901. *The Inhibitory Effects of Mercury and of Hydrogen in the Gas-phase Oxidation of* n-*Hexane.*

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During the initial stages of the oxidation of *n*-hexane in the region 260—290°, new inhibiting effects have been observed due to mercury atoms and to molecular hydrogen. The mercury is oxidised, and its inhibitory action may involve a chemical process such as $RO_2 + Hg \longrightarrow RO + HgO$. Inhibition by molecular hydrogen resembles, but is less marked than, the effect previously observed in the oxidation of acetaldehyde in the region 120—220°. This inhibition is tentatively ascribed to deactivating collisions of an energy-rich chain carrier with hydrogen molecules. Both these inhibiting effects suggest that a reaction of the type $RO_2^* + RH \longrightarrow RO{\cdot}OH + R$ is a critical chain-propagating step in the oxidation mechanism of paraffin hydrocarbons.

A reaction scheme for the oxidation of gaseous hydrocarbons in the " low-temperature " region (below about 320°) previously put forward (Ubbelohde, *Proc. Roy. Soc.*, 1935, **152**, *A*, 354) includes the processes :

Initiation : $RH + X \longrightarrow R + XH$ . . . . (i)

where X is some hydrogen acceptor which may be an atom or a free radical.

Main reaction chain : $R + O_2 \longrightarrow RO_2^*$ . . . . (ii)

$RO_2^* + RH \longrightarrow RO{\cdot}OH + R$ . . . . . (iii)

(An asterisk against a radical stresses that an energy content significantly higher than the thermal average is important in the reaction.)

Arguments in support of this scheme frequently involve rather indirect experimental evidence. One difficulty in obtaining direct evidence is that initial reaction products readily undergo further oxidation and decomposition at the temperatures required to establish chain oxidation of the parent hydrocarbon. A suggestive comparison may be made with the oxidation of acetaldehyde. This readily occurs at least 80—90° below the temperature of oxidation of the hydrocarbon in similar mixtures. An oxidation mechanism corresponding to that for the hydrocarbon is generally accepted. It is interesting to consider how far the oxidation of the hydrocarbon is determined by the sluggishness of specific steps in the reaction chain.

In its broadest aspects this problem is reviewed elsewhere (Small and Ubbelohde, unpublished). The present paper is the outcome of attempts to " trigger " the initiation of reaction chains so as to facilitate step (i) above. A possible method might be to use photo-excited mercury atoms. At low pressures, direct collisions between excited mercury atoms and hydrocarbons lead to rupture of the C–H bonds with the initial production of alkyl radicals (for refs., see Steacie, " Atomic and Free Radical Reactions," Reinhold, 1946). These alkyl radicals should follow a reaction scheme as above. Another method might be to add hydrogen to a hydrocarbon + oxygen/nitrogen mixture so as to make use of hydrogen atoms produced by the reaction (Cario and Franck, *Z. Physik*, 1922, **11**, 161) $Hg^* + H_2 \longrightarrow 2H + Hg$ (for discussion on HgH formation, see Laidler, *J. Chem. Phys.*, 1942, **10**, 43; Steacie, *Ann. N.Y. Acad. Sci.*, 1941, **41**, 187). Hydrogen atoms (actually produced in a discharge tube, and not by mercury) are known to attack hydrocarbons at low pressures and liberate in the first instance alkyl radicals as in the reaction $RH + H \longrightarrow H_2 + R$ (Badin, *J. Amer. Chem. Soc.*, 1950, **72**, 1550).

Neither of these photochemical methods of " triggering " could be developed as planned. Blank experiments with hydrogen and with mercury (separately or together) added to the oxidation mixture showed unexpected inhibiting effects. These are of considerable interest for the elucidation of oxidation mechanisms and are discussed below. Analysis showed that the mercury was oxidised, but only during the co-oxidation of hydrocarbon molecules. This oxidation is attributed to labile oxygen carriers such as the RO_2 radical, which are destroyed by a process such as $RO_2 + Hg \longrightarrow HgO + RO$. The inhibiting effect of hydrogen, though definite, was less marked than in the oxidation of acetaldehyde at lower temperatures (Small and Ubbelohde, *J.*, 1950, 723—728). It is attributed to the efficiency of collisions with hydrogen for the dispersal of activation energy in labile chain carriers such as RO_2^*.

