

## EFFECT OF LIGHT ON THE COMBUSTION OF HYDROCARBONS

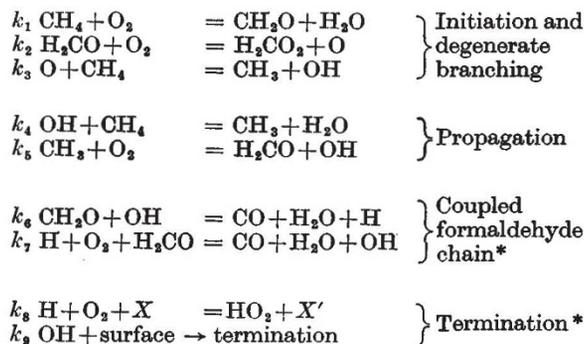
By PROF. R. G. W. NORRISH, F.R.S., and D. PATNAIK

Department of Physical Chemistry, University of Cambridge

THE slow combustion of hydrocarbons in general takes place by a kinetic process which Semenov<sup>1</sup> described as a chain reaction showing 'degenerate branching'. According to this conception, the hydrocarbon is first oxidized to a moderately stable intermediate, which is itself oxidized to the final products, namely, carbon monoxide, water, etc. Thus a stationary concentration of the intermediate is built up during the reaction, which reaches a maximum at the time of maximum velocity. According to Semenov's conception, the intermediate is responsible for the starting of new chains by an alternative reaction with oxygen, and a delayed or degenerate branching results.

In the case of methane<sup>4</sup> and ethylene, the intermediate may be identified with formaldehyde, which, as shown by Bone, Haffner and Rance<sup>2</sup> and by Harding and Norrish<sup>3</sup>, reaches a maximum concentration at the point of maximum velocity, and which when added to the reactants in the right amount (c. 1.0 per cent) completely removes the induction period<sup>4</sup>.

The complete scheme derived for the oxidation of methane<sup>4</sup>, based on the work of Norrish and Foord on methane<sup>4</sup> and Axford and Norrish<sup>5</sup> on the oxidation of formaldehyde, is as follows:



\* Reactions (7) and (8) are only formally to be regarded as ternary reactions. The transition complex  $\text{HO}_2$  formed with c. 50 k.cal. is unstable unless deactivated (reaction (8)), and reactive only if it encounters a formaldehyde molecule (reaction (7)) before it decomposes, or is deactivated.

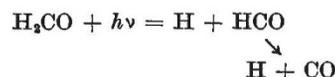
In this mechanism, the concentration of formaldehyde, initially zero, grows very slowly at first, during the induction period; and later, as the delayed branching by reaction (2) takes effect, at an ever-increasing rate. But the rate of the oxidation of formaldehyde by reactions (6) and (7), which as is generally agreed depends approximately on the square of its concentration, grows still faster, so that eventually a stationary concentration is reached when its rate of destruction is equal to its rate of production. At this point the velocity of reaction must cease to increase; it settles down to a steady value which finally falls off as the reactants are consumed. Thus we get the familiar S-shaped pressure-time curves. A similar scheme has been derived for the oxidation of ethylene<sup>6</sup>.

The steady rate is readily shown to be given by the kinetic equation<sup>6</sup>

$$\frac{-d(\text{Hy})}{dt} = \frac{k_4}{k_6} \left( k_2(\text{Hy})(\text{O}_2) + \frac{k_2 k_4 k_7 (\text{Hy})^2 (\text{O}_2) P d}{2k_7 k_9 \sigma + 2k_8 k_6 P^2 d} \right), \quad (1)$$

where (Hy) stands for methane or ethylene,  $\sigma$  the specific surface activity per square cm. for termination by reaction (9),  $P$  the total pressure in the system and  $d$  the diameter of the reaction vessel. The first term on the right-hand side represents the initiation process, the second the propagation; and the former is generally negligible in comparison with the latter. With methane, the first term in the denominator is large compared with the second, which can be neglected; with ethylene, which oxidizes at a lower temperature, the two terms are of comparable magnitude. This circumstance is responsible for minor differences in their oxidation kinetics.

This general view of the oxidation of methane and ethylene led us to the conclusion that the combustion reaction should be accelerated by light, which is known to dissociate formaldehyde into free radicals, for the degenerate branching reaction (2) would now be augmented by the photochemical process



as a chain-starting mechanism.

