254. *The Oxidation of* n-*Paraffins from Propane to Nonane by Nitrous Oxide.*

By E. J. Smith.

An exploratory study of the slow oxidation of propane and other *n*-paraffins up to nonane has been made. The reactions are chain processes involving alkyl radicals; in typical cases they are inhibited by small amounts of nitric oxide and by reaction products. The latter effect is doubtless due to the presence of olefins produced in the simultaneous hydrocarbon pyrolysis both by direct unimolecular breakdown and by thermal decomposition of intermediate alkyl radicals. These stable pyrolysis products are not readily attacked by nitrous oxide at 550° and their formation limits the extent of the oxidation, especially with the higher members of the series. Some tentative conclusions regarding the mechanism of the oxidation are given.

The slow oxidation of hydrogen (Melville, *Proc. Roy. Soc.*, 1933, **142**, *A*, 524; 1934, **146**, 737) and methane (Robinson and Smith, *J.*, 1952, 3895) by nitrous oxide are chain reactions in which oxygen atoms arising from thermal decomposition of the oxide initiate the processes by the respective steps, $H_2 + O \longrightarrow OH + H$, $CH_4 + O \longrightarrow CH_3 + H$. The work on hydrocarbons is being continued by Dr. P. L. Robinson, and this paper describes exploratory observations on the corresponding oxidation of propane and other paraffins up to *n*-nonane. Interesting differences from the behaviour of methane have been observed which are undoubtedly related to the fact that at the temperatures employed (500—600°) all these hydrocarbons are " cracked," producing shorter saturated hydrocarbons (principally methane and ethane), olefins, and hydrogen. These pyrolyses are well known as sources of alkyl radicals and involve, simultaneously, free-radical chain and non-chain molecular mechanisms (Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458; **201**, 18; Ingold, Stubbs, and Hinshelwood, *ibid.*, 1950, **203**, 486; **208**, 285). Both modes of decomposition appear to give the same products in practically the same proportions. The present work suggests that both have an important bearing on the behaviour of the hydrocarbon towards nitrous oxide.

The molecular products, in typical cases, have been shown to react very slowly with nitrous oxide; but the alkyl radicals simultaneously produced must react readily, initiating a cycle terminating in the production of carbon monoxide, carbon dioxide, and water vapour.

EXPERIMENTAL

Materials.—The hydrocarbons used, with the exception of the propane, were presented by Imperial Chemical Industries Limited through the courtesy of Dr. Holroyd. The purity of the *n*-octane and *n*-pentane is given as 90—95%, and that of the remainder as better than 99%. The only further treatment they received was a thorough degassing in the apparatus. The propane, from a cylinder, was washed with pyrogallol, dried, and condensed at −180°; large head and tail fractions were rejected and the remainder given three bulb-to-bulb distillations. Nitrous oxide was taken from a cylinder and treated as described by Robinson and Smith (*loc. cit.*). Nitric oxide, prepared from copper and nitric acid, was freed from nitrogen dioxide with 30% sodium hydroxide, dried, and condensed at −180°. The frozen product was pumped free from nitrogen and distilled several times to rid it of nitrous oxide. The purified nitric oxide was stored in a cooled trap attached to the quenching bulb of the apparatus.

Apparatus.—The apparatus used in the methane work (*loc. cit.*) was modified for work with less volatile hydrocarbons above pentane. The mixing bulb *E* was enveloped in a steam-jacket, and all adjacent leads and taps were also kept at 100° by resistance heating and asbestos lagging. After being outgassed, the hydrocarbons were vaporised from trap *I*, and the required pressure of nitrous oxide was admitted afterwards. Taps between the storage section and reaction vessel were lubricated with silicone grease. Mixtures of the gaseous hydrocarbons with nitrous oxide were prepared in a series of 3-l. bulbs attached to the line and furnished with individual mercury manometers.

Results.—The oxidations proceed at a convenient rate at 500—600° and can be approximately represented by the stoicheiometric stages :

$$(a)\quad C_nH_{2n+2} + (2n+1)N_2O \longrightarrow nCO + (n+1)H_2O + (2n+1)N_2$$

$$(b)\quad CO + N_2O \longrightarrow CO_2 + N_2$$

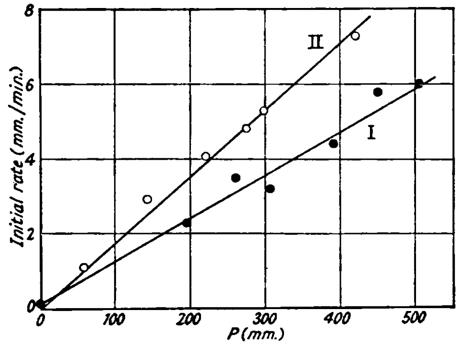
Since the decomposition of nitrous oxide alone is very slow at these temperatures, the extent of the reaction, expressed in terms of ($CO + CO_2$) and the other products shown above, may be calculated from the pressure change in the closed vessel. Table 1 gives data for 585° showing the amounts of carbon monoxide and dioxide found by analysis after complete reaction, as well as values for the total carbon oxides, calculated from the pressure increase on the basis of the above reactions. All are expressed as percentages of the gaseous contents of the reaction vessel after removal of water vapour.

