cally gave 5.1%.[5] 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 $2[(C_6H_5)_2-SiO]_4 \cdot C_6H_6$ 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°.

(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.

Cracking of Paraffin Hydrocarbons in the Presence of Aluminum Chloride

BY V. I. KOMAREWSKY AND S. C. ULICK

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

(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).

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Experiment no. →	7	10	11	16	15	18	20	21	22
Hydrocarbon charged →			n-Heptane			n-Octane	n-Hexane	Octene-1	Neohexane
Temp., ±2°C.	100	100	100	100	100	125	70	122	50
Moles AlCl₃/mole H.C.	0.036	0.083	0.083	0.15	0.2	0.2	0.38	0.2	0.2
Time, hours	3	3	10	10	3	3	3	1	3
i-Butane, wt. %[a]	57.6	53.8	58.3	65.6	58.0	65.9	67.0	30.1	No reaction
i-Butane, moles[b]	1.11	1.00	1.05	1.18	1.10	1.30	1.00	0.58	
i-Pentane[a]	4.4	16.0	11.1	8.7	7.5	5.7	5.0	2.5	
i-Hexanes[a]	5.4	2.5	6.3	3.2	6.3	2.0	9.0	....	
i-Heptanes[a]	10.2	8.2	4.7	3.2	9.2	2.0	....	....	
							3.3 (i-octanes)		
Unsaturated oil[a]	22.4	19.5	19.6	19.3	19.0	21.1	19.0	67.4	
% H in unsatd. oil	12.8	12.0	12.2	11.6	11.9	10.9	....	12.4	
Unreacted hydrocarbon[c]	81.0	60.0	62.1	15.9	6.2	0	0	0	
% Reaction	19.0	40.0	37.9	84.1	93.8	100	100	100	
% Recovery	98.1	93.8	88.6	98.7	96.2	96.8	95.0	90.8	

[a] % by weight of hydrocarbon reacted.　[b] Calculated on the bases of hydrocarbon cracked.　[c] % by weight of hydrocarbon charged.

TABLE II

MATERIAL BALANCE AND COMPOSITION OF THE PRODUCTS

Experiment no.	16	18	20
		Charged, g.	
Hydrocarbon	n-C₇H₁₆, 150.0 g.	n-C₈H₁₈, 150.0 g.	n-C₆H₁₄, 150.0 g.
Catalyst	AlCl₃, 30.0 g.	AlCl₃, 35.0 g.	AlCl₃, 88.0 g.
		Products, g.	
Non-condensable gas		Traces hydrogen	
Isobutane	81.5	95.7	95.5.
Isopentane	10.8	8.3	7.1
Isohexanes[a]	3.9	3.0	12.8
Isoheptanes[a]	3.9	3.0	..
Isoöctanes[a]	..	4.6	..
Unreacted heptane	23.8	..	..
Lower layer hydrocarbons	24.1	30.7	27.1
Loss	2.0	4.7	7.5

[a] See the distillation curves, fig. 1, 2 and 3. Further isolation of isomers was not attempted.

octene-1 c. p., b. p. 121.1–121.4°, n^{20}D 1.4095 were prepared according to a previously described procedure[4]; n-heptane Westwaco Chemical Company c. p., b. p., 98.4°, n^{20}D 1.3876; 2,2-dimethylbutane (neohexane) Phillips Petroleum Company c. p., b. p., 49.5°, n^{20}D 1.3690; aluminum chloride c. p. Merck and Company; hydrogen chloride, Harshaw Chemical Company.

Apparatus and Procedure.—The apparatus was an all-glass system with ground glass joints. The three-necked reaction flask was fitted with a mercury seal, a wide blade stirrer, a dropping funnel for introduction of hydrocarbon, a tube sealed to the bottom of the flask for introduction of gases (hydrogen chloride or nitrogen) and a condensing system. The condensing system consisted of water condenser, two graduated traps placed in Dewar flasks and cooled with Dry Ice–ethylene dichloride mixture, a safety trap and a gas holder with an overflow device, permitting the collection and the measurement of gases at atmospheric pressure. Cylinders of nitrogen and anhydrous hydrogen chloride were connected through sulfuric acid bubblers to the gas inlet tube of the reaction flask. A capillary flow meter was used for regulating and measurement of the incoming hydrogen chloride.

