

XCIV.—*Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons.*

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It is usually stated that nitric acid—concentrated, fuming, or mixed with sulphuric acid—has little or no action on the paraffins, whilst in one or other form it acts readily on the unsaturated and aromatic hydrocarbons, yielding nitro-compounds in the latter case. It has, however, been observed by Konowaloff (*Ber.*, 1892, 25, Ref. 108) that normal hexane and octane yield secondary nitro-compounds when heated with dilute nitric acid in sealed tubes at 130—140°.

Hydrocarbons of the polymethylene series are not attacked by a mixture of sulphuric and nitric acids at the ordinary temperature, nor readily on moderate heating. With fuming nitric acid, the behaviour of pentamethylene and hexamethylene differs widely from that of their methyl derivatives, for the two former compounds are only attacked when heated, and yield chiefly the corresponding dibasic acids—glutaric and adipic acids—whilst the methyl derivatives, and especially methylpentamethylene, are acted on rapidly at the ordinary temperature with evolution of heat, and the molecule is for the most part broken down.

With less concentrated nitric acid at a high temperature, pentamethylene and hexamethylene give secondary nitro-compounds in addition to the dibasic acids, and the methyl derivatives yield tertiary nitro-compounds (Markownikoff, *Ber.*, 1897, 30, 974 and 1222; *Annalen*, 1898, 301, 201; Zelinsky, *Ber.*, 1897, 30, 389).

It is quite true that at the ordinary temperature the paraffins remain practically unacted on by nitric acid in any form, and that the normal paraffins are very slowly decomposed by fuming nitric acid when heated on a water bath, but we have observed that the iso-paraffins—isoheptane, iso-octane, di-isobutyl—are very readily attacked when heated with the fuming acid, a moderate yield of nitro-compound being obtained in each case.

Isohexane.

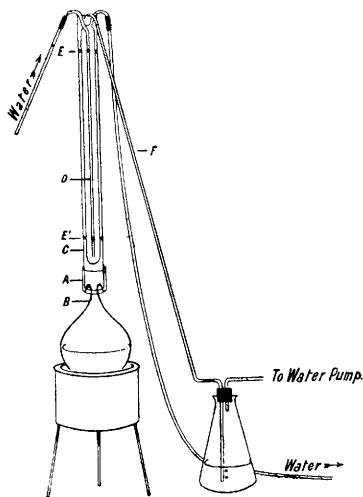
The attempt to separate normal hexane from light petroleum by fractional distillation, after removal of benzene, was only partially successful, owing to the presence of methylpentamethylene, which boils only about 3° higher than the paraffin. In order to remove the naphthene, the fractions from about $66-70^{\circ}$ were separately heated with fuming nitric acid in a flask of special form provided with a reflux condenser (see Fig. 1). A

piece of wide tubing, A, is sealed to the narrow neck, B, of the round-bottomed flask, and the wide tube is pushed down over the narrow one so as to form a ring-shaped depression in which the tube C fits loosely. The condenser, D, is an internal one, somewhat like that recommended by Sudborough and Feilmann (*J. Soc. Chem. Ind.*, 1897, 16, 979), and is centred by five internal projections in the wide vertical tube in each of two horizontal planes E, E'. A little strong nitric acid in the ring-shaped depression prevents the escape of nitrous fumes below, and the gases which reach the top of the tube are carried off through a bent tube, F, connected with a wash bottle and a water pump. It is not necessary to carry on the operation in a draught chamber.

Taking the fractions in descending order of temperature, it was observed that the loss of weight reached a minimum at about 69° , just above the true boiling point of normal hexane, increasing rapidly at lower temperatures. Also, whilst the higher fractions, rich in methylpentamethylene, gave diminishing amounts of a liquid nitro-compound (separated by diluting the acid with water) the fraction from $68.85-68.95^{\circ}$ yielded no nitro-compound at all, and the lower ones, containing isohexane, gave increasing quantities of a solid nitro-compound.

Details of the results obtained with the fractions below 69.03° , including one from $62.6-63.05^{\circ}$, very rich in isohexane, are given in the table below. Each fraction was heated for 5 days with about its own volume of fuming nitric acid (renewed on the second and

FIG. 1.



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fourth days), but in the case of the lowest fraction the treatment was extended to 6 days, and a fourth quantity of acid was used.

Temperature range.	Weight of fraction.		Percent- age loss.	Remarks.
	Before.	After.		
68·95—69·03	113·2	89·8	20·7	Trace of liquid nitro-compound.
68·85—68·95	84·4	66·1	21·7	Acid nearly clear on dilution.
68·7 —68·85	73·5	57·1	22·3	A few small crystals on standing.
68·35—68·7	83·0	60·8	26·7	0·6 gram solid nitro-compound.
67·85—68·35	51·0	32·0	37·3	1·1 " " " "
66·4 —67·85	79·4	37·4	52·9	4·9 " " " "
62·6 —63·05	89·2	6·5	92·7 {	12·0 " " " " also some liquid, b. p. about 194°.