TABLE 1.

Hydrocarbon	P_{Hy} (mm.)	P_{N_2O} (mm.)	ΔP_∞ (mm.)	($CO + CO_2$), %, calc.	CO, % found	CO_2, % found	($CO + CO_2$), % found	% of hydrocarbon finally oxidised
Propane	21	226	112	19·7	1·87	19·2	21·1	88·9
n-Pentane ...	20	338	148	18·0	0·3	19·3	19·6	74
n-Nonane ...	15	407	91	12·2	1·03	11·3	12·3	33·7

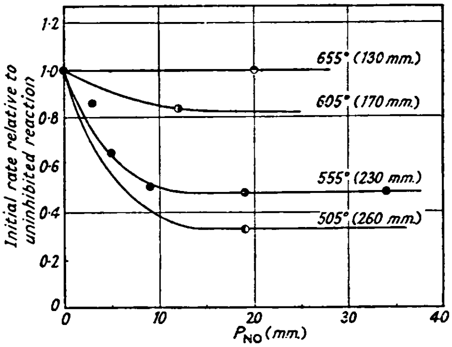
As with methane, little carbon monoxide remains at the end of the reaction although it is relatively abundant in the earlier stages. In a duplicate run with 19 mm. of propane and excess of nitrous oxide the amounts of carbon monoxide and dioxide found for the semi-completed reaction (ΔP = 52 mm.) were 5·3% and 3·8% respectively. Clearly, carbon monoxide is a primary oxidation product and is further oxidised in the subsequent stage (*b*). Table 1, col. 9, gives the percentage of hydrocarbon oxidised finally, as calculated from ΔP_∞, the reaction being assumed to be completed when no measurable pressure change occurred in 20 min. Any subsequent creep in pressure is attributable to side reactions among the products or to decomposition of residual nitrous oxide. The diminishing extent of the oxidation on ascent of the homologous series is very striking. A reason for this incomplete oxidation is the concurrent formation by thermal decomposition of the hydrocarbon, of products which are either not readily oxidised themselves or which actively inhibit the oxidation process by removing radicals responsible for its propagation. For example, propylene, an established inhibitor, is produced in the pyrolysis of butane and higher paraffins. Confirmation that this side-decomposition could explain incomplete oxidation was obtained by experiments on *n*-nonane and *n*-pentane : 34 mm. of *n*-nonane were heated at 525° for some hours during which the pressure rose to 61 mm.; 270 mm. of nitrous oxide were then added and the pressure rose at a rate of 0·25 mm./min. This is slow compared with the 8·5 mm./min. given by a mixture of 60 mm. of fresh *n*-nonane with 240 mm. of nitrous oxide at the same temperature. On another occasion, 100 mm. of a 1 : 4 mixture of *n*-pentane and nitrous oxide were heated for 4 hours at 525°; the initial rate of pressure change was 15 mm./min. Afterwards some of the material was removed from the reaction vessel, leaving a pressure of 140 mm., and to this were added 100 mm. of fresh mixture. The initial rate was now 9 mm./min. and had thus been reduced by 40% owing to inhibition by olefins formed in the previous run. Steacie and MacDonald (*Canad. J. Res.*, 1935, **12**, 711) have similarly observed that the reaction between ethylene and nitrous oxide (involving decomposition, polymerisation, and oxidation of the olefin) was slow at 530°.

FIG. 1. *Dependence of initial rate on partial pressure of each reactant at* 523°.



I, P_{N_2O} variable, $P_{C_3H_8}$ = 50 mm.
II, $P_{C_3H_8}$ variable, P_{N_2O} = 50 mm.

FIG. 2. *Inhibiting influence of nitric oxide on oxidation of propane by* N_2O.



(1 : 3 mixtures) : pressures as stated.

The decrease in the completeness of oxidation on passing from propane to *n*-nonane is understandable because of the increasing proportion of molecular, *i.e.*, non-chain, decomposition on ascent of the homologous series. Inhibition studies (Stubbs and Hinshelwood, *loc. cit.*) have shown that the " apparent chain length " for paraffin decomposition (a measure of the proportion of molecules decomposing by a chain path) is 10·0 for propane, 5·0 for pentane, and 3·7 for *n*-nonane at 530° and 100 mm.