After charging the catalyst and flushing the reaction vessel with dry nitrogen, the flask was immersed in the oil-bath and heat regulated to the desired temperature. Stirring was started after the introduction of hydrocarbon

(4) Komarewsky, Ulick and Murray, THIS JOURNAL, **67**, 557 (1945).

and establishing a constant rate (2 liters per hour) of hydrogen chloride introduction.

The analysis of the products was carried out as follows: the liquid product (upper layer) after alkali wash and calcium chloride drying was fractionated by means of a high temperature Podbielniak column with heligrid packing; the condensable gases were analyzed in a Podbielniak hydrobot apparatus and the composition of the non-condensable gases was determined in a Goeckel absorption and combustion apparatus. The lower layer was decomposed with ice water, extracted with benzene, dried and vacuum distilled for further investigation. The results are presented in Tables I and II and Figs. 1, 2, 3 and 4. Table I gives the over-all results. Table II presents the material balance and analysis of products for three representative experiments with heptane (expt. 16), octane (expt. 18) and hexane (expt. 20). Figures 1, 2 and 3 are the corresponding distillation curves of the products. Figure 4 illustrates the effect of catalyst concentration on the amount of heptane reacted. The special rate experiment with heptane was conducted in the same manner with the exception of the fact that the product formed was withdrawn and analyzed for its butane-pentane content at equal time intervals (ten minutes). The data and re-
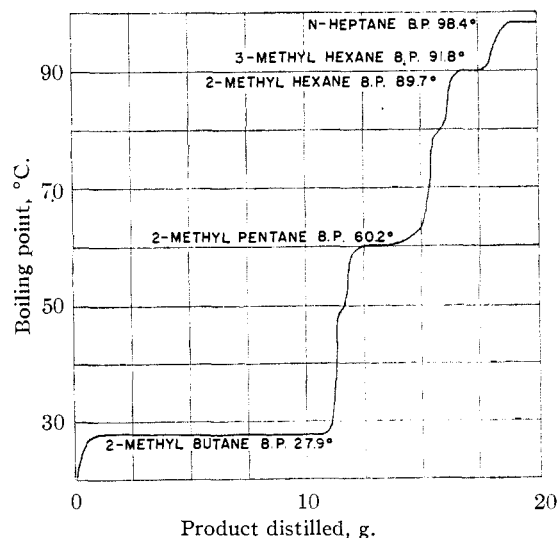

Fig. 1.—Distillation of the liquid product from experiment 16.
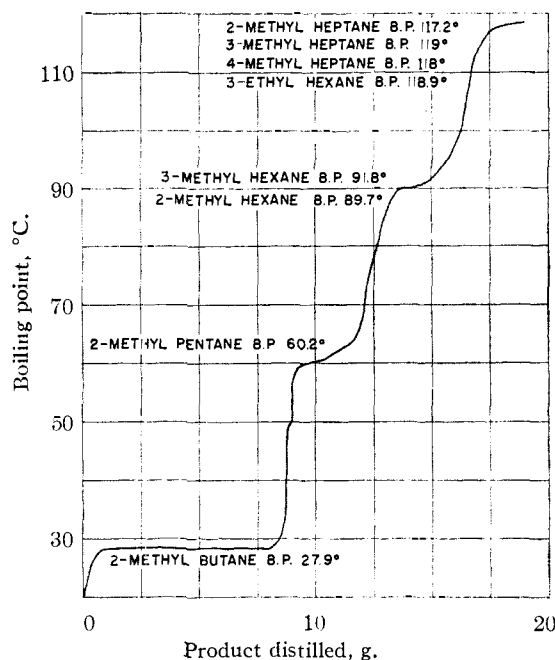
Fig. 2.—Distillation of the liquid product from experiment 18.