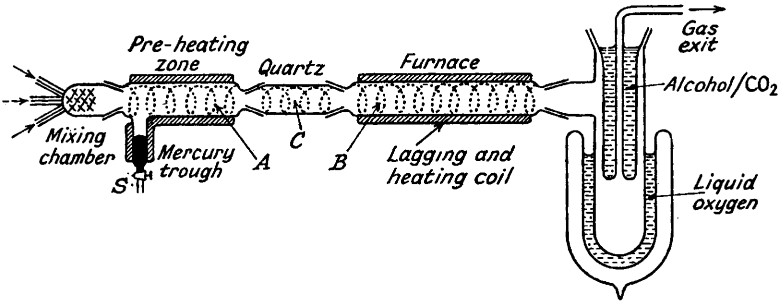
EXPERIMENTAL

Procedure.—Since the emphasis of the experiments was on the *initial* stages of oxidation, a flow method was used throughout. In essence, each unit volume of the gas mixtures used passes through the reaction chamber in a time determined by its length and cross-section, and the volume flow velocity. The temperature of the reaction chamber was thermostatically controlled. By analysing the products for various reaction temperatures, the temperature of onset of rapid oxidation could be obtained for any given mixture. The time of flow represents a " dynamic " induction period for the build-up of the oxidation chains at this temperature. These dynamic induction periods are easier to control than when " static " induction periods are measured, since the walls of the apparatus reach a stationary state.

Except in details given below, the general apparatus was as previously described (Small and Ubbelohde, *loc. cit.*).

To test the action of hydrogen, mixtures of hydrocarbon vapour with constant proportions of oxygen and diluent gases such as nitrogen or nitrogen + hydrogen were passed at constant rate through a Pyrex reaction vessel, scrupulously cleaned with hot nitrating acid and washed with distilled water before each test. Unchanged hydrocarbon and any reaction products were collected in cooled traps, or were scrubbed from the exit gases by bubblers containing distilled water. From measurements of the percentage of aldehydes, acids, and peroxides produced, the temperature for onset of rapid reaction was obtained under the conditions of the test.

FIG. 1.



In other inhibitory studies mercury was introduced by diffusion from a subsidiary vessel attached to the main reaction system and heated to various temperatures up to 50°. Mercury and any reaction products containing mercury were collected in the condensing traps and were analysed as described below.

Apparatus.—The main lines of experimental procedure may be summarised by reference to Fig. 1. Mercury was held in a side limb *S* at a carefully controlled temperature and vaporised into the gas flow. The quartz joining tube was used in other experiments not described here. It was found essential, particularly in the comparative experiments, to measure the temperature of the gases by means of a thermometer placed axially in the gas flow, since the furnace walls, though kept at constant temperature electrically, do not respond quickly to changes in a flow system.

Purification of Materials.—Commercial *n*-hexane was kept for at least 10 days over 20% oleum with occasional shaking. A black, viscous tar was formed from which the hydrocarbon was removed by decantation. The decanted hexane was repeatedly washed with concentrated aqueous sodium hydroxide and then gently refluxed with the same reagent. It was washed with water and dried (Na_2SO_4) for 24 hours. Fractional distillation under oxygen-free nitrogen in a 16″ column packed with porcelain rings gave a middle fraction, b. p. 67·5—68·5°. This was held in a carburettor kept in a thermostat at 41° to give a partial pressure of 280 mm.

Following methods discussed by Wichers (*Rev. Sci. Instr.*, 1942, **13**, 501), distilled mercury was placed in a large Buchner flask and covered with 2N-nitric acid containing a few drops of hydrogen peroxide. Filtered air was drawn through this mercury for several days, with periodic renewal of the oxidising mixture. Amalgams of base metals are reported to react readily under this treatment. The addition of hydrogen peroxide is to ensure the complete removal of sulphur compounds in view of their possible action as inhibitors. After this treatment the mercury was washed, dried, and stored until required.

Hydrogen, Air, and Nitrogen.—These gases, taken from cylinders, were normally used without purification. In a few special experiments they were passed separately through quartz tubes heated to 600° and then through liquid-air traps before use. This procedure was adopted to remove possible volatile impurities derived from the steel cylinders, but the results obtained showed no detectable difference from those in which cylinder gases were used directly. Rates of flow of these gases were determined by means of calibrated flow-meters.

Methods of analysis of peroxide, acids, and aldehydes were as previously described (*J.*, 1950, 723).

Results.—(a) *Progressive dilution of a reaction mixture with nitrogen.* By using apparatus similar to that described, but somewhat simpler methods for the collection of products, it was established that progressive dilution with nitrogen raised the temperature of onset of rapid oxidation as shown in Fig. 2.

