CCCCXIV.—*Ionisation and Chemical Change during Slow Combustion.*

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DURING the period of slow combustion, important changes occur in a gas mixture rendering it sensitive to inflammation. Bone, Fraser, and Witt have recently demonstrated (*Proc. Roy. Soc.*, 1927, *A*, **114**, 442) that with mixtures of methane and oxygen when an electric spark is passed there is a definite lag or induction period before main combustion occurs. Ionisation has sometimes been detected during the slow combustion of a hydrocarbon, alcohol, etc., in air, and is associated with the formation of a fine mist (Bennett, *Trans. Faraday Soc.*, 1927, **23**, 295).

It has been found that a system containing liquid droplets is more ionised and more sensitive to ignition than the corresponding vapour mixture. Many different mixtures of *n*-hexane and air have been passed through a horizontal glass tube, heated in an electric furnace to 675°, without ignition occurring, but if the tube was tilted or held vertically, a fine mist passed back against the stream and then ignition often occurred as low as 550°. When hexane was sprayed down the tube ignition occurred at 570°. A similar behaviour was observed with a number of substances, as shown in Table I. The apparatus employed was the same as described by Callendar (*Engineering*, 1927, **123**, 147) and Bennett (*loc. cit.*); and the spontaneous ignition temperature given is the minimum observed on varying the mixture strength. The rate of flow through the tubes was the same for both spray and vapour.

TABLE I.

Spontaneous ignition temperatures of vapour or spray of some liquids in air; heated-tube method.

Substance.	Spray.	Vapour.
m-Xylene	610°	710°
n-Butyl alcohol	635	725
Undecane (b. p. 198—208°)	506	550
Benzyl alcohol	546	571
Amyl ether	516	591
Cymene (b. p. 174—176°)	571	606

The minimum ignition temperature obtained with a falling temperature was often much lower than with a rising temperature. Thus, with a mixture of acetylene and air a sharp explosion first occurred at 340° with a rising temperature, but on lowering the temperature the mixture continued to catch fire at intervals even below 300° without violence, indicating that something remained in the tube from the previous combustion which rendered the fresh gas mixture sensitive to ignition.

Chemical changes occur below the ignition temperature, and these were usually more marked and occurred at lower temperatures with the liquid drops present than with the vapours alone. Thus with cymene at 370° the aldehyde and peroxide tests were given by the liquid drops but not by the vapour; lime-water was turned milky at 425° by the products from the spray, but it was necessary to raise the temperature to 440° in the case of the vapour before the presence of carbon dioxide could be definitely demonstrated. Table II gives some results obtained with a spray in quartz tubes with light from the mercury-vapour lamp. The electrical conductivity was measured in the manner described by Bennett (*loc. cit.*).

TABLE II.

Chemical and ionisation changes during the slow combustion of (*a*) cymene; (*b*) amyl ether; (*c*) undecane.

	Temp.	Observations.
(*a*)	275°	Aldehyde and peroxide tests given.
	300	Fog formed; slight ionisation.
	400	Dense, white fog, with pronounced ionisation; carbon dioxide present.
(*b*)	120	Aldehyde and peroxide tests given.
	300	Slight ionisation; white fog formed.
(*c*)	150	Aldehyde and peroxide tests given.
	275	Slight ionisation; white fog formed.
	450	Pronounced ionisation; dense white fog and nearly complete combustion of undecane to aldehydes, acids, CO_2, etc.

Although the high degree of ionisation is regarded as an accompaniment of, rather than as the direct cause of, detonation in the internal-combustion engine (Symposium on Gaseous Reactions, *Trans. Faraday Soc.*, October, 1926), yet the important rôle that can be played by electron emission follows from Callendar's nuclear-drop theory, the electron being capable of acting as a nucleus (Aeronautical Research Committee, R. and M. 1013, H.M.S.O.).

