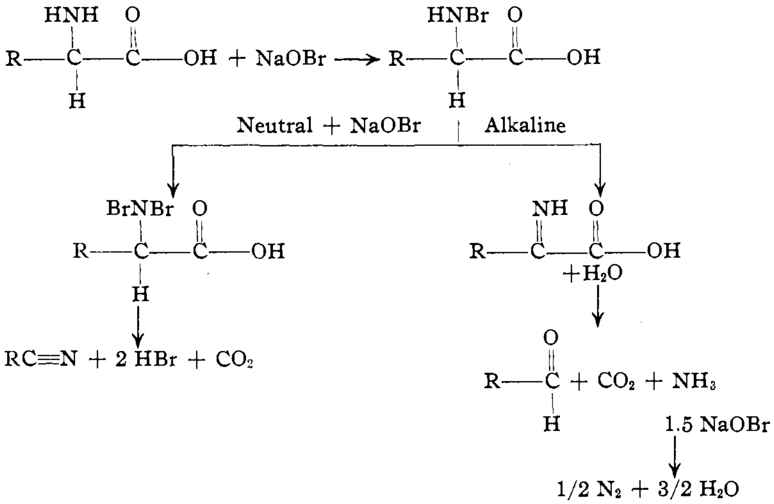
aldehyde, but with substances, such as uric acid, in which the oxidation products are of a more complex nature.

From the data here presented and the work of previous workers we suggest the following scheme for the oxidation of amino acids by sodium hypobromite. This embodies Langheld's, Dakin's and Goldschmidt's results, with certain modifications based on our own experiments.



The first step of the reaction is bromination of the amino group. In alkaline solution there is a greater tendency for this group to split off hydrogen bromide with the probable formation of an imine, which hydrolyzes to the aldehyde, ammonia and carbon dioxide. The formed ammonia reacts further with 1.5 moles of hypobromite reagent. In less alkaline solution there is a greater tendency for the formation of the dibromo substitution product and subsequent nitrile formation.

Summary

The amino acids react with sodium hypobromite to form aldehydes or nitriles with one carbon atom less than the original amino acid, ammonia and carbon dioxide. The extent of the aldehyde or nitrile production depends upon the alkalinity, and the greater the alkalinity the greater the tendency for the production of aldehyde at the expense of nitrile. Furthermore the longer the carbon chain of the amino acid the greater is the amount of nitrile formed. A quantitative study of the amounts of nitrogen and of carbon dioxide liberated as well as of the amounts of sodium hypobromite reacting with the various amino acids and some derivatives has been made under varying experimental conditions.

OMAHA, NEBRASKA RECEIVED MARCH 16, 1936

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

Alkylation of Paraffins with Olefins in the Presence of Aluminum Chloride

BY V. N. IPATIEFF, ARISTID V. GROSSE, HERMAN PINES AND V. I. KOMAREWSKY

As previously stated the catalytic alkylation of paraffins[1] consists in the direct addition of an olefin to a paraffin, for instance

$$\underset{\text{Hexane}}{C_6H_{14}} + \underset{\text{Ethylene}}{C_2H_4} \xrightarrow{\text{Catalyst}} \underset{\text{Octanes}}{C_8H_{18}} \xrightarrow{\text{Catalyst}} \underset{\text{Decanes}}{C_{10}H_{22}}, \text{ etc.}$$

Both normal and *i*-paraffins can be alkylated in the presence of aluminum chloride, in contrast to boron fluoride.[1] Paraffins from butane to dodecane have been used in our experiments and the reaction is general for paraffins with the possible exception of methane and ethane, which, up to the present, have not been alkylated. Olefins that can alkylate in the presence of aluminum chloride are ethylene, propylene and butylenes; higher molecular weight olefins have not been used yet.

In the presence of aluminum chloride, the main reaction of alkylation is complicated by side reactions. The elucidation of these side reactions was important for the understanding of general hydrocarbon reactions involving aluminum chloride (especially cracking) and was accomplished step by step, investigating the action of aluminum chloride on individual paraffins and olefins, as described in separate articles.[1,2,3]

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

(2) V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

(3) V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **58**, 915 (1936).

It was first established that "*autodestructive alkylation*" of the paraffins takes place. This reaction consists in the splitting of a paraffin into a lower paraffin and an olefin which alkylates another molecule of the paraffin to a higher paraffin; it causes the formation of intermediate paraffins, for instance, pentanes, heptanes and nonanes in the case expressed by the equation above. Secondly, polymerization of the olefins used takes place, yielding in the case of ethylene, for instance, large amounts of paraffins.[3] Thirdly, compound formation with aluminum chloride takes place yielding characteristic deep red-brown viscous lower layers of addition compounds.

These three different reactions take place simultaneously, but the extent of each reaction varies depending on the individual hydrocarbons used and the experimental conditions (temperature, pressure, time, etc.).

In this paper experimental data will be given on the alkylation of (1) hexane with ethylene at atmospheric pressure, (2) under pressure and (3) iso-butane with ethylene.

Experimental Part

1. Alkylation of Hexane with Ethylene.—It was first investigated at ordinary pressure and later in autoclaves under pressure. For the experiments under atmospheric conditions a continuous apparatus was built which allowed any unreacted portion of a paraffin to be alkylated over and over again without exposing it to air or moisture and avoiding losses.