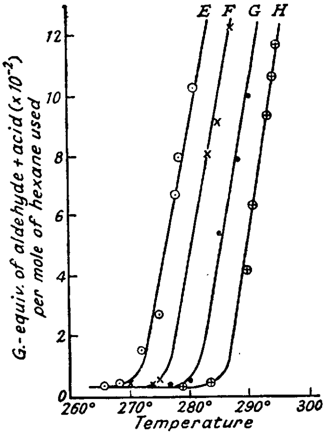


FIG. 2. *Variation of concentration of diluting nitrogen.*

Area of cross section of reactor = 11·9 sq. cm.
Length of reactor = 45 cm.

Flow rates, in g.-mols./sec. × 10^3.

Curve	C_6H_{14}	O_2	N_2
E	0·272	0·081	0·508
F	0·272	0·081	0·682
G	0·272	0·081	0·891
H	0·272	0·081	1·128

(b) *Comparison of the inhibitory effects of nitrogen and hydrogen.* In these experiments, the aim was to keep a constant reference mixture and to introduce the diluent gases in corresponding proportions so that the total flow rate was the same in both cases. The flow rates were as shown in Table 1. In Fig. 3, Curve *X* shows the oxidation characteristics for a convenient reference mixture. From Curves *Y* and *Z* it is evident that hydrogen has a more powerful inhibitory effect on the oxidation of *n*-hexane than has an equal amount of nitrogen, under the same experimental conditions. The temperature of onset of rapid oxidation is almost 10° higher in the presence of diluting hydrogen, and the whole reaction curve is displaced to higher temperatures.

TABLE 1. *Comparison of effects of nitrogen and hydrogen as diluents.* (Flow rates in mole/sec. × 10^3. Area of cross-section of tube = 14·4 sq. cm. Length of tube = 50 cm.)

Curve	C_6H_{14}	O_2	N_2	Diluent	Total flow rate	Temp. of steep rise
X	0·316	0·109	0·440	Absent	0·865	264°
Y	0·316	0·109	0·440	0·469 N_2	1·334	280
Z	0·316	0·109	0·440	0·469 H_2	1·334	289

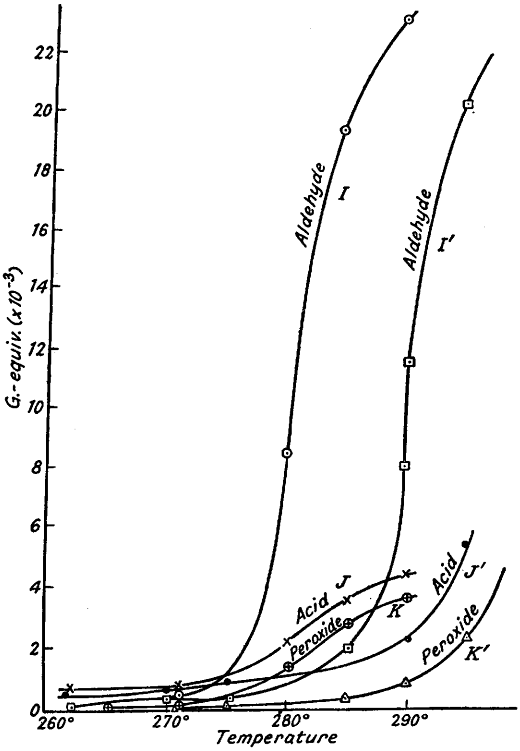
Fig. 4 shows the actual yields of oxidation products obtained in these experiments. With the reaction mixtures as in Table 1, mixture *Y* gave *I*, *J*, and *K* as plots of the aldehyde, acid, and peroxide content of the condensed material, and mixture *Z* gave *I'*, *J'*, and *K'*. The amount of each product is seen to be substantially reduced when hydrogen is present in the reaction mixture. It may be significant that the production of peroxides is almost completely suppressed.

(c) *Effects of changing the concentrations of hexane and oxygen in the reaction mixture.* The oxygen concentration could be altered by replacing some of the diluting nitrogen by oxygen. As in the experiments with hydrogen, the total diluent concentration was kept constant.

