of two different batches were placed under high vacuum at 90–100° for twenty minutes. The weight losses found were 4.5 and 4.7%. Analysis of a sample by still another method involving the determination of the volatile constituent directly as benzene colorimetri-

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(5) Kipping, *J. Chem. Soc.*, **125**, 2291–2297 (1924).

cally gave 5.1%.[6] The formula indicated requires 4.69% benzene.

Cryoscopic Data.—The additional molecular weight data presented in this paper were obtained by the standard techniques.[7] The large tube procedure with camphor seemed to be more satisfactory for this work although both the large and small tube procedures gave satisfactory results using naphthalene as a standard.

Preparation of Samples for X-Ray Examination.—The trimer and the tetramer readily form supersaturated solutions in benzene and in benzene–alcohol. This makes it possible to grow crystals of the various forms, particularly by seeding, which are suitable for single crystal X-ray examination. The conditions leading to the formation of any particular form from solutions other than by seeding have not been investigated.

The fine grinding necessary to prepare the powder samples had no effect on the crystal structure of the polymorphs I_4 and II_4. However, after short grinding in an agate mortar, A_4 immediately gave a melting point of 200–201° instead of 188–190°, which is that observed for the unpowdered material.

Since A_4 is stable indefinitely in contact with its mother-liquor, it was possible to prepare powders suitable for X-ray examination by grinding in contact with the mother liquor.

Summary

1. Two polymorphs of hexaphenylcyclotrisiloxane have been characterized by X-ray diffraction methods: an orthorhombic form identical with that described by Kipping and Robison, and a triclinic form, each of which, as well as their mixture, melts at 188–189°.

2. Two stable polymorphs of octaphenylcyclotetrasiloxane have been characterized in like manner. One is triclinic and is identical with that described by Kipping and Robison. The other is monoclinic and is identical with the form described by Burkhard, Decker and Harker. Both of these forms as well as their mixture melt at 200–201°.

3. A metastable polymorph of octaphenylcyclotetrasiloxane melting at 187–189° and a crystalline substance with the formula $2[(C_6H_5)_2SiO]_4 \cdot C_6H_6$ have also been isolated and their relationship to the two stable polymorphs have been described.

4. Hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane in equimolar proportions form a eutectic melting at 164–165°.

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[6] *U. S. Bureau of Mines Reports Investigation*, No. 3287 (1935).

[7] Reilly and Rae, "Physico Chemical Methods," D. Van Nostrand Co., New York, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, ILLINOIS INSTITUTE OF TECHNOLOGY]

Cracking of Paraffin Hydrocarbons in the Presence of Aluminum Chloride

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The reactions of pure paraffin hydrocarbons in the presence of aluminum chloride have been studied extensively. Of particular importance are more recent works in which modern distillation techniques have been used in identification of the reaction products, as well as careful experimentation to avoid any undesirable influence of impurities.[1] As a result of these studies, the products were demonstrated to be composed of isomers of the charged hydrocarbon, higher and lower boiling paraffins and highly unsaturated hydrocarbons combined with aluminum chloride in the so called lower layer. The formation of these products clearly indicates that the following reactions take place: isomerization, cracking to lower boiling hydrocarbons and alkylation (destructive alkylation) with the production of hydrocarbons boiling higher than the original material charged. Part of the unsaturated fragments formed by cracking combines with aluminum chloride into a lower layer. It was recently shown[2] that by suitable use of promoters as well as aluminum metal it was possible to influence the reaction by increasing isomerization while decreasing cracking. In a previous study of the action of aluminum chloride on natural hydrocarbon mixtures from this Laboratory,[3] it was found that by increasing the reaction time higher yields of lower boiling isoparaffins were obtained in the reaction product. It was of interest to follow this observation with pure hydrocarbons, to study the effect of time upon the nature and distribution of the reaction products and, if possible, to determine the kinetics for these reactions with pure hydrocarbons. In the following work the action of aluminum chloride–hydrogen chloride on n-hexane, heptane and octane was studied at the boiling point of each hydrocarbon under carefully controlled conditions. In addition the reactions with octene-1 and neohexane were carried out. These last hydrocarbons were studied for elucidation of some questions of reaction mechanism.

Experimental

Material Used.—n-Hexane C. P., b. p. 68.7°, $n^{20}D$ 1.3750; n-octane C. P., b. p. 125.6°, $n^{20}D$ 1.3976 and

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[1] Grummitt, Sensel, Smith, Burk and Lankelma, THIS JOURNAL, **67**, 910 (1945).

[2] Grummitt, Case and Mitchell, *Ind. Eng. Chem.*, **38**, 141 (1946).

[3] Komarewsky and Warson, *Ind. Eng. Chem.*, **37**, 323 (1945).