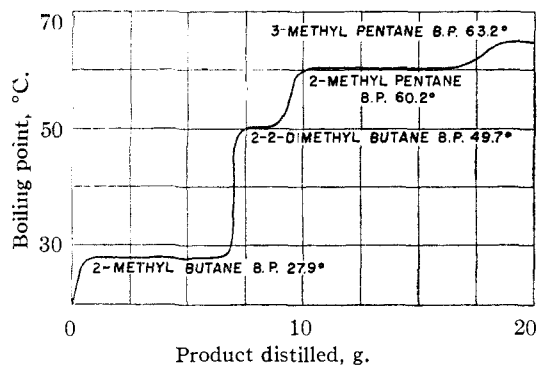

Fig. 3.—Distillation of the liquid product from experiment 20.

sults of this rate experiment are presented in Table III and Fig. 5.

Table III

Rate Experiment

Charged n-C$_7$H$_{16}$, 60.0 g.; AlCl$_3$, 12.0 g.; temperature, 100°C.

Time, min.	Isobutane formed, g.	Isopentane formed, g.
0	0	0
10	7.0	3.1
20	14.0	4.2
30	21.5	
40	28.0	
50	32.5	
60	34.0	

Examination of the results reveals the following facts.

1. Effect of aluminum chloride concentration: The dealkylation of n-heptane is a direct function of aluminum chloride concentration. **Figure 4** shows a straight line relationship between the amount of n-heptane reacted and
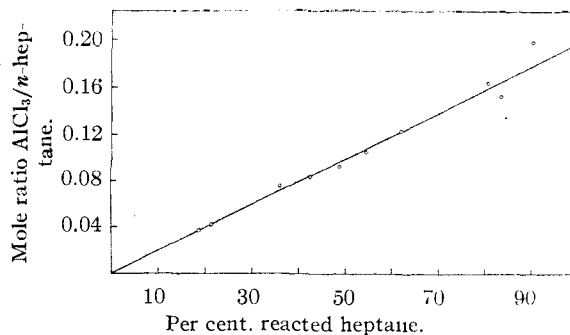

Fig. 4.—Relation between the concentration of aluminum chloride and reacted n-heptane.

the amount of catalyst used. It was found that 0.2 mole of aluminum chloride is required per each mole of n-heptane reacted.

2. Effect of time: Time has a marked influence at the amount of lower paraffins formed. In a special rate experiment (Table III, Fig. 5) the formation of isobutane and isopentane was measured at equal time intervals. It was found that the reaction of dealkylation of n-heptane to isobutane and to a minor extent to isopentane proceeds with a constant rate.
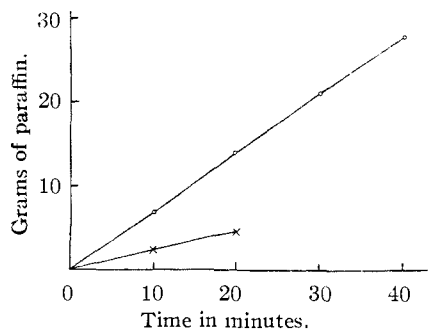

Fig. 5.—Rate experiment with n-heptane: ⊙, i-butane; ×, i-pentane; charged n-heptane, 60 g.; AlCl$_3$, 12 g.; temperature, 100°.

3. Nature of reaction products: In distinction with other investigators, it was found that methane, ethane, propane as well as hydrocarbons boiling higher than the hydrocarbons charged are absent in the reaction product. In experiments with n-heptane the only hydrocarbons formed are isobutane, isopentane, isohexanes and isoheptanes. The amount and hydrogen content of the lower layer hydrocarbons are constant within experimental error.

4. Suggested reaction mechanism: All these facts indicate that under the conditions studied[5] n-hexane, n-heptane and n-octane undergo predominantly the reaction of dealkylation to isobutane and unsaturated fragments which combine with aluminum chlorides. The reaction of isomerization to paraffins, containing the same amount of carbon atoms as the hydrocarbon charged, proceeds only to a minor extent. The reaction of destruction alkylation does not take place at all. A slight excess of isobutane formation (more than 1 mole) can be explained by secondary reaction of depolymerization of polymers formed in the lower layer. E. g., octene-1 (expt. 21) under the action of aluminum chloride combines with the catalyst, forming a homogeneous, viscous liquid and produces 0.58 mole of isobutane; similar reactions might explain the excess isobutane formation. Whether in all these reactions isomerization precedes dealkylation and depolymerization is still an open

(5) The hydrocarbon is heated to its boiling point and only then is subjected to the action of aluminum chloride.

question. The fact that no traces of n-butane are found in the reaction products supports the theory that isomerization preceeds cracking. The stability of neohexane under the conditions studied (expt. 22) indicates the opposite point of view.