Table 2 shows the flow rates of the various components used in these experiments, and Fig. 5 plots the results obtained. Curve *L* shows the previously observed oxidation characteristics of a reference hexane–oxygen–nitrogen mixture, additional nitrogen being used as the inert diluent. The curve rises steeply at 275°, in good agreement with earlier observations on the same reaction mixture. When some of the diluting nitrogen is replaced by oxygen, all other conditions remaining constant, this curve becomes modified to *M*. Rather unexpectedly, compared with the same amount of diluent nitrogen, the added oxygen appears to exercise an inhibiting effect on the *initial* stages of the reaction. Rapid oxidation does not set in until a temperature of 284° is attained, whereas with diluent nitrogen the same reaction started at 275°. In these experiments with an oxygen-rich mixture, temperature control during the progress of a run was more difficult than in previous cases. Once oxidation started, a sharp temperature rise was noted in the mixture, dense white fumes were emitted from the exit tube, and on one occasion a mild thermal explosion occurred at approx. 295°. The overall results

FIG. 3. *Comparison between effects of nitrogen and hydrogen.*

FIG. 4. *Effect of replacing some nitrogen by hydrogen on the initial oxidation of hexane.*



I, J, K. $C_6H_{14} : O_2 : N_2 = 2{\cdot}9 : 1 : 8{\cdot}3$.
I′, J′, K′. $C_6H_{14} : O_2 : N_2 : H_2 = 2{\cdot}9 : 1 : 4{\cdot}0 : 4{\cdot}3$.

TABLE 2. *Variation of oxygen concentration.* (Flow rates in mole/sec. × 10^3.)

				Diluent		
Curve	C_6H_{14}	O_2	N_2	N_2	O_2	Total flow rate
L	0·272	0·081	0·325	0·357	—	1·035
M	0·272	0·081	0·325	0·183	0·175	1·035

seem to involve the action of molecular oxygen as a chain breaker in some initial reaction step. However, once a sufficient concentration of chain carriers has been built up, oxidation takes place at a greater rate than is ever attained in the absence of diluent oxygen. No explanation of this effect is attempted here.

Experimentally the amount of hydrocarbon entering the combustion chamber could be varied by changing the temperature of the thermostatted carburettor. Fig. 6 shows that in the temperature and concentration range studied any variation of the hydrocarbon concentration produces little observable effect on the temperature for onset of rapid oxidation. Table 3 shows the flow rates for two different hydrocarbon mixtures. The decreased hydrocarbon in mixture (*b*) slightly decreases the total flow rate. This may compensate slightly for a decrease in oxidation rate, but the net effect of the change is outside the limits of experimental error. All points lie substantially on the same curve. Hence, in these experiments the hydrocarbon concentration does not appear to have a critical influence on the temperature required for the onset of rapid oxidation.

(d) *The inhibitory action of mercury vapour.* In these studies the apparatus used permitted analysis of peroxide, aldehyde, and acid content of the condensed material.

FIG. 5. FIG. 6.

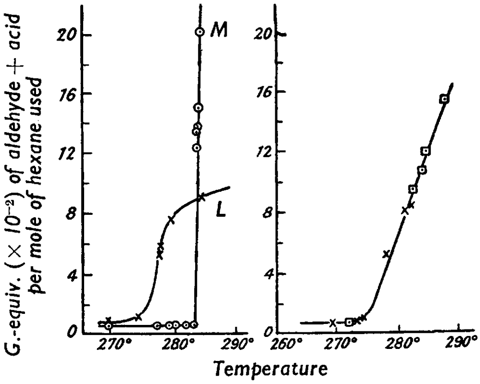


FIG. 5. *Effect of replacing some nitrogen by oxygen in the initial oxidation of hexane.*

FIG. 6. *Effect of variation of hydrocarbon concentration on initial oxidation of hexane.*

The reaction mixture consisted of hexane + oxygen + nitrogen in a fixed ratio. Either nitrogen or hydrogen was added in equal proportions and the effect of mercury vapour was investigated. Table 4 shows the flow rates in these experiments. Mercury inhibited the reaction chains in both systems. The overall effect is illustrated in Fig. 7, where the total yield of peroxide, aldehyde, and acid is plotted against the reaction temperature. Table 4 indicates the substantial reduction in each of the reaction products when mercury vapour is present in the reaction system at furnace temperatures close to 285°. In these experiments it was also established that the inhibition was not sensitive to the exact concentration of mercury introduced into the reacting mixture. For brevity, only variations of the mercury concentration in a system containing diluting hydrogen will be reported here.

TABLE 3. *Variation of hexane concentration.* (Flow rates in mole/sec. × 10³.)

