moved from the extract and the residue dissolved in petroleum ether. This solution, after standing in a refrigerator, gave 0.45 g. of N-phenyl-O,N-bis(1-cyano-1-methylethyl)-hydroxylamine, m.p. 93–94° (recrystallized from aqueous alcohol) with no depression on admixture with a sample prepared from nitrosobenzene according to Gingras and Waters.[8]

Anal. Calcd. for $C_{14}H_{17}N_3O$: N, 17.28. Found: N, 16.94%.

The insoluble part in petroleum ether gave, on filtration, 70 mg. of 2,3,5-tricyano-2,3,5-trimethylhexane, m.p. and mixed m.p. 81–82°.

Reaction of m-dinitrobenzene with α,α'-azobisisobutyronitrile. To a solution of 6.72 g. of m-dinitrobenzene in 20 cc. of toluene heated on a boiling water bath 6.56 g. of α,α'-azobisisobutyronitrile was added in small portions over 2 hr., and the mixture was heated for a further 3 hr. to complete the reaction. Hydrogen cyanide was evolved during the reaction. The reaction mixture was subjected to steam distillation and after recovery of tetramethylsuccinonitrile, acetone was isolated as 2,4-dinitrophenylhydrazone (0.85 g.) from the distillate. The residue from the steam distillation was extracted with ether, the ether removed and the residue was treated with petroleum ether. An insoluble part in this solvent was extracted with benzene and evaporation of the benzene gave 0.5 g. of N-(m-nitrophenyl)-O,N-bis(1-cyano-1-methylethyl)hydroxylamine, m.p. 159–159.5° (from benzene).

Anal. Calcd. for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.44;

mol. wt., 288. Found: C, 58.62; H, 5.88; N, 19.3%; mol. wt. (Rast), 278.

Reaction of nitromethane with α,α'-azobisisobutyronitrile. α,α'-Azobisisobutyronitrile (8.2 g.) was added gradually during 2 hr. to nitromethane (30 g.) under reflux and the refluxing was continued for a total of 6 hr. No hydrogen cyanide was detected in the nitrogen evolved during this period. The reaction mixture was distilled through a Vigreux column and the recovered nitromethane was shown to contain no acetone. On slow sublimation at 100° of the solid residue from the distillation, 5.27 g. of tetramethylsuccinonitrile was obtained. The residue was extracted with ether and evaporation of the ethereal solution gave 1.09 g. of 2,3,5-tricyano-2,3,5-trimethylhexane, m.p. 81–82°.

Reaction of tetranitromethane with α,α'-azobisisobutyronitrile. To a solution of 4.0 g. of tetranitromethane in 15 cc. of toluene heated on a boiling water bath, 5.0 g. of α,α'-azobisisobutyronitrile was added in small portions during 2 hr. and the mixture was heated for a further 6 hr. Some nitrogen dioxide was evolved. The reaction mixture was distilled with steam and acetone was isolated as 2,4-dinitrophenylhydrazone (0.6 g.) from the distillate after separation of tetramethylsuccinonitrile. No tractable products could be isolated from the viscous residue from the steam distillation.

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Oxidation of *n*-Octane with White Fuming Nitric Acid[1]

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The heterogeneous reactions of *n*-octane with white fuming nitric acid at −5°, 4°, and 27° have been investigated, using infrared spectroscopy as the main analytical tool. The effect of added phosphorus pentoxide, nitrogen pentoxide, sulfuric acid, and water was studied. The vigor of the reaction is a function of both the temperature and the concentration of nitrogen pentoxide. It is suggested that the nitrogen pentoxide in the white fuming nitric acid is responsible for its higher reactivity compared with the reactivity of aqueous nitric acid.

The principal products formed from the low temperature reaction include initially an alkyl nitrate (presumably 2-octyl nitrate) and subsequently 2-octanone. At higher temperatures carbon-carbon scission occurs and a mixture of carboxylic acids is obtained.

The reaction of white fuming nitric acid with alkanes is of interest as a model, controllable system for certain hypergolic (spontaneous ignition) reactions. The liquid phase heterogeneous reaction of *n*-octane with white fuming nitric acid has been investigated in order to determine the initial attack involved and the course of the reaction.