If the rate of absorption of light by formaldehyde is given by  $k(\text{H}_2\text{CO})I$ , where  $I$  is the incident intensity, the rate equation now becomes modified to

$$\frac{-d\text{Hy}}{dt} = \frac{k_4}{k_6} \left( k_2(\text{Hy})(\text{O}_2) + k(\text{Hy})I + \frac{k_2 k_4 k_7 (\text{Hy})^2 (\text{O}_2) P d + k k_4 k_7 (\text{Hy})^2 I P d}{2k_7 k_9 \sigma + 2k_8 k_6 P^2 d} \right). \quad (2)$$

Subtracting the rate in the dark ( $R_D$ ) from the rate in the light ( $R_L$ ) we obtain:

$$R_L - R_D = \frac{k_4}{k_6} \left( k(\text{Hy})I + \frac{k k_4 k_7 (\text{Hy})^2 I P d}{2k_7 k_9 \sigma + 2k_8 k_6 P^2 d} \right); \quad (3)$$

or, keeping  $\sigma$ ,  $I$  and  $d$  constant:

$$R_L - R_D = (\text{Hy}) + \frac{a(\text{Hy})^2 P}{b + cP^2}. \quad (4)$$

If, in addition, the total pressure  $P$  be kept constant by making up with nitrogen,

$$R_L - R_D = (\text{Hy}) + K(\text{Hy})^2. \quad (5)$$

These predictions have all been confirmed. We used a cylindrical quartz reaction vessel (diameter 3.4 cm., volume 175 c.c.) in a horizontal electric furnace lined with polished aluminium with a quartz window 7 cm. in diameter at one end. A beam of light of high intensity obtained from a high-pressure point-source mercury arc, burning 1 kW., and 'cooled' by passing through 50 cm. of water contained in a tank with parallel quartz sides, was focused into the furnace by means of a searchlight mirror of polished aluminium. The reaction was followed by pressure change, measured by a glass spoon gauge sensitive to a pressure of 0.05 mm. mercury. Fig. 1 shows a typical result.

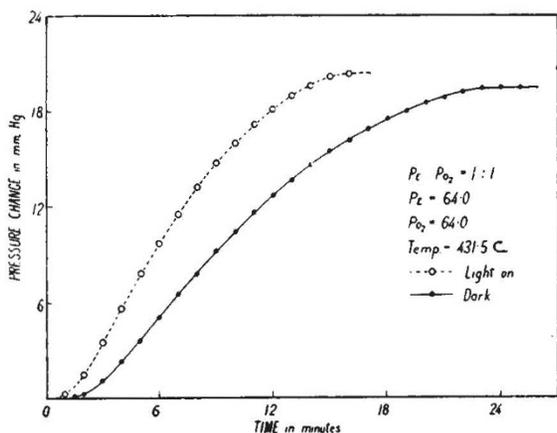


Fig. 1. Effect of light on the slow oxidation of ethylene

When the light beam was passed through a colour filter of 0.5 per cent solution of quinine hydrochloride 7 cm. thick, which cuts out all light of wave-length shorter than 3600 Å., the acceleration due to the light was very nearly (90 per cent) suppressed. The formaldehyde absorption spectrum extends from 3750 Å. to beyond 2500 Å., whereas the spectrum of the lamp extended to 2450 Å.; thus the active light lies in the ultra-violet in the region covering the absorption band of formaldehyde. With a more concentrated solution of quinine hydrochloride (2.5 per cent) cutting out all light of less than 4000 Å., the effect was completely suppressed.

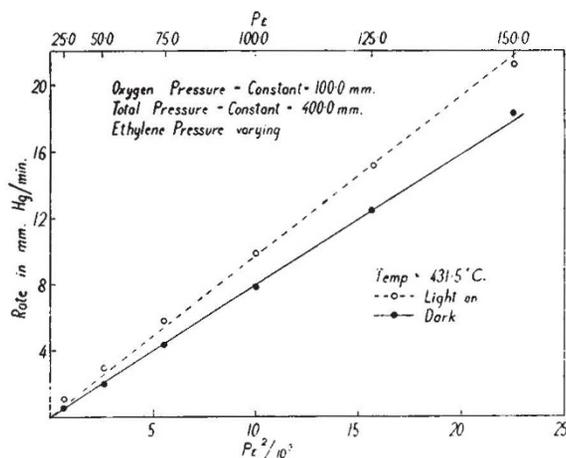


Fig. 2. Effect of light on the slow oxidation of ethylene; ethylene pressure varying, total pressure constant