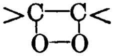
The coincidence of mist formation and ionisation during the slow combustion of a large number of substances raised the question as to whether ionisation was due to the development of surface (compare Simpson, *Phil. Trans.*, 1909, *A*, **209**, 379) or whether it was the result of chemical change, and this matter is under investigation.

Although it is not certain whether all gaseous reactions are accompanied by ionisation (compare Trautz and Henglein, *Z. anorg. Chem.*, 1920, **110**, 257), the results shown in Table III indicate that at higher temperatures slight ionisation occurs with some mixtures. Moreover, Brewer (*Proc. Nat. Acad. Sci.*, 1926, **12**, 560) has observed ionisation during the catalytic oxidation of a number of organic substances, *e.g.*, xylene, acetone, etc.

TABLE III.

Mixture with air.	Composition (% by vol.).	Temp. of initial combustion.	Temp. when slight ionisation first observed.
Carbon monoxide	48·5	465°	500°
,, ,,	9·0	460	460
Carbon monoxide and hydrogen	22% CO 11% H_2	430	430
Hexane	5	350	650
Ethyl ether	10	173	400

In no case was ionisation observed below the temperature of initial oxidation, *i.e.*, when aldehydes were first detected, and usually only slight ionisation was observed at higher temperatures even when oxidation was extensive. This delay might appear to throw some light on the mechanism of chemical reaction during the combustion of hydrocarbons. The scission of the oxygen molecule into atoms would probably result in profuse liberation of electrons so that hypotheses of oxidation and combustion at moderate temperatures which involve this atomic separation (*e.g.*, the hydroxylation theory) are not so convincing as those in which the oxygen molecule is regarded as being incorporated as a whole, *i.e.*, when O = O becomes — O — O — in the formation of peroxides from hydrocarbons :

$R{\cdot}CH_3 + O_2 \rightarrow R{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}H$; $>C{:}C< + O_2 =$  $\underset{O-O}{>C-C<}$.

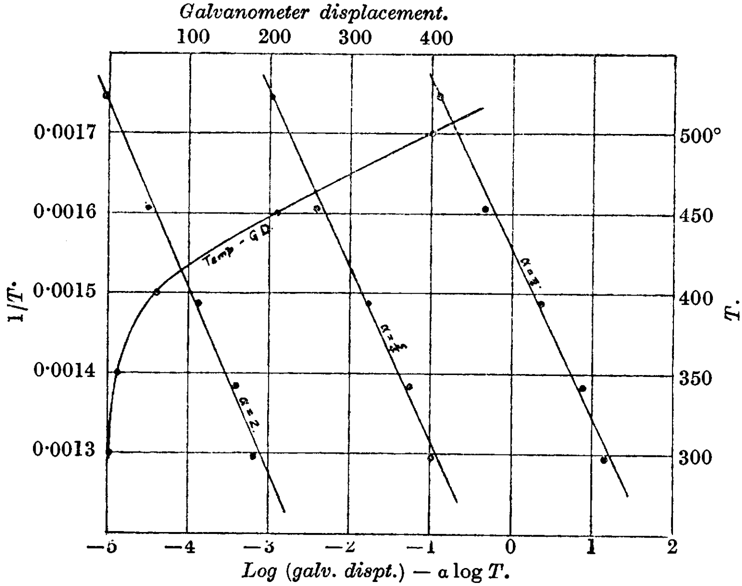
The formula $i = \theta T^{\alpha} e^{-\phi/T}$ (where $\alpha = \frac{1}{2}, \frac{5}{4}$, or 2 ; i = current ; T = temperature ; and θ and ϕ are constants) satisfies cases of thermionic emission, ionisation in flames, and ionisation in liquid drops–air systems during slow combustion, since in each case, within the limits of experimental error, all points plotted with axes ($\log i - \alpha \log T$) and $1/T$ fall on straight lines (Bennett, *loc. cit.*).

