

All fractions, with the exception of Nos. 13 and 14, were stable to nitrating mixture and permanganate solution, indicating the absence of aromatics and olefins; all were free from chlorine except a trace in No. 1.

The above data definitely prove that we have a formation of paraffins from hexane and ethylene. As can be seen from the amount of fraction 2, over 50% of the original hexane took part in the reaction.

On the average 2.0 to 2.5 molecules of ethylene reacted with 1 molecule of hexane.

3. Alkylation of Isobutane with Ethylene under Pressure.—The procedure and equipment were the same as in the previous experiment, but the ethylene (init. pressure, 15 atm.) was absorbed more rapidly so that only ten refillings were made in approximately ten hours. Using 62.3 g. of isobutane and 22.4 g. of aluminum chloride, 95.6 g. of ethylene was added. The upper and lower layers weighed 142.0 and 31.8 g., respectively. No gas condensable at -78° was obtained; the uncondensable gas consisted of pure ethylene (75%) and air (25%), corresponding to 4.9 g. of ethylene, leaving an unaccounted for loss, then, of only 1.6 g.

These data show that practically all the *i*-butane reacted. On the average, one molecule of *i*-butane condensed with three molecules of ethylene; it reacts

easier than any of the other paraffins investigated so far.

The upper layer (135 g.) was separated, at 750 mm., into seven fractions with the following boiling ranges and weights: 25–50, 50–70, 70–100, 100–125, 125–160, 160–185, 185–200°; 7.4, 11.5, 24.3, 24.6, 13.3, 13.0, 13.6 g. (residue and losses were 25 g. and 2 g.). Their refractive indices and densities at 20° were: 1.3624, 1.3720, 1.3853, 1.3992, 1.4086, 1.4178, 1.4244; 0.6398, 0.6540, 0.6789, 0.7039, 0.7224, 0.7414, 0.7543. Their percentages of hydrogen and carbon were: 16.50, 16.00, 15.95, 15.65, 15.55, 15.35, 15.20; 83.28, 83.90, 83.85, 84.15, 84.40, 84.35, 84.00.

A comparison of these analytical data with the theoretical carbon and hydrogen figures for paraffins of the same boiling range together with their physical constants, again shows that the hydrocarbons of the upper layer are *paraffins*.

Summary

The alkylation of paraffins with olefins in the presence of aluminum chloride is described.

Experimental data on the alkylation of *n*-hexane with ethylene and of *i*-butane with ethylene are given.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Polymerization of Ethylene with Aluminum Chloride

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A preliminary study of the polymerization of ethylene under pressure in the presence of aluminum chloride was made by one of us some thirty years ago.¹ It has recently been augmented by the work of H. M. Stanley,² A. W. Nash,³ and H. T. Waterman and A. J. Tulleners.⁴ These workers used low-boiling paraffin hydrocarbons as what they considered "inert solvents" for the polymerization. In view of our discovery of the reaction of paraffins with olefins,⁵ their results are not characteristic for ethylene polymerization. Furthermore, since we required detailed information of the behavior of ethylene in the presence of aluminum chloride for the elucidation of the reaction of paraffins with olefins in the presence of aluminum chloride, the work was repeated using glass reaction liners to eliminate any possible catalytic effects of the autoclave walls.

(1) V. N. Ipatieff and Routala, *Ber.*, **46**, 1748 (1913).

(2) H. M. Stanley, *J. Soc. Chem. Ind.*, **49**, 349T (1930).

(3) A. W. Nash, H. M. Stanley and A. R. Bowen, *J. Inst. Petroleum Tech.*, **16**, 830 (1930).

(4) H. T. Waterman and A. J. Tulleners, *Chimie et industrie*, Special No., June, 1933, 496–505; see also H. T. Waterman, J. Over and A. J. Tulleners, *Rec. trav. chim.*, **53**, 699 (1934).

(5) V. N. Ipatieff and A. V. Grosse, *THIS JOURNAL*, **57**, 1616 (1935).

It is first discovered that aluminum chloride when really pure does not react with pure ethylene even under pressures up to 50 atmospheres at 10–50° and that the presence of traces of hydrogen chloride or moisture is necessary for the reaction.