Figs. 2-5 show that  $R_L$  and  $R_D$  conform to equations (1) and (2), and that  $R_L - R_D$  is independent of  $(O_2)$  and approximately proportional to  $(Hy)^2$ , as is required by equation (4) if the terms in  $Hy$  (initiation) are small compared with the terms in  $Hy^2$  (propagation), and if  $b$  is large compared to  $cP^2$ , as it is in the case of methane. With ethylene we kept the total pressure  $P$  constant by adding nitrogen, and therefore  $R_L - R_D$  is given by equation (5). Under these conditions, when  $(Hy)$  is small the first term in equation (5) preponderates, and  $(R_L - R_D)$  is more nearly proportional to  $(Hy)$  than  $(Hy)^2$ . The fact that the experimental points for low  $(Hy)$  in Fig. 2 lie above the line is in accord with this.

By working close to the ignition limit with ethylene ( $C_2H_4 = 225$  mm.,  $O_2 = 318$ , temp.  $431^\circ C.$ ) we were

readily able to convert a 'slow' dark reaction into an ignition by irradiation; but in this region equation (1) is no longer obeyed owing to the large measure of self-heating as the ignition limit is approached.

These results accord well with the reaction scheme based on formaldehyde outlined above, and confirm the kinetic formulæ previously deduced. They show, in effect, that the degenerate branching process can be powerfully affected by light without altering the character of the reaction; and the effect is all the more striking when it is remembered that the initial reactants are completely transparent to the light used.

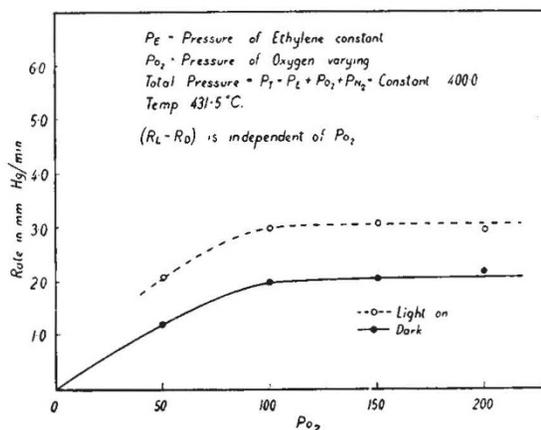
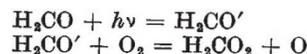


Fig. 3. Effect of light on the slow oxidation of ethylene; oxygen varying, total pressure constant

By using the weaker colour filter (0.5 per cent quinine hydrochloride) it was shown that the effect still persists feebly in light the spectrum of which lies between 3600 Å. and 4000 Å. Now the pre-dissociation limit of formaldehyde as shown by the threshold of fluorescence is at c. 3000 Å., and it must therefore be concluded that some such reactions as



take place in this region; that is, that reaction (2) is somewhat enhanced by light which excites, but does not split, the formaldehyde molecule.

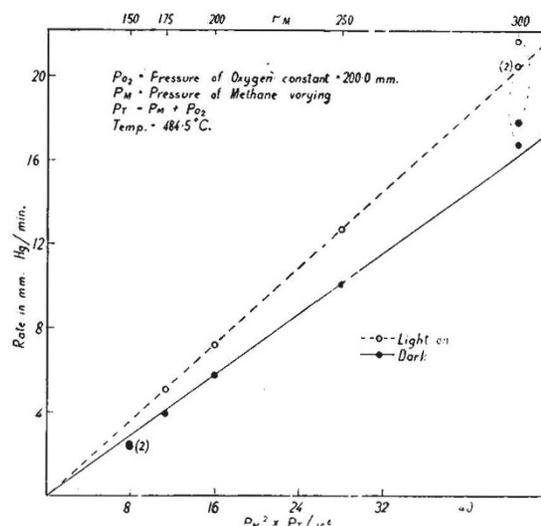


Fig. 4. Effect of light on the slow oxidation of methane; methane varying