	C_6H_{14}	O_2	N_2	Diluent N_2	Total flow rate
a	0·272	0·081	0·325	0·357	1·039
b	0·144	0·081	0·325	0·357	0·907

TABLE 4.

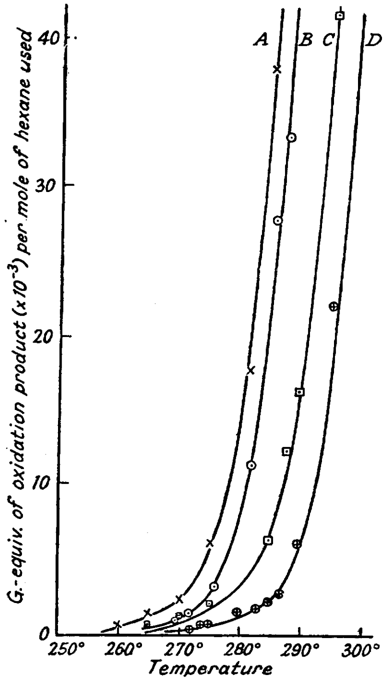
	Reaction mixture, mole/sec. × 10³ (C_6H_{14} 0·316, N_2 0·44, O_2 0·109)				Reaction products, g.-equiv. × 10³			
	Furnace temp.	Diluent	Hg	Total flow rate	Peroxide	Aldehyde	Acid	Total product
a	285°	0·469 N_2	—	1·334	2·813	19·1	3·5	25·41
b *	286	0·469 N_2	+	1·328	0·818	14·8	3·09	18·71
c	287	0·469 H_2	—	1·328	1·023	5·98	1·7	8·70
d *	285	0·469 H_2	+	1·338	0·12	0·373	0·936	1·43

* The mercury trough was held at 30° in (*b*) and (*d*).

The mercury trough *S* was held at various temperatures. The results shown graphically in Fig. 8 for varying concentrations of mercury all fall substantially on the same curve *E*. Curve *C* plots the oxidation characteristics for the uninhibited reaction.

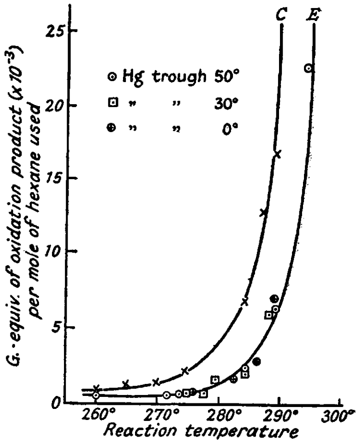
Table 5 records detailed analytical data at 285°, *i.e.*, near the bend of Curve *E*, or just before the onset of rapid oxidation, in the presence of mercury. At this critical part of the reaction curve minor temperature changes during the progress of a run have an appreciable influence on the quantity of oxidation products formed. This probably explains the slight differences in the yields of products *b*, *c*, and *d* in Table 5. However, this variation is imperceptible when the points are plotted in Curve *E*.

FIG. 7. *Effect of mercury vapour on oxidation of* n-*hexane.*



A, Standard mixture.
B, Standard mixture with mercury.
C, Mixture with some hydrogen.
D, Mixture with mercury.

FIG. 8. *Variation of mercury concentration.*



Examination of condensate for compounds of mercury. A detailed examination of the condensed reaction products was carried out in an attempt to determine the rôle played by the mercury. In particular, it was considered to be of prime importance to establish whether the formation of any organo-mercury compounds could account for the observed inhibitions, by a radical-removing reaction such as $Hg + R \longrightarrow HgR$. Large-scale runs were carried out, and reaction products were collected in a trap of about 500-c.c. capacity chilled in carbon dioxide–alcohol. The condensate normally separated into hydrocarbon and aqueous layers together with a sludge containing finely divided mercury. Repeated filtration through sintered-glass crucibles removed all traces of the grey sludge containing mercury, and the hydrocarbon and the aqueous layer were obtained as clear colourless solutions.

TABLE 5 (*units as for Table* 4).