Previous work on the liquid phase reactions between alkanes and nitric acid has involved mainly aqueous solutions of nitric acid. The nitration of *n*-octane carried out by Konovalov[3] at 130° (sealed tube) with dilute nitric acid (sp. gr. 1.075) produced a fair yield of 2-nitrooctane. Worstall[4]

reported the formation of primary mono- and dinitrooctanes in the reaction of this hydrocarbon with a mixture of nitric acid (sp. gr. 1.42) and sulfuric acid at the reflux temperature. The use of fuming nitric acid (sp. gr. 1.52) resulted in extensive oxidation of the hydrocarbon.

The literature yields the following generalizations concerning the liquid phase reactions of alkanes and nitric acid. Dilute nitric acid is preferable for nitration,[5] concentrated nitric acid favors oxidation and polynitroalkane formation,[3] while fuming nitric acid leads to both vigorous oxidation and polynitration.[4,6] Tertiary carbon atoms are nitrated most readily.[7] In the light of the above data and of Hass' signal successes with

(1) This work was conducted under Office of Naval Research Contract Nonr-630(00).

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vapor phase nitration of alkanes,[8] it has generally been assumed that alkanes undergo reaction with nitric acid only under vigorous conditions. The present investigation shows that alkanes will react with white fuming nitric acid at room temperature or below.

It should be noted that the research cited above was directed toward the synthesis of nitroalkanes and not to the complete elucidation of the reaction between alkanes and nitric acid. Considerable confusion has arisen because of the failure of previous workers to specify the identity of the nitric acid used. Even the designation of the specific gravity of the nitric acid is of little use for concentrations of acid above 90%, in which region the density of the acid changes little with composition.

Recent spectroscopic and cryoscopic investigations of the nature of analytically anhydrous nitric acid have demonstrated the presence of 1–2% nitrogen pentoxide.[9] The presence of nitrogen pentoxide results in a significant difference in the reactivities of white fuming nitric acid and of aqueous nitric acid on alkanes as shown in the present work. In this connection the work of Titov and Shchitov[10] is of major significance. They studied the reactions of nitrogen pentoxide with cyclohexane, n-heptane, and n-octane in carbon tetrachloride solution. The principal products of these reactions were alkyl nitrate and nitroalkane. They also observed that the addition of a mixture of phosphorus pentoxide and "anhydrous" nitric acid to cyclohexane in carbon tetrachloride solution gave similar results.

In the present work, infrared spectroscopic analysis has been utilized in order to investigate the products present at low conversions of the reaction of n-octane and white fuming nitric acid in order to determine the initial oxidation product as well as the further sequence of oxidation products.

EXPERIMENTAL

Materials. n-Octane was obtained from the Matheson Co., n_D^{20} 1.3964. 2-Octyl nitrate was synthesized according to the method of Ferris,[11] n_D^{20} 1.4261. 2-Octyl nitrite was synthesized according to the method of Kornblum and Oliveto,[12] n_D^{20} 1.4089. 2-Octanone, obtained from the Eastman Kodak Co., was purified by means of the bisulfite addition compound, n_D^{20} 1.4142. 2-Octanol was an Eastman Kodak Co. product, n_D^{20} 1.4261. White fuming nitric acid was obtained from the General Chemical Division of Allied Chemical and Dye Corp., and was found by titration with standard base to contain 102–103% nitric acid. Cerate ion analysis of a similar sample of white fuming nitric acid

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indicated the concentration of nitrogen dioxide to be 0.02–0.03 g./ml.[13]

General procedure. One volume of the hydrocarbon was added cautiously by means of dropping funnel to two volumes of white fuming nitric acid contained in a 125-ml. Erlenmeyer flask which was equipped with a reflux condenser and magnetic stirrer, and submerged in a small water bath. The liquid, heterogeneous mixture was stirred vigorously at a constant rate for 0.25–5 hr., and poured over ice. The oil layer was separated, washed twice with water, and dried over anhydrous sodium sulfate; the reaction mixture was then submitted for infrared analysis. It was shown that this treatment did not affect any of the postulated products of the reaction.

Runs were made routinely at 27 ± 2° and 4 ± 1°. The 27° runs were conducted in a water bath; the 4° runs although conducted in an ice bath, did not attain 0° because of heat transfer from the magnetic stirrer. Occasionally the violence of a reaction raised the internal temperature to 50° or more. An ice-salt mixture was employed to obtain a temperature of −5 ± 2° and a circulating water bath maintained a temperature of 19 ± 1°.