Kinetic Measurements with Propane.—In the curves (Fig. 1) the rates are from the initial slopes of pressure–time curves and have been corrected for simultaneous non-chain pyrolysis of the hydrocarbon. Stubbs and Hinshelwood's data were used for this purpose, the maximum correction applied at the highest propane pressure being 5%. The results point to a first-order reaction with respect to each reactant, and suggest a rate equation of the form $dp/dt = k_1[C_3H_8] + k_2[C_3H_8][N_2O]$. The measurements are limited to pressure only, and it is by no means necessary that the rate-determining stage remained exactly the same over the wide range of relative concentrations used. Hence it is unsafe to draw detailed conclusions. Qualitatively, however, the fact that the rate is more sensitive to the hydrocarbon concentration than to the nitrous oxide concentration presents an interesting contrast with methane where the rate depends almost upon the square of the nitrous oxide concentration. It implies, as might be expected from the lower temperature, that initiation is not as before through oxygen atoms. Alkyl radicals, readily formed in the thermal decompostion of propane at this temperature, can now initiate the oxidation sequence. The first term in the rate equation supports this view of initiation *via* propane.

Inhibition Experiments.—It is suggested that olefins simultaneously formed by hydrocarbon decomposition reduce the amount of hydrocarbon oxidised by removing free radicals and starting a competing polymerisation process. Nitric oxide is more effective than olefins in removing alkyl radicals, and the influence of small quantities upon a standard 1 : 3 mixture of propane and nitrous oxide was studied. Various pressures of highly purified nitric oxide were added to the standard mixture, and their influence on the reaction rate was determined. Control experiments without nitric oxide were performed before and after each run to prove that the inhibition was real. Fig. 2 shows, for various pressures of nitric oxide and at several temperatures, the rates relative to that of the uninhibited reaction. The curves for 505°, 605°, and 655° involve the assumption that a maximum interference occurs when 20 mm. of nitric oxide are present.

TABLE 2. *Initial rates of hydrocarbon consumption during oxidation at* 525° (*mm./min.*).

Hydrocarbon	p_{initial} = 100 mm.	p_{initial} = 300 mm.	Hydrocarbon	p_{initial} = 100 mm.	p_{initial} = 300 mm.
Propane	0·133	0·79	*n*-Octane	0·27	0·77
n-Butane	0·12	0·60	*n*-Nonane	0·16	0·47
n-Pentane	0·16	0·95	2 : 2 : 4-Trimethylpentane		
n-Heptane	0·32	0·93	(" *iso*octane ")	0·2	0·48

At the lower temperatures nitric oxide has a marked retarding effect on the oxidation, which is taken as confirming the presence of alkyl radicals. This effect decreases at higher temperatures and vanishes above 655°. The residual reaction would normally be attributed to a concurrent non-chain decomposition reaction; but this could hardly account for its magnitude here which is 12 mm./min. at 555°, and a non-chain oxidation process cannot be envisaged. The explanation is to be sought either in a reaction involving the product of the radical–nitric oxide step, or, more probably, in the catalytic influence of nitric oxide on the decomposition of nitrous oxide, leading to additional initiation *via* oxygen atoms. Hinshelwood and Musgrave (*Proc. Roy. Soc.*, 1932, *A*, **135**, 23) have demonstrated the powerful catalytic influence of nitric oxide in promoting the decomposition of nitrous oxide.

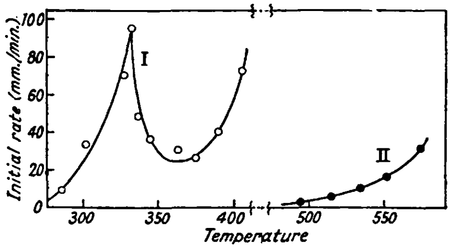


FIG. 3. *Temperature dependence of initial rate of oxidation of propane.*

I, $C_3H_8 : O_2 = 1 : 3$, pressure 410 mm. (maximum rates).

II, $C_3H_8 : N_2O = 1 : 2$, pressure 400 mm.

Activation Energies.—The activation energies for the oxidation of propane, *n*-butane, and *n*-pentane were deduced from rate measurements with standard mixtures at four individual temperatures and were respectively 44, 45, and 47 kcals. The apparent gradation could suggest a common step in the mechanisms, whose activation energy is subject to some structural influence, and may be significant. Without more knowledge of the probable steps in the mechanisms further speculation is unwarranted.

The absence of any complex temperature-dependence in the oxidation of propane by nitrous oxide is shown by Fig. 3, which contrasts the behaviour of a standard propane–oxygen mixture. The latter exhibits the pronounced " low-temperature " reaction generally attributed to branching chains involving peroxides. This should be precluded in the nitrous oxide combustion and the lower curve confirms this.