	Furnace temp.	Temp. of Hg bath	Peroxide	Aldehyde	Acid	Total product
a	287°	(absent)	1·023	5·98	1·7	8·703
b	285	30°	0·12	0·373	0·936	1·429
c	285	50	0·05	0·483	0·65	1·184
d	284	0	—	0·516	0·27	0·786

The hydrocarbon layer was washed with water to remove all water-soluble compounds and was then dried and carefully fractionated, distillation being carried up to 69·5°. A little low-boiling material and a considerable quantity of unchanged hexane were collected. The undistilled residues of fractionation were concentrated in this process by a factor of about 200. To test for the possible presence of mercury alkyls of low volatility, the fractionation residues were decomposed by warming with concentrated nitric acid. On dilution of the resulting acid solution, spot tests with diphenylcarbazide and *p*-dimethylaminobenzylidenerhodanine gave negative tests for mercury, and it was therefore concluded that the observed inhibition could not be explained by mercury compounds in the hydrocarbon layer. On the other hand, the clear aqueous layer gave strong spot tests with the above reagents. Hence, mercury compounds formed in the oxidation are predominantly confined to the aqueous layer. Benzene, chloroform, and ether were tried in turn as extracting agents for mercury compounds in the freshly formed aqueous material. Tests with Schiff's reagent showed that a small amount of aldehyde was removed in these extractions, but spot tests failed to show traces of mercury compounds in any of these solvents. Thus reaction products containing mercury remained strongly held in the aqueous solution.

Gentle heating of the aqueous solution under reduced pressure at 16 mm. removed traces of the organic substances referred to above and left a solution with the following properties: (i) The purple colour with Schiff's reagent developed after a short delay. It was equally strong in the presence of an equal volume of 10% sulphuric acid, showing the residual aldehyde to be formaldehyde (see Egerton, Smith, and Ubbelohde, *Phil. Trans.*, 1935, **234**, 433). (ii) The aqueous solution liberated iodine from acidified potassium iodide. The yellow coloration was equally positive after the solution had been boiled and suggests that the peroxide present is stable, and is probably hydrogen peroxide. (iii) Strong tests for mercury were obtained with the above spot-test reagents. When the clear solution was boiled a grey deposit of mercury was obtained. (iv) *The solution had acidic properties.* Hence, this mercury compound which is so strongly held in the aqueous layer has properties consistent with those of mercury formate. Test solutions made up by dissolving either mercuric or mercurous oxide in dilute formic acid gave practically identical reactions.

The most plausible explanation for the formation of mercury formate is that the oxide present in the condensed material reacts with formic acid produced in the oxidation and is then retained in the aqueous layer as the formate. The decomposition of the solution on boiling can be represented by the equations:

$$2Hg(H{\cdot}CO_2)_2 \longrightarrow Hg_2(H{\cdot}CO_2)_2 + CO_2 + H{\cdot}CO_2H$$

$$Hg_2(H{\cdot}CO_2)_2 \longrightarrow 2Hg + H{\cdot}CO_2H + CO_2$$

The possibility is not excluded, however, that the formaldehyde reduces a soluble salt of mercury, such as the acetate, on heating.

In another experiment freshly formed sludge from a typical run was extracted with aqueous formic acid and filtered. The clear solution obtained gave even stronger spot tests for mercury. It was decomposed by boiling or on storage for several days and produced a grey mercury deposit. This indicates that only some of the oxides of mercury formed when hydrocarbon is passed through the reaction tube in the presence of mercury become dissolved. Apparently insufficient acid is produced in the oxidation to dissolve all the oxide and therefore much of it remains in the mercury sludge. The experiments were repeated in the absence of hexane, all other conditions remaining as before. After the run had been in progress for an hour the condensed material consisted of distinct globules of metallic mercury. This was extracted as before with aqueous formic acid but the clear filtered solution gave only the faintest of spot tests for mercury with the reagents mentioned above.

The important conclusion therefore is that no appreciable oxidation of the mercury takes place when hydrocarbon is absent from the reaction mixture.

DISCUSSION

All the observations in this paper refer to the *initial* build-up of reaction chains in the oxidation of hydrocarbons, *i.e.*, to the transition from the "induction period" to the onset of rapid oxidation. This may explain why the various concentration effects observed differ from those found in static reaction systems.

In a typical example, for the mixture F in Fig. 2 the total volume of gas flowing = 29·78 c.c./sec.; cross-sectional area of tube = 11·9 sq. cm.; linear flow rate =

29·78/11·9 cm./sec.; length of tube = 45 cm. Therefore, each c.c. of gas remains 45 × 11·9/29·78 = 17·9 sec. in the tube at the temperature of the reaction. Hence, at the temperature of onset of rapid oxidation the " dynamic " induction period is 17·9 sec.

One difference between static and dynamic induction periods is that in a flow system a steady state is set up and that chains from one cross-section in the flow system can diffuse into neighbouring cross-sections.