Reactions were run using white fuming nitric acid alone, as well as white fuming nitric acid with added phosphorus pentoxide (Mallinckrodt Chemical Co.), nitrogen pentoxide, sulfuric acid (Baker and Adamson, 96% sulfuric acid), and water. The phosphorus pentoxide was added to the nitric acid at 0° prior to the introduction of the hydrocarbon. The nitric acid–nitrogen pentoxide mixture was prepared from a sample of distilled nitrogen pentoxide,[13] formed from the reaction of white fuming nitric acid and phosphorus pentoxide.

All infrared spectra were determined using a Perkin-Elmer Double Beam Recording Infrared Spectrophotometer Model 21 employing matched 0.1-mm. cells with sodium chloride windows. The analytical data and summary of the runs are given in Table I.

RESULTS

Effect of nitrogen pentoxide. The reaction of white fuming nitric acid with n-octane produced, in general, oxidation products although a small amount of nitration was observed. It was observed that the most vigorous stage of reaction at 27° occurred with the addition of the first few milliliters of hydrocarbon to the nitric acid. This implied the presence of some substance in the nitric acid which produced a vigorous reaction and which was consumed rapidly. The assumption that this substance was nitrogen pentoxide accounted for this rapid diminution of rate.

Several experiments bore out this theory. There was a remarkable reduction in total reaction in going from *ca.* 100% acid to 97.5% and 95% acids. On the other hand, by adding nitrogen pentoxide as such to the white fuming nitric acid, or by adding phosphorus pentoxide which forms nitrogen pentoxide according to the equation:

$$P_2O_5 + 6HNO_3 \longrightarrow 3N_2O_5 + 2H_3PO_4$$
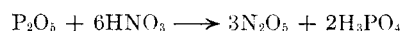
the amount of total reaction was markedly increased. These results are presented in Table I, Runs 8–12. It should be noted that the 27° runs utilizing additional nitrogen pentoxide or

(13) We acknowledge the assistance of Dr. George Gibson in these experiments.

TABLE I

OXIDATION OF n-OCTANE WITH WHITE FUMING NITRIC ACID

Run	n-Octane Ml.	Oxidant White Fuming HNO$_3$, Ml.	Oxidant Other	Temp., °C.	Time, Hr.	Overall Reaction, %[h]	Infrared Product Analysis-Mole, %[a,f] RCO$_2$H[b]	RCOR[c]	RONO$_2$[d]	RNO$_2$[e]	
1	7	12.5	P$_2$O$_5$[m]	-5	1.25	13	0	0	100	0	
2	5	10		4	2.0	3	0	68	25	7 ·	
3	5	5	H$_2$SO$_4$[l]	4	0.25	0.7	0	0	100	0	
4	14	25	P$_2$O$_5$[m]	4	1.5	26	0	0	99	1	
5	14	25	P$_2$O$_5$[m]	4	4.0	29	9	67	18	6	[i]
6	3	6	N$_2$O$_5$[n]	4	2.0	14	0	50	37	13	
7	5	10		19	2.0	2	63	1	20	6	
8	8	20	H$_2$O (5%)	27	3.0	0.06	89	0	0	0	
9	8	20	H$_2$O (2.5%)	27	5.0	0.28	84	0	0	6	
10	1	2		27	6.0	2.2	77	0	0	8	[g,o]
11	3	6	N$_2$O$_5$[n]	27	2.3	5.5	48	0	0	14	[i]
12	3	6	P$_2$O$_5$[m]	27	2.5	7.3	65	0	0	10	[o,i]
13	5	12	NaNO$_2$	27	1.0	0	0	0	0	0	[o]
		Oxidation of Intermediate Compounds									
14	2-Octanol	4		4	0.25	—	0	91	7	2	[i]
15	2-Octanone	2		27	2.0	76	57	24	0	1	[g]
16	2-Octyl Nitrate	5		4	1.0	31	0	28	69	3	[i]
17	"Octyl" Nitrate	9		4	2.0	31	0	28	69	3	[k]