The diluted nitric acid from the lowest fraction was found to contain a considerable quantity of acetic acid, some propionic acid, and very small quantities of oxalic and succinic acids.

The hydrocarbon remaining after treatment with nitric acid was in each case shaken repeatedly with strong sulphuric acid, until the latter gave no turbidity on dilution, then with caustic soda, and finally with water; after this, it was dried with phosphorus pentoxide and weighed.

Each fraction was distilled over sodium wire and it was found that, after a few fractionations (omitting the lowest fraction) to remove the last traces of nitro-compounds, the boiling point was quite constant at 68·95°, and the sp. gr. at 0°/4° rose only from 0·67693—0·67713, whereas, before treatment, the range of temperature was from 66·4 to 69·03° and of sp. gr. from 0·6793 to 0·6803. The remaining hydrocarbon therefore consisted of practically pure normal hexane (b. p. 68·95°; sp. gr. 0·67697) and both the pentamethylene, which raised the specific gravity, and the isohexane, which lowered the boiling point, had been eliminated.

The solid nitro-compound crystallised from light petroleum in hexagonal plates; recrystallised from petroleum or from alcohol, the melting point was 85·5—86·0°. Heated in an open tube with a free flame, it decomposed with slight explosion. The substance was analysed, with the following results.

	Found.		Calculated for $C_6H_{11}(NO_2)_3$.
	I.	II.	
C	32·85	32·15	32·57 per cent.
H	5·37	5·26	4·97 " "
N	19·45		19·00 " "

It was therefore a trinitro-derivative of isohexane, and was probably a tertiary compound, as it appeared to give no reaction with nitrous acid and no sodium salt.

Isoheptane.

A specimen of nearly pure isoheptane, prepared from the crude heptanes from petroleum by bromination, separation of the mono-bromides, and reduction of the isoheptylic bromide, was heated for a short time with fuming nitric acid, when it diminished quickly in volume, and the acid, on dilution, gave a considerable amount of a liquid nitro-compound.

A further quantity of less pure isoheptane, mixed with its own volume of normal hexane to dilute it, was heated with fuming nitric acid on the water bath for 2 days. As the acid, on dilution, again gave a liquid nitro-compound, it was distilled with steam until the oil had almost ceased to come over; the residue, on cooling, deposited crystals in small quantity. The solid nitro-compound, crystallised from a mixture of alcohol, water, and ether, melted at 194° with immediate decomposition. On recrystallisation, it was obtained in well-formed plates which melted at the same temperature.

The percentage of nitrogen was found to be 17.64. Calculated for $C_7H_{13}(NO_2)_3 = 17.87$.

Iso-octane.

A specimen of iso-octane from petroleum, treated in the same manner as isoheptane, was quickly acted on, and gave a liquid nitro-compound, but in this case no solid could be separated by distillation with steam.

Isopentane.

The boiling point of pure isopentane is too low for any reaction to take place with fuming nitric acid. It was thought possible, however, that a mixture of isopentane and normal hexane might give a high enough temperature, but the action was slow and the acid, on dilution, remained quite clear. The remaining hydrocarbon, when distilled, left a very small, semi-solid residue which, after being dried on a porous plate and recrystallised from dilute alcohol, melted at 192° with immediate decomposition. The quantity was too small for a nitrogen determination, but on heating it in a dry test tube, large quantities of red fumes were evolved. It thus resembled the trinitro-derivative of isoheptane very closely indeed.

Di-isobutyl.

A small quantity of di-isobutyl (from isobutylic bromide and sodium) mixed with its own volume of normal hexane, was heated for two days with fuming nitric acid on the water bath.

The acid, when diluted, became but slightly turbid, but the remaining paraffin, after being washed with dilute caustic soda, deposited crystals.

By recrystallisation from benzene and light petroleum, the nitro-compound was obtained in large, colourless plates melting at 91.0° .

The percentage of nitrogen was found to be 16.65. Calculated for $C_8H_{15}(NO_2)_3 = 16.86$.

General Conclusions.

The normal paraffins are less easily attacked by fuming nitric acid than any other hydrocarbons, and next to them come the polymethylene compounds with no side chains. Of the remaining hydrocarbons, the aromatic compounds, the methyl derivatives of the polymethylene hydrocarbons, and the iso-paraffins—which are all characterised by the presence of $\equiv CH$ groups—are much more readily attacked, the first two classes of hydrocarbons at the ordinary temperature, the iso-paraffins when heated moderately on a water bath. Compounds of the general formula, $(CH_3)_3C \cdot C_nH_{2n+1}$, have not yet been studied, but, as they contain no $\equiv CH$ group, it seems probable that they would resemble the normal paraffins in their behaviour with nitric acid.

A recent observation by Aschan (*Ber.*, 1898, 31, 1801) is of considerable interest in connection with this subject. Aschan finds that di-isopropyl and isopentane are rapidly attacked by chlorosulphonic acid at the ordinary temperature; he has not yet, however, studied the action of this reagent on other paraffins, but expresses the intention of doing so. It will be interesting to know whether the normal paraffins are less easily attacked than the iso-compounds.

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