In one typical experiment, 25 g. of pure aluminum chloride was placed in a 750-cc. glass liner in an Ipatieff rotating bomb, vacuum sublimed, *in situ*, 2 times and then 15 atm. of pure dry ethylene was pressed in at 33–36°; the reaction was negligible (pressure drop less than 0.2 atm. per hour). At the end of the experiment, absolutely pure pearl-white leaflets of aluminum chloride were recovered.

In an identical experiment, the addition of 3 g. of pure dry hydrogen gas caused an immediate, approximately exponential drop in pressure with a half-period of about fifteen to twenty minutes.

In the presence of hydrogen chloride, as well as with aluminum chloride of ordinary purity, the reaction product consists of two layers. The *upper layer* is water-white and consists of paraffins.

The *lower layer* is dark red-brown in color, much more viscous than the upper, and consists of addition compounds of aluminum chloride with unsaturated *cyclic* hydrocarbons. At a maximum, about 10 molecules of ethylene are condensed by 1 molecule of aluminum chloride.

The ratio of masses of the two layers depends on the ratio of ethylene condensed by a certain quantity of aluminum chloride as shown in the table.

ORDINARY C. P. ALUMINUM CHLORIDE USED WITHOUT ADDITIONAL HYDROGEN CHLORIDE AT 20-30°

Number of experiment	1	2	3	4
Molecules C ₂ H ₄ polymerized by 1 molecule AlCl ₃	3.3	4.2	6.5	9.2
C ₂ H ₄ polymerized by 100 g. AlCl ₃ , g.	69	89	138	193
Upper layer, g.	22	35	76	102
Lower layer (hydrocarbon part), g.	47	54	62	91

The composition of the lower layer in the last experiment (No. 4) corresponds to the formula C_nH_{2n-x} · 2 AlCl₃ (x from 2 to 6).

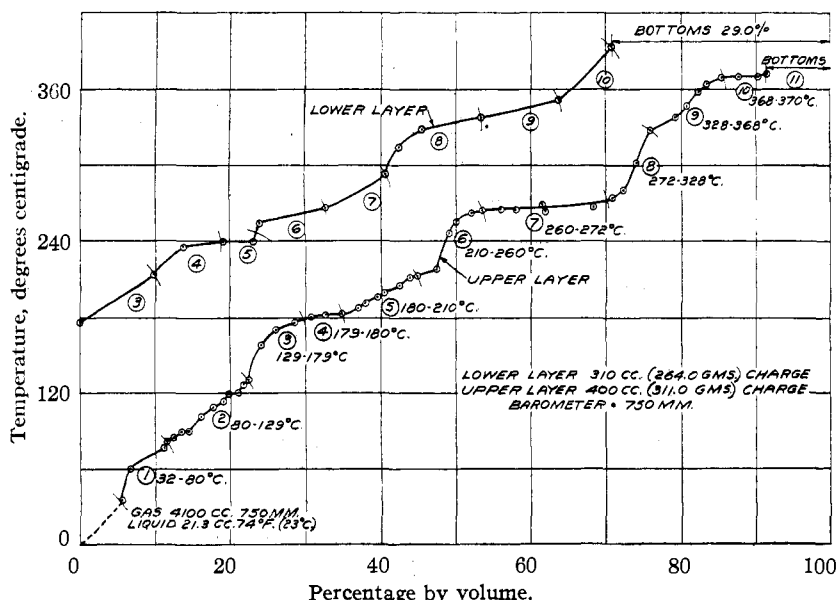


Fig. 1.—Distillation analysis of hydrocarbons obtained from upper and lower layer in the C₂H₄ + AlCl₃ (+ HCl) reaction.

The reaction products from four condensations at 25-30° and 20 atmospheres using in each case 3 atmospheres of hydrogen chloride at the start of the runs and condensing from 150-200 g. of C₂H₄ per 100 g. of aluminum chloride were combined for investigation.