[a] The product analyses are expressed in mole % of the total water-insoluble product. The product analyses are reproducible to ±5%. Several assumptions were made in the calculations: (1) the validity of Beer's Law in these systems; (2) the validity of the standards (the standards were chosen to reproduce individual absorption peaks but do not imply that the products had the identical structure except for functional groups) (see footnotes b–f); (3) the independence of the extinction coefficient of a given functional group from the structure of the rest of the molecule. [b] Calculated from the 1712 cm.$^{-1}$ absorption peak using n-heptanoic acid (in n-octane) as standard. [c] Calculated from the 1724 cm.$^{-1}$ absorption peak using 2-octanone as standard. [d] Calculated from the 1642 cm.$^{-1}$ absorption peak using 2-octyl nitrate as standard. [e] Calculated from the 1560 cm.$^{-1}$ absorption peak using 2-nitrooctane as standard. [f] In reactions carried out at 19° and 27° (runs 7–12 and 15), another component was detected by infrared analysis, having an absorption band at 1604 cm.$^{-1}$ This substance may be an alkyl nitrite (2-octyl nitrite shows absorption peaks at 1643 and 1604 cm.$^{-1}$) or a polynitro compound in which the absorption band of the nitro group has been shifted to the 1604-cm.$^{-1}$ region. A. I. Titov and M. K. Matveeva, Doklady Akad. Nauk, S.S.S.R., 83, 101 (1952) and Sbornik Statei, Obshchei Khim. Akad. Nauk, S.S.S.R., 1, 246 (1953) report the formation of cyclohexyl nitrite from cyclohexane and nitric acid or nitrogen oxides. It is possible that the sample of white fuming nitric acid used in the present experiments contained enough dissolved nitrogen dioxide to account for the formation of alkyl nitrite in these cases. [g] The water-insoluble carboxylic acid fraction was identified in the following fashion. The reaction product, washed with water was extracted with dilute aqueous sodium bicarbonate. The acrid material obtained from acidification of the bicarbonate extract was distilled in vacuo (b.p. 80–85°/3 mm.). The neutralization equivalent of the fraction from Run 11 was 116 ± 1 and from Run 16 was 121 ± 1. p-Toluides of each of these acid samples melted in the range of 58–62°, considerably lower than the toluides of pentanoic, hexanoic, or heptanoic acids. [h] The over all % reaction is the percentage of the reactant found as the total water-insoluble product. The abnormally low yields found in some of the higher temperature runs are probably due to extensive disruption producing water-soluble products which were not isolated. The percentages are reproducible to ±5%. [i] An experiment fourfold as large produced an uncontrollable reaction evolving heat and copious fumes of nitrogen dioxide. [j] The ketone was isolated by stirring the reaction product (washed free of carboxylic acid with sodium bicarbonate) for several hours with a strong, aqueous solution of Girard's Reagent T. The aqueous phase was acidified with hydrochloric acid, warmed gently for an hour on a steam bath, and extracted with ether. The ketone was recovered from the ether extract, and converted into a 2,4-dinitrophenylhydrazone, m.p. 57–58°, after recrystallization from ethanol. A mixture of this sample and an authentic sample melted at 57–58°. [k] A solution of what was presumably an octyl nitrate in n-octane was prepared from the reaction of n-octane with 100% nitric acid and phosphorus pentoxide at −5° according to Run 1. Its infrared spectrum was identical with that of authentic 2-octyl nitrate from 1000–4000 cm.$^{-1}$ [l] The molar ratio of the sulfuric acid to the nitric acid was 4:1. [m] The molar ratio of the octane to the phosphorus pentoxide was 1:1 in runs 5 and 6; and 1:0.8 in runs 13 and 4. [n] The molar ratio of the nitrogen pentoxide to the nitric acid was 1:10. [o] Nitrogen dioxide was liberated.

phosphorus pentoxide were accompanied by vigorous evolution of nitrogen dioxide and boiling of the reaction mixture.

Main oxidation products. At 4° or lower, with a reaction time of 1.5 hr. or less, using mixtures of phosphorus pentoxide and nitric acid (Runs 4 and 1) an alkyl nitrate is almost the sole product. At 4° nitric acid alone produced a mixture of alkyl nitrate and ketone with the latter predominating

(Run 2). At 19° the main products of the oxidation with nitric acid were carboxylic acid, ketone, and alkyl nitrate (Run 7). At room temperature the reaction of nitric acid and n-octane gave mainly carboxylic acid (Run 10).
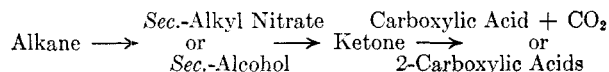
The alkyl nitrate exhibited an infrared spectrum identical with that of authentic 2-octyl nitrate. However, the infrared spectra of other octyl nitrates are practically indistinguishable from that

of 2-octyl nitrate. It may be concluded that the alkyl nitrate produced is an octyl nitrate or mixture of octyl nitrates. The ketone produced in the oxidation was isolated and identified as 2-octanone. The water-insoluble carboxylic acid fraction produced in the oxidation was isolated and shown to have an average molecular weight equivalent to that of hexanoic acid, probably a mixture of pentanoic, hexanoic, and heptanoic acids, since the p-toluidide of this fraction melted lower than the toluidides of either one of the individual acids.