The rate of chemical action, dc/dt, is expressed by the above equation if $\alpha = \frac{1}{2}$ and $i = dc/dt$. Richardson concluded that since ϕ in the case of chemical action differs from that in the case of thermionic emission the emission cannot be due to chemical action, but Brewer (*loc. cit.*) has now accounted for this difference.

In the light of these conclusions it seems probable that the processes occurring at the beginning of and during combustion are (*a*) a thermionic emission and (*b*) the formation of centres of chemical change from ions as soon as they are liberated (compare Lind and Bardwell, *J. Amer. Chem. Soc.*, 1926, **48**, 2335).

FIG. 1.

Undecane (liquid drops) + air.



Action of Iron Carbonyl, Lead Tetraethyl, Aniline, etc., on Slow Combustion and Ionisation.

The presence of iron carbonyl, lead tetraethyl, etc., even in small quantities exerts a great influence on slow combustion, delaying spontaneous inflammation and altering the temperature at which appreciable combustion begins. Some results are given in Tables IV and V.

TABLE IV.

The influence of lead tetraethyl and iron carbonyl on spontaneous ignition temperature.

Substance, spray in air.	Spontaneous ignition temp.
m-Xylene	610°
,, plus 0·3% (vol.) lead tetraethyl	650
,, ,, 0·5% (vol.) lead tetraethyl	688
,, ,, 1·0% (vol.) iron carbonyl	700
n-Butyl alcohol	635
,, ,, plus 1% (vol.) lead tetraethyl	687

TABLE V.

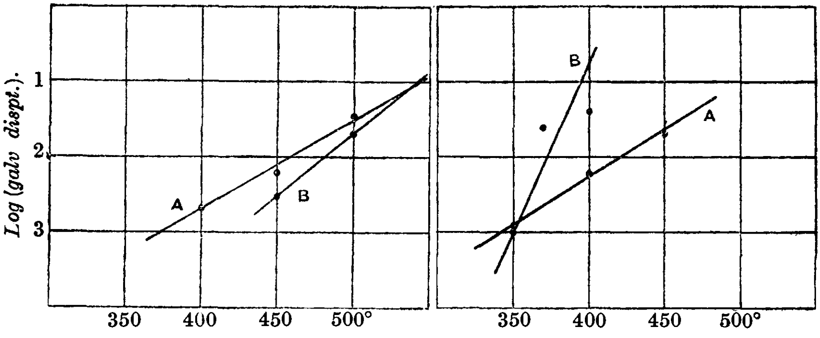
The influence of iron carbonyl, lead tetraethyl, etc., on chemical change and ionisation during slow combustion.

Substance.	Temp. of initial combustion.*	Ionisation.
Undecane, spray in air	200°	Very slight at 275°.
,, plus 0·2% iron carbonyl	238	Not detected until 330°.
,, ,, 0·5% lead tetraethyl	305	Less than with undecane alone, below 350°.
,, ,, 20% *m*-toluidine	248	The same as with undecane.
,, ,, 20% *m*-xylidine	275	,, ,, ,,
,, ,, 20% *m*-cresol	310	Not detected until nearly 400°.
,, ,, 20% carbon disulphide	230	,, ,, ,,

* *I.e.*, as measured by the appearance of aldehydes.

The action of iron carbonyl, lead tetraethyl, and other " anti-knockers " appears to be the inhibition of peroxide formation during the period of slow combustion (Callendar, *loc. cit.*), and although below a temperature of about 400°, iron carbonyl and lead tetraethyl reduce the rate of chemical change, yet at higher temperatures there is a higher yield of water and carbon dioxide. This is shown in Table VI.

FIG. 2.



A *Hexane vapour.*
B ,, ,, + *iron carbonyl.*

A *Undecane : liquid drops.*
B ,, ,, ,, + *iron carbonyl.*

It will be seen from Fig. 2 that the ionisation curves for a very rich mixture of hexane and a spray of undecane containing iron carbonyl cross those for the " undoped " fuel, indicating that the initial decrease in chemical change is accompanied by a decrease in electron emission, whilst increased ionisation at higher temperature results from increased combustion, probably at the surface of the metal particles produced by the thermal decomposition of the metallic compounds.