According to the theory of degenerate chain reactions (Lewis and von Elbe, " Combustion, Flames and Explosions of Gases," Acad. Press, N.Y., 1951) the duration of the induction period τ_1 in seconds is given by

$$\tau_1 = 8{\cdot}1 \times 10^{-12} \times p^{-0{\cdot}66} \times e^{15{,}000/T} \text{ (for } n\text{-heptane)}$$

$$\phi = 8{\cdot}1 \times 10^{-12}$$

where ϕ is the branching parameter for the multiplying of reaction chains. In systems showing two-stage ignition, τ_1 is defined as the time between the beginning of the reaction and the appearance of a cool flame; p is the pressure (in atm.) and T is the absolute temperature. The inhibiting effects due to mercury and to hydrogen refer to this chain-branching process. There is reason to believe that the same step in the reaction chain is being affected in both cases, though by different mechanisms.

Mercury. Here the inhibitory action might in principle be chemical, in processes such as

$$R + Hg \longrightarrow HgR \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iv)}$$

or $$RO_2 + Hg \longrightarrow HgO + \text{decomposition products} \quad . \; . \; . \quad \text{(v)}$$

or it might involve merely an energy-transfer deactivation due to collision with mercury.

The lowest excited energy state of the mercury atom is obtained on irradiation with the 7371·7 Å line and lies approx. 38 kcal. above the ground state. As is discussed more fully elsewhere (Small and Ubbelohde, unpublished) only reaction (ii) above, which may be written $R + O_2 \longrightarrow RO_2^*$ to denote the formation of an energy-rich radical, could be sufficiently exothermic to be capable of leading to excitation on collision with mercury atoms. However, in view of the evidence for chemical attack on the mercury, the possibility of deactivation merely by energy transfer to the mercury from a labile radical is an unnecessary hypothesis and is provisionally discarded.

In spite of careful search no evidence could be found for any attack on the mercury by R radicals to form mercury alkyls. Such alkyls are fairly well known (Rice and Polly, *Ind. Eng. Chem.*, 1935, **27**, 915; Frey and Hepp, *J. Amer. Chem. Soc.*, 1933, **55**, 3358) and from their properties it would be expected that, if appreciable concentrations accumulate in the reaction system, they would have been detected in the collectors. Though the present evidence does not exclude the possibility that temporary association occurs in the gas phase between the mercury atoms and the R radicals, this possibility must be left for further proof. Temporary association would not necessarily seriously affect the oxidation, since mercury alkyls probably decompose to give free alkyl radicals in the first instance.

The quite extensive oxidation of the mercury observed when hydrocarbons are being co-oxidised gives strong support that inhibition occurs by some process such as (v) above.

It has not yet proved possible to investigate the rôle of mercury on other oxidations such as that of acetaldehyde. In contrast with the present findings at the temperature for onset of rapid oxidation, mercury is indifferent as an antiknock (Egerton and Gates, *J. Inst. Pet. Tech.*, 1927, **13**, 244). It may be that in a system undergoing active oxidation, such as the gases ahead of a flame front in the region of " knock," the higher temperatures and pressures suppress any specific effect due to mercury atoms.

Hydrogen. The effect due to molecular hydrogen parallels that previously observed in the oxidation of acetaldehyde (Small and Ubbelohde, *J.*, 1950, 723). No simple chemical explanation can be suggested. From energy considerations a reaction such as

$$H_2 + RO_2^* \longrightarrow RO{\cdot}OH + H \quad . \; . \; . \; . \; . \; . \; . \quad (a)$$

would be not more likely to occur than

$$RH + RO_2^* \longrightarrow RO{\cdot}OH + R \quad . \; . \; . \; . \; . \; . \; . \quad (b)$$

Even if reaction (*a*) did occur, the hydrogen atoms produced should, on the basis of present knowledge, be able to continue the oxidation chain by producing fresh alkyl radicals (Badin, *loc. cit.*).