The apparatus consisted principally of two glass flasks: the alkylation reaction proceeded under rapid mechanical stirring in the first flask, and when enough reacted product had formed, the clear upper layer was siphoned over to the second flask, and the fractions corresponding to the unreacted hexane were distilled back into the first flask where the alkylation reaction was again continued, whereas the higher boiling product remained in the second flask. This procedure could be repeated as many times as necessary.

The details of an experiment were as follows. Pure (99.6%) ethylene was passed into 147.7 g. of nearly pure normal hexane (b. p. 67.8° (750 mm.), $d^{29.9}_{4}$ 0.6562, n^{25}_{D} 1.3768) at 29–33°, whereby the mixture warmed up to about 40°. As the absorption of ethylene slackened, a little dry hydrogen chloride was passed into the reaction mixture and from time to time fresh aluminum chloride was added up to a total of 25.1 g. Only a little of the ethylene passed through unabsorbed. The process was stopped after fifteen hours when a total of 48.7 liters (N. T. P.) or 61.3 g. had been absorbed.

Two layers were formed as with ethylene alone. The brown lower one (60.5 g.) contained practically all of the aluminum chloride combined with high boiling hydrocarbons; the upper colorless mobile one (158.0 g.) contained only traces of aluminum chloride. The whole upper layer was separated, at 760 mm., into eight fractions by means of a 40 × 2.5-cm. column, packed with glass rings, and insulated with a 25 mm. layer of magnesia. The reflux ratio was 10:1; the rate of distillation 0.5 to 1 cc. per minute.

The eight fractions had the following boiling ranges and weights: 20–45, 45–85, 85–125, 125–170, 170–235, 235–275, 275–300, 300–350°; 9.9, 49.2, 25.6, 25.6, 24.5, 7.5, 4.7, 3.9 g. The higher seven fractions had the following refractive indices (D-line) and densities at 20°: 1.3784, 1.3953, 1.4132, 1.4300, 1.4436, 1.4506, 1.4588; 0.6630, 0.7047, 0.7326, 0.7649, 0.7920, 0.8089, 0.8209. Their percentage contents of hydrogen and carbon were: 16.2, 15.8, 15.5, 15.2, 14.7, 14.6, 14.5; 83.4, 83.9, 84.2, 84.7, 85.0, 85.2, 85.0.

All fractions were free from halogens, unsaturated and aromatic hydrocarbons.

A careful comparison of the physical data of the several fractions with those of pure paraffins, together with the analytical data, leaves no doubt that all our fractions consist of paraffins. About 75% of the hexane was transformed during the reaction. It can also be seen immediately that the higher boiling products, that is, fractions 3–8 and bottoms, cannot be due to the polymerization of ethylene alone, since the latter weighs only about half as much as the former. The reaction proceeds with greater velocity in the presence of aluminum bromide because its solubility in hydrocarbons is much greater.

2. Alkylation of Hexane with Ethylene under Pressure.—The procedure was as previously described, except that the temperature was 25° and the pressure of the ethylene 15 atm. The pressure usually dropped after two to three hours to 2–4 atm., whereupon fresh ethylene was added, a total of twelve such additions being made during the thirty-six hours. Using the same amount of hexane as in the previous experiment (150 g.) and 30 g. of aluminum chloride, a total of 100–110 g. of ethylene was usually absorbed. After the reaction an upper layer of about 225 g., a lower layer of 50–55 g. and a trace ($\simeq$0.2 g.) each of a gas condensable at −78° and of an uncondensable gas (ethylene) was obtained.

The water-white clear upper layers from two such experiments were combined, washed, dried (charge, 440 g.) and separated by ordinary and vacuum fractionation (above 175°) into fourteen fractions: 25–50, 50–75, 75–100, 100–125, 125–150, 150–175, 175–190, 190–220, 220–250, 250–275, 275–305, 305–335, 335–365 and 365–400° (all temperatures corrected to 760 mm. pressure, partly by means of the G. G. Brown chart[4]). Their weights were as follows: 8.8, 150.2, 21.7, 36.3, 24.1, 37.4, 8.2, 45.8, 24.1, 26.3, 18.9, 12.8, 7.9 and 6.2; residue 0.5 g., and losses 0.8 g.

Their corresponding refractive indices (D-line) and densities at 20° were: 1.3589, 1.3766, 1.3857, 1.3962, 1.4058, 1.4147, 1.4230, 1.4270, 1.4337, 1.4405, 1.4481, 1.4547, 1.4599 and 1.4659; 0.6550 at 0°, 0.6604, 0.6785, 0.7032, 0.7198, 0.7375, fr. 7 not det., 0.7628, 0.7755, 0.7889, 0.8055, fr. 12 not det., 0.8304, fr. 14 not det. Their percentage contents of hydrogen and carbon were, except fractions Nos. 1, 7, 12 and 14, beginning with fraction No. 2:

16.5	16.1	16.0	15.8	15.5	15.06	15.11	14.90	14.63	14.31
83.8	83.3	84.0	84.4	84.3	84.88	84.94	84.85	85.05	85.17

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[4] G. G. Brown and H. B. Coats, Circular Series No. 2, Dec., 1928, Dept. of Eng. Research, University of Michigan, Ann Arbor.

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.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 16, 1935

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

Polymerization of Ethylene with Aluminum Chloride

BY V. N. IPATIEFF AND ARISTID V. GROSSE

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.

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.

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(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).