TABLE VI.

The influence of lead tetraethyl on the quantity of carbon dioxide in the oxidation products of *n*-hexane at different temperatures.

	% CO_2 in oxidation products,	
Temp.	without lead tetraethyl.	with about 0·25% lead tetraethyl.
265°	Trace	Nil
300	2·1	Trace
400	1·9	3·3

Experiments with hydrogen, and with hydrogen–air, hexane–air, coal-gas–air, and acetylene–air mixtures, with and without puffs of iron carbonyl, lead tetraethyl, and nickel carbonyl, were made at temperatures up to 600°, and usually the addition of the organo-metallic compound was found not appreciably to increase ionisation. By a special device, only a trace of iron carbonyl, etc., was allowed to enter the stream of gases, and then only for a few seconds while the reading was being taken. With carbon monoxide–air mixtures there was a rapid movement on the galvanometer scale as the "doped" gas mixture passed across the electrodes, followed by a return to the normal reading after the puff had passed. The fouling of the electrodes and tube caused much difficulty in measuring the ionisation, and they had frequently to be thoroughly cleaned during the experiments.

The mixture (67% CO + 33% H_2)–air gave very striking results. As a puff rich in iron carbonyl was passed through the combustion tube at 500° along with the mixture, the current passing between the electrodes increased approximately 2000-fold. The actual readings were :

Temp.	Galvanometer displacement (mm.).	Remarks.
430°	3	Without $Fe(CO)_5$.
500	25	,, ,,
500	450 (with shunt, 100)	With $Fe(CO)_5$.
500	35	After passage of puff.

It will be noticed that (1) after the puff had passed through the tube the conductivity decreased to its former order of magnitude, (2) there was a slight persistence of increased conductivity, (3) the galvanometer reading did not increase suddenly, but at first it moved gradually and then rapidly accelerated till, when the spot had reached the end of the scale, its velocity was very great. The state of ionisation tends to remain unchanged.

Some typical results with the less effective mixtures are given in Table VII.

A mixture of air and iron carbonyl was passed through the combustion tube and did not cause any movement of the galvanometer.

TABLE VII.

Mixture.	Strength of mixture.	Temp.	Galvanometer displacement (mm.).	Remarks.
CO plus air	Weak	520°	0	—
,, ,, ...	,,	600	2	—
,, ,, ...	,,	550	2	With lead tetraethyl.
,, ,, ...	,,	600	7	,, ,, ,,
Hydrogen–air ...	Rich	(335—650)	0	—
Iron carbonyl ...	,,	,,	0	—
Hydrogen plus air	50%	(525—600)	0	—
,, ,,	,,	,,	2	With lead tetraethyl.
,, ,,	,,	,,	5	With iron carbonyl.
,, ,,	10%	(450—570)	40	With lead tetraethyl.
Coal-gas–air	50%	610	10	—
,, ,, ...	,,	,,	20	With iron carbonyl.
Acetylene–air ...	Weak	(150—470)	0	—
,, ,, ...	,,	470	1	With nickel carbonyl. On addition of iron carbonyl, temp. of electrodes rose suddenly to 800° and mixture exploded.
,, ,, ...	,,	500	—	

The addition of a puff of the hydrogen–carbon monoxide mixture increased the conductivity to a high degree, as described before. The temperature was not increased by the puff and it must therefore be concluded that the ionisation was due to chemical change.

The characteristic action of lead tetraethyl and iron pentacarbonyl on the slow combustion of the gases mentioned was to delay spontaneous ignition and to lower the temperature at which slow combustion began by 50—100°. However, at 600° the amount of oxidation of carbon monoxide was not appreciably affected by the presence of small amounts of these substances.

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