The *upper layer* was separated, washed with dilute sodium hydroxide and water and dried. The *lower layer* cannot be distilled as such and was decomposed slowly with ice (to avoid overheating). The orange-red hydrocarbon layer which separates was thoroughly washed with water, after diluting with ether, and dried. Both layers were then separately fractionated by means of a high-temperature Podbielniak column,⁶

(6) W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119, 135 (1933); the rate of distillations used was 0.5 to 1 cc./min.

partly in a vacuum of 10 mm. The two distillation curves are shown on Fig. 1.

Data Obtained from Upper Layer Fractions

A charge of 311 g. (400 cc.) was separated into 11 fractions (for their numbers see Fig. 1), with the following boiling ranges (at 750 mm.) and weights: -10 to +32° (mostly butanes), 32-80, 80-129, 129-179, 179-180, 180-210, 210-260, 260-272, 272-328, 328-368, 368-372°; 11.4, 16.1, 31.3, 20.7, 15.5, 30.9, 27.2, 53.9, 16.7, 31.9, 19.6 g.; residue 27.0 g.

The higher ten fractions had the following refractive indices (*n*_D²⁰) and densities (*d*₄²⁰): 1.3702, 1.3930, 1.4100, 1.4145, 1.4192, 1.4315, 1.4381, 1.4471, 1.4553, 1.4590; 0.6692, 0.7012, 0.7369, 0.7471, 0.7570, 0.7810, 0.7934, 0.8118, 0.8235, 0.8463; residue, 1.4668, 0.9530. Their

percentage contents of hydrogen and carbon were: 16.11, 15.77, 15.37, not detd., 15.27, not detd., 15.09, not detd., 14.61, not detd.; 82.56, 83.29, 83.69, not detd., 84.19, not detd., 84.81, not detd., 85.60, not detd., residue 14.14, 84.51. Molecular weights of fractions 0, 5, 7 and 9 were: 56.5 (butanes), 187, 253 and 339.

All fractions were water white (except No. 10 which was slightly yellow) and stable to potassium permanganate solution and nitrating mixture, except No. 9 and No. 10, indicating the absence of aromatic and unsaturated hydrocarbons. All fractions contained *traces* of alkyl chlorides, especially noticeable in No. 1.

The combustion analysis data prove that the hydrocarbons of the upper layer are principally paraffins in agreement with H. M. Stanley. In the higher fractions (for instance No. 9) the slight deficiency in hydrogen content (14.61% instead of 15.06% for a paraffin of this boiling range) and reactivity toward potassium permanganate solution shows the presence of unsaturates and possibly naphthenes.

Data Obtained from Lower Layer Fractions

A charge of 264 g. (310 cc., excluding ether used as a diluent) was separated into ten fractions (for their numbers see Fig. 1) with the following boiling ranges (at 750 mm.) and weights: 33-34, 34-35 (ether), 175-212, 212-236, 236, 236-264, 264-292, 292-336, 336-350, 350-392°; 50, 50, 25.8, 23.4, 10.2, 25.2, 20.9, 34.2, 27.8, 18.8 g.; residue, 77.6 g. Discarding fractions 1 and 2 (ether), the higher eight fractions had the following indices of refraction (*n*_D²⁰) and densities (*d*₄²⁰): 1.4525, 1.4704, 1.4738, 1.4765, 1.4797, 1.4833, 1.4865, 1.4887; 0.8108, 0.8401, 0.8481, 0.8571, 0.8607, 0.8686, 0.8742, 0.8747; residue, 1.5036, 0.9040. Their percentage contents of hydrogen and carbon were: 13.36, 12.97, 12.94, 13.01, 12.96, 13.01, 12.95,

12.79; 86.40, 86.77, 86.65, 86.72, 86.75, 86.87, 86.73, 86.75; residue, 11.77, 84.10. Bromine numbers, determined by Francis⁷ method, for these fractions were: 177, 201, 183, 162, 165, 152, 324, 148. Molecular weights, determined by the freezing point method in benzene, for fractions 5 and 9 were: 201, 324.

The residue can be distilled completely in high vacuum (≤ 0.005 mm.). The molecular weight of the highest fraction (250° at 0.005 mm.) was 600 (freezing point method, in benzene), *i. e.*, corresponds to $(C_2H_2)_n$ ₂₀₋₂₅.

