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Modern Views on Combustion.

THE study of the combustion of gaseous mixtures and vapours of fuels in air has recently received considerable attention from physicists, chemists, and engineers, with special regard to the subject of detonation or knocking in the internal combustion engine. Two years ago, an important discussion on the subject of gaseous explosions, under the chairmanship of Prof. H. B. Dixon, was held in London under the auspices of the Faraday Society, when several valuable papers were read by eminent workers in this branch of science. Since that time, however, discoveries have been reported which throw new light on the mechanism of combustion and on the function of traces of water, lead tetra-ethyl, etc., on ignitibility.

Hexane burns in air or oxygen with the formation of carbon dioxide and water in accordance with the chemical equation

$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$ + heat of reaction;

but little was known of the mechanism whereby the atoms are rearranged to form new molecules. The isolation of aldehydes from the products of combustion of hydrocarbons led Profs. Armstrong and Bone to the well-known hydroxylation theory of the combustion of hydrocarbons, by which the oxygen atoms are assumed to become interposed between the carbon and hydrogen, forming dihydroxyl compounds which lose water and form aldehydes.

Recently, new ideas have been advanced with regard to the intermediate and initial steps of combustion, and these arose from extensive investigations on the cause of detonation. Thus, in papers by Prof. H. L. Callendar and the staff of the Air Ministry Laboratory, Imperial College of Science, evidence was given that the first step in the combustion of gaseous systems was the development of nuclei, either of ionised molecular aggregates or of small liquid particles condensed in the engine cylinder charge during adiabatic compression. These nuclei sensitise the gas mixture to self-ignition on heating by acting as centres of oxidation. The significance of ionisation on gaseous reactions has been shown by the interesting results of Prof. Bone and his co-workers, obtained during researches on the influence of the energy of the electric spark on ignitibility of dried gaseous systems. Still more recently, the work of Finch and Hodges, of the Imperial College of Science, has also shown that whereas moisture may accelerate combustion of carbon monoxide in a region of comparatively weak ionisation, it has little or no influence in a region of sufficiently intense ionisation.

The inhibitory action of traces of lead tetraethyl, iron carbonyl, thallium vapour, etc., is better understood by the explanation involving the provision of nuclei which are rendered innocuous by the attachment of molecules of the inhibiting substances. It is interesting in this connexion to recall the similar conclusions of Prof. Dixon and Lord Rayleigh with regard to the inhibition of phosphorescence by traces of ethylene and other organic vapours.

On the chemical side, Prof. Callendar and his co-workers concluded that the nuclear particles became centres of peroxidation, the collision of a fuel molecule with one of oxygen resulting in the formation of a highly reactive and explosive organic peroxide, for example, an alkyl hydrogen peroxide, by the direct incorporation of the oxygen molecule, rather than in the formation of hydroxyl compounds, which involves a separation of the oxygen molecules into atoms. The primary formation of peroxides accounts at once for autoxidation and detonation.

Autocatalytic action during the combustion of gaseous mixtures has also recently been reported by White (carbon disulphide), Hinshelwood (hydrogen), and others. The peroxidation in gaseous mixtures affords a link with the interesting work by Moureu and Dufraisse and others on the mechanism of inhibitors on the oxidation and polymerisation of liquid substances such as acrolein.

The careful studies by Egerton and Gates, an outline of which is given by Mr. Egerton in the following pages of our Supplement, of the action of a large number of organic substances and metallic vapours on the self-igniting temperatures of fuel–air mixtures, shed further light on the difficult problem of detonation and indicate the complexity of gaseous reactions.