Summary

1. Paraffin hydrocarbons (n-hexane, n-heptane and n-octane) when subjected to the action of aluminum chloride–hydrogen chloride at temperature of their boiling point or slightly above, are cracked to lower boiling isoparaffin.

2. Cracking with the production of iso-

butane is the predominant reaction.

3. Cracking consists in the dealkylation of paraffin and polymerization–depolymerization of the cracked fragments to produce isoparaffins.

4. The amount of dealkylation reaction is a direct function of catalyst concentration.

5. No destructive alkylation to form hydrocarbons boiling higher than the charge takes place under these conditions.

6. A reaction mechanism to explain the above facts is proposed.

CHICAGO, ILLINOIS   RECEIVED MAY 20, 1946

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

# The Nitration of Melamine and of Triacetylmelamine[1]

BY JAMES CASON[2]

Melamine has been nitrated with nitric acid in acetic anhydride by Whitmore and co-workers,[3] but the product obtained was not purified and analyzed. We have repeated this preparation and have obtained the highly unstable nitration product in a crystalline condition by low temperature acidification of the purified sodium salt. Analyses of the nitration product, its sodium salt and its potassium salt indicate for the nitration product the formula $C_3H_{3-4}N_7O_5$. It will be noted that this substance contains only one nitrogen atom more than melamine but contains five oxygen atoms. The salts contain two atoms of metal and one molecule of water. On the basis of the evidence obtained nothing can be suggested concerning the structure of this compound.

In order to study the nitration of triacetylmelamine it was necessary to develop an improved method for preparing this substance. Although diacetylmelamine may be readily obtained by heating melamine with acetic anhydride, the triacetyl derivative is obtained only with difficulty. Ostrogovich[4] used 200 cc. of acetic anhydride for the conversion of 0.5 g. of melamine to the triacetyl derivative. By improvements in the procedure, including recycling the acetic anhydride it has been found possible to convert 120 g. of melamine to the triacetyl derivative in 99% yield, using only 450 cc. of anhydride. The difficulty of introducing the third acetyl group into melamine may be associated with the occurrence of a tautomeric change prior to acetylation[4,5]; however, it is also possible that the very low solu-

(1) This paper is based entirely on work done for the Office of Scientific Research and Development under Contract OEMsr-790 with Vanderbilt University.

(2) Present address: Department of Chemistry, University of California, Berkeley.

(3) Work carried out under the direction of Dean F. C. Whitmore at Pennsylvania State College under a contract with the Office of Scientific Research and Development.

(4) Ostrogovich, Gazz. chim. ital., 65, 566 (1935).

(5) McClellan, J. Ind. Eng. Chem., 32, 1181 (1940).

bility of diacetylmelamine is responsible for this difficulty.

If triacetylmelamine has the structure, I, nitration with nitric acid in acetic anhydride would
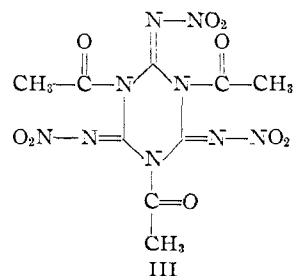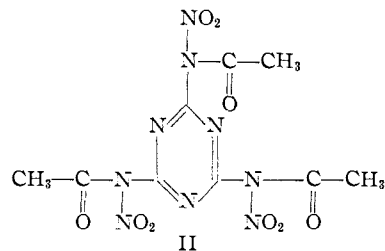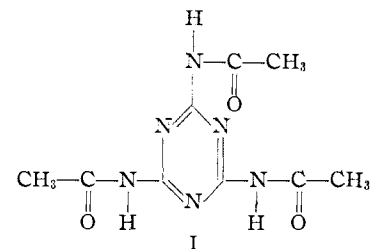
be expected to give the corresponding nitramide, II. Actually, the compound obtained when nitration was carried out at 20–25° did not have any of the properties that would be expected of II. This nitration product, which has been designated as TM-1, is too unstable to be purified, but analyses of the crude substance and of its stable sodium