All fractions have a yellow to orange-red color deepening with increasing molecular weight, and a pleasant terpene-like odor. All react at once with nitrating mixture and potassium permanganate solution; all fractions are free from chlorine.

The combustion analysis, molecular weight, and bromine number determinations show that we have unsaturated hydrocarbons containing on the average from two to three double bonds per molecule. The hydrocarbons are completely soluble in 96% sulfuric acid at 0° showing the absence of paraffins and naphthenes.

In order to determine further the character of these hydrocarbons, fractions 3 and 6 were exhaustively hydrogenated with nickel oxide at 255 to 280° under 100 atm. hydrogen pressure. The product from fraction 3 had the following constants: b. p. (750 mm.) 175 – 220° ; n_D^{20} 1.4366; d_4^{20} 0.7901; C, 85.52; H, 14.58; and that from fraction 6 had: b. p. (760 mm.) 230 – 275° ; n_D^{20} 1.4568; d_4^{20} 0.8304; C, 85.53; H, 14.37. Both products were water white, *insoluble* in 96% sulfuric acid and absolutely stable toward nitrating mixture. All these properties prove them to be naphthenes (calcd. C, 85.62; H, 14.38), so that our original fractions are *cyclic unsaturated hydrocarbons* of the type of terpenes,⁸ since diolefins or polyolefins would give paraffins on hydrogenation.

Discussion of Results

It can be seen from the facts mentioned that our reaction is not a *true polymerization*, as contrasted to the action of boron fluoride.⁵ Very probably true polymerization to monoolefins is the first reaction step (mechanism see below).

The monoolefins are transformed by cyclic or intramolecular alkylation into naphthenes, which either as such or at the moment of their formation are converted by means of a reaction of hydrogenation–dehydrogenation or hydrogen disproportionation into a mixture of paraffins and un-

(7) A. W. Francis, *Ind. Eng. Chem.*, **18**, 821 (1926); see also S. P. Mulliken and R. L. Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).

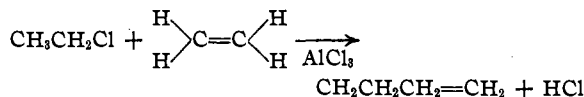
(8) This conclusion is further supported by the fact that limonene combines directly with aluminum halides forming addition compounds very similar in physical and chemical properties to the lower layer.

saturated naphthenes. The latter combine with aluminum chloride forming the lower layer.

It is proposed to call such a polymerization, conjoined with hydrogen disproportionation, a "*conjunct polymerization*." The same picture applies also to polymerization with sulfuric and phosphoric acids.⁹

The paraffins not being able to combine with aluminum chloride form the upper aluminum chloride-free layer. Evidently some of the final paraffins are due to direct alkylation of the initially formed paraffins with ethylene, since we showed that direct alkylation of paraffins is possible under similar conditions.¹⁰

The role of hydrogen chloride is a decisive one as in its absence, as we have shown, the catalytic mechanism does not work. As previous evidence indicates,¹¹ the mechanism of olefin formation consists in the addition of hydrogen chloride to C_2H_4 , catalyzed by aluminum chloride, leading to C_2H_5Cl , which reacts in the presence of aluminum chloride with another molecule of ethylene (or higher olefin) losing hydrogen chloride



The latter is thus being continuously regenerated for the catalytic cycle.

Summary

The polymerization of ethylene with aluminum chloride and the nature of products obtained are described. Since the polymerization is conjoined with a hydrogenation–dehydrogenation reaction, the products are not true polymers of ethylene but consist of a layer of paraffins and a layer of unsaturated cyclic hydrocarbons, combined with aluminum chloride. The term "*conjunct polymerization*" is suggested for such a type of polymerization.

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(9) V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, **127**, 1364 (1935).

(10) V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarevsky, *THIS JOURNAL*, **58**, 913 (1936).

(11) E. Berl and J. Bitter, *Ber.*, **57**, 95 (1924). H. T. Waterman, J. J. Beendertse and A. J. Tulleners, *Rec. trav. chim.*, **53**, 715 (1934).