When possible physical explanations are examined, the first point to consider is how far the diffusion of an active radical such as R or RO_2 through the diluent mixture is likely to be affected by the change from $C_6H_{14} + N_2 + O_2$ to $C_6H_{14} + N_2 + H_2 + O_2$. If by any process a radical R is produced, after a lapse of time t it will be found in a " reaction shell " of radius r where $r^2 = 6Dt$ (cf. Ubbelohde, *Nature*, 1933, **131**, 328). The effect of introducing hydrogen can be qualitatively inferred from a comparison of the diffusion coefficients D of the hexyl radical in pure nitrogen and pure hydrogen severally as extreme cases. More accurate calculations are not warranted owing to the complexity of diffusion in mixed gases. For the binary diffusion coefficients D_{12}

$$D_{12} = (\bar{c}_1^2 + \bar{c}_2^2)^{\frac{1}{2}}/[3\pi(N_1 + N_2)\sigma_{12}^2]$$

where $\bar{c}_1$ and $\bar{c}_2$ are the root-mean-square velocities, N_1 and N_2 the number of molecules/c.c., and σ_{12} the sum of the collision radii (cf. Partington, " An Advanced Treatise on Physical Chemistry," Longmans, 1949). Then

$$\frac{D_{12}\text{ (hexyl/nitrogen)}}{D_{12}\text{ (hexyl/hydrogen)}} = \frac{(\frac{1}{85} + \frac{1}{28})^{\frac{1}{2}}}{(\sqrt{3{\cdot}2} + \sqrt{5{\cdot}18})^2} \times \frac{(\sqrt{2{\cdot}4} + \sqrt{5{\cdot}18})^2}{(\frac{1}{2} + \frac{1}{85})^{\frac{1}{2}}} = 0{\cdot}270$$

[Collision diameters for nitrogen and hydrogen are taken from Schuil (*Phil. Mag.*, 1939, **28**, 683), and those for *n*-hexyl are assumed equal to those for *n*-hexane (Cummings, McCoubrey, and Ubbelohde, *J.*, 1952, 2725).]

It is evident that hydrogen increases the size of the reaction cell appreciably. This might affect diffusion to the walls, though the difference is hardly large enough to explain the effects observed in the mixtures actually used.

Another way of expressing the influence of hydrogen is to compare, as extreme cases, the number of collisions between similar mixtures of hexane with hydrogen and nitrogen severally :

$$\frac{\text{Number of collisions, hexane–nitrogen}}{\text{Number of collisions, hexane–hydrogen}} = \frac{(\sqrt{3{\cdot}2} + \sqrt{5{\cdot}18})^2}{(\sqrt{2{\cdot}4} + \sqrt{5{\cdot}18})^2} \times \frac{(\frac{1}{85} + \frac{1}{28})^{\frac{1}{2}}}{(\frac{1}{2} + \frac{1}{28})^{\frac{1}{2}}} = 0{\cdot}344$$

Obviously, in the presence of hydrogen the number of collisions with non-reacting species increases. The opportunity for disposal of activation energy stored in a radical such as RO_2^* must be increased by this fact.

A suggestive physical rôle of hydrogen could be its deactivating influence on an energy-rich chain carrier. When the various steps above are examined for heat balance, it seems likely that considerable energy is liberated in step (ii), whereas step (iii) proceeds with the absorption of energy. Exact values are difficult to establish owing to gaps in our knowledge of bond energies, but approximate estimates are discussed elsewhere (Small and Ubbelohde, unpublished). As has been previously pointed out (Ubbelohde, *loc. cit.*, p. 372), the intervention of an energy-rich chain carrier could explain certain features of the low-temperature oxidation of hydrocarbons such as the negative temperature coefficient. The new finding that hydrogen acts as an inhibitor lends support to this suggestion. In studies of the transition from pseudo-unimolecular to bimolecular thermal decomposition of complex molecules, collisions with hydrogen have been found (Hinshelwood, *Proc. Roy. Soc.*, 1927, *A*, **114**, 94; *A*, **115**, 223) much more effective than collisions with other atoms and molecules such as He, N_2, CO, CO_2, CH_4, for the activating collision

$$\text{Deactivated complex molecule} + H_2 \longrightarrow \text{Complex molecule}^* + H_2$$

The effectiveness of collisions with hydrogen is also established for the activation of ethylene vibrations (Richards and Reid, *J. Chem. Phys.*, 1934, **2**, 206). Application of the statistical principle of " detailed balancing " shows that hydrogen must also be much more effective than the other molecules in the reverse collision process.

Our suggestion is that this explains the inhibiting effect of hydrogen in the early stages of hydrocarbon oxidation. Some form of energy-rich RO_2^* radical is produced in step (ii), and if this loses its energy of activation before completing step (iii) the reaction chain may be partly or wholly broken unless the RO_2 survives till it again becomes activated. A comparatively long survival time of deactivated RO_2 would explain why inhibition of the oxidation chains by mercury is not sensitive to the amount of mercury.

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[*Received, May* 30*th*, 1952.]