Dependence of the Rate of Oxidation on the Hydrocarbon Structure.—Table 2 shows rates of oxidation of a series of normal paraffins under standard conditions, *viz.*, a 1 : 4 mixture of hydrocarbon and nitrous oxide at 525° and at two initial mixture pressures. In deriving the rates, the initial rates of pressure change were each multiplied by a factor $1/2n$, where n is equal to the number of carbon atoms in the particular hydrocarbon, in accordance with the stoicheiometry previously stated. A correction was also introduced for the decomposition of the hydrocarbon by the molecular side reaction, Hinshelwood and Stubbs's data being used. The oxidation rate is seen to increase as the hydrocarbon chain lengthens, and after reaching a maximum, decreases again beyond heptane. As a matter of interest 2 : 2 : 4-trimethylpentane was tested for comparison with isomeric *n*-octane, and a pronounced drop in rate was observed on passing from the straight to the branched skeletal chain.

DISCUSSION

The experimental work described is in the nature of a preliminary survey and the conclusions are accordingly tentative. Reasons have been given indicating that the oxidation of paraffin hydrocarbons by nitrous oxide involves alkyl radicals, and since pyrolysis of the hydrocarbons occurs readily at the temperatures employed, these radicals must be formed at an early stage of the reaction. It is convenient to summarise the main steps in the decomposition chain reaction in view of the probable connection of this with the oxidation process. These are as follows (see Steacie, " Atomic and Free Radical Reactions," 1946) : (i) Initial breakage of a C–C bond in the hydrocarbon molecule, forming two alkyl radicals; rupture occurs predominantly in the positions $\overset{1}{\mathrm{C}}-\vdots-\overset{2}{\mathrm{C}}-$ and $\mathrm{C}-\overset{2}{\mathrm{C}}-\vdots-\overset{3}{\mathrm{C}}-$. (ii) Hydrogen abstraction from a fresh hydrocarbon molecule by radical attack; this produces a saturated compound such as methane or ethane and a larger alkyl radical. (iii) Thermal decomposition of alkyl radicals to yield olefins and smaller radicals or hydrogen atoms; fission occurs more readily at the C–C bonds than at the stronger C–H bonds, as Bywater and Steacie (*J. Chem. Phys.*, 1951, **19**, 172, 319) have shown in the case of propyl and butyl radicals. The methyl radical, which can only decompose by rupture of C–H bonds, is stable up to 900°.

Process (i) appears to provide the most feasible initiation step for the oxidation process also, since oxygen atoms are not formed from nitrous oxide at the temperatures used, and the direct bimolecular step $\mathrm{RH} + \mathrm{N_2O} \longrightarrow \mathrm{R} + \mathrm{OH} + \mathrm{N_2}$ requires the simultaneous rupture of two bonds. The oxidation mechanism could then feasibly proceed by the formation of alkoxy-radicals in the step (iv) $\mathrm{R} + \mathrm{N_2O} \longrightarrow \mathrm{RO} + \mathrm{N_2}$ and their subsequent breakdown to aldehyde and simpler fragments in the established manner (Bell, Raley, Rust, Seubold, and Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 242). The final stable oxidation products probably arise from further oxidation stages, whose elucidation has not been attempted here.

The increasing rate of oxidation on passing from propane to *n*-heptane resembles the similar trend observable in the decomposition rate and (although to a much greater degree) in the rate of oxidation of *n*-paraffins by molecular oxygen. Such effects are attributable *inter alia* to increasing ease of initial rupture of the skeletal chain, and of hydrogen-atom removal in radical attack, as the hydrocarbon chain length increases.

In considering the reasons for reversal of this trend in the cases of *n*-octane and *n*-nonane, one should note the very low percentage of hydrocarbon returned as carbon oxides when *n*-nonane was allowed to react completely with nitrous oxide (Table 1). This cannot be entirely accounted for by the simultaneous molecular decomposition of the hydrocarbon into non-oxidisable substances; the decomposition of large alkyl radicals by process (iii) must be responsible for some of the olefins formed. Hence, unimolecular decomposition of radicals must always compete to some extent with their bimolecular removal by nitrous oxide in (iv), and since in the former process one of the products is a stable molecule not readily oxidised, such decomposition will tend to decrease the rate of the overall oxidation process. Radicals larger than methyl are increasingly stabilised by resonance, especially when the chain is branched (Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377), and the activation energy of processes such as (iv) could therefore be expected to increase and lead to a relatively greater loss of radicals by unimolecular breakdown as the hydrocarbon chain length increases. This retardation, coupled with gradual simultaneous decrease in the previous accelerating influences, seems to offer at least a qualitative explanation of the observed decrease in oxidation rate beyond *n*-heptane. The large decrease observed for 2 : 2 : 4-trimethylpentane is in accordance with this explanation in view of the enhanced resonance stabilisation of branched-chain radicals.

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