In order to demonstrate the hypothesis of a stepwise reaction involving the sequence: alkane → alkyl nitrate → ketone → carboxylic acid, the following experiments were performed. 2-Octyl nitrate was treated with nitric acid producing 2-octanone which was isolated and identified (Runs 16 and 17). 2-Octanone was treated with nitric acid producing a (water-insoluble) carboxylic acid fraction whose neutralization equivalent was 121 ± 1, indicating approximately equal amounts of hexanoic and heptanoic acids (Run 15).

DISCUSSION

Reaction path. Using the previous data, the following reaction scheme can be postulated

$$\text{Alkane} \longrightarrow \begin{array}{c} \textit{Sec.-}\text{Alkyl Nitrate} \\ \text{or} \\ \textit{Sec.-}\text{Alcohol} \end{array} \longrightarrow \text{Ketone} \longrightarrow \begin{array}{c} \text{Carboxylic Acid} + CO_2 \\ \text{or} \\ \text{2-Carboxylic Acids} \end{array}$$

This scheme satisfies all the data presented above and implies that the nitroalkane(s) be considered as by-products.

The decision as to whether the alcohol or alkyl nitrate is the initial oxidation product proved difficult. Under one set of reaction conditions nitrate was detected exclusively. 2-Octanol was converted to nitrate although the reverse was not observed, probably owing to the lack of water in the reaction mixture. Both 2-octanol (Run 14) and 2-octyl nitrate were converted to 2-octanone. These experiments do not permit an unambiguous assignment of the roles of alkyl nitrate and alcohol. The results can be explained by (1) the primary formation of alcohol with subsequent esterification to alkyl nitrate and oxidation to ketone; or (2) the primary formation of alkyl nitrate followed by oxidation to ketone. It should be pointed out that the chromic acid oxidation of alcohols has been demonstrated to proceed through an ester intermediate.[14]

The oxidation of ketone to acid involves the rupture of a carbon-carbon bond and may result in

the formation of two carboxylic acids or of one carboxylic acid and carbon dioxide. There was some ambiguity in the identification of the carboxylic acid fraction. Since the only ketone isolated was 2-octanone, there might seem to be justification to assume that the water-insoluble carboxylic acids produced would be those derived from 2-octanone, namely hexanoic and heptanoic acids. However, there is no reason to exclude the formation of other octanones. Therefore, the carboxylic acid fraction could conceivably contain all normal alkanoic acids containing two to seven carbon atoms.

Mechanism of the initial attack. It has been shown that the ease of attack of an alkane by white fuming nitric acid is directly related to its nitrogen pentoxide content. This result is consistent with the results of Titov and Shchitov[10] on the facile oxidation of alkanes with nitrogen pentoxide. It is possible that the nitrogen pentoxide reaction occurs by a primary dissociation into NO_2 and NO_3 radicals or into the nitronium cation and the nitrate anion. If it is assumed that the oxidation occurs in the nitric acid phase, attack by an ionic species such as nitronium ion is indicated since Millen demonstrated that nitrogen pentoxide exists as nitronium nitrate in 100% nitric acid.[9] However, it is more probable that the oxidation process occurs in the hydrocarbon phase, and in such a situation, it is probable that the species that attacks the alkane is the NO_3 radical as postulated by Titov and Shchitov. It has been demonstrated by Ogg[15] that nitrogen pentoxide dissociates in the gas phase according to the equilibrium:

$$N_2O_5 \rightleftharpoons NO_2 + NO_3$$

In a nonpolar organic solvent such as n-octane this equilibrium would also be expected to exist. Titov and Shchitov have demonstrated that the initial attacking agent in the N_2O_5 oxidation in an organic solvent is the NO_3 radical by means of kinetic studies, the effect of solvent on the rate of oxidation and the effect of N_2O_4 on the rate of the reaction and on the relative product formation. It is reasonable to extrapolate this hypothesis to the present two-phase system involving white fuming nitric acid and n-octane. It should be noted that gas phase nitration and other substitution reaction of alkanes normally proceed by free radical mechanism;[16] the reactions under study appear to be members of the same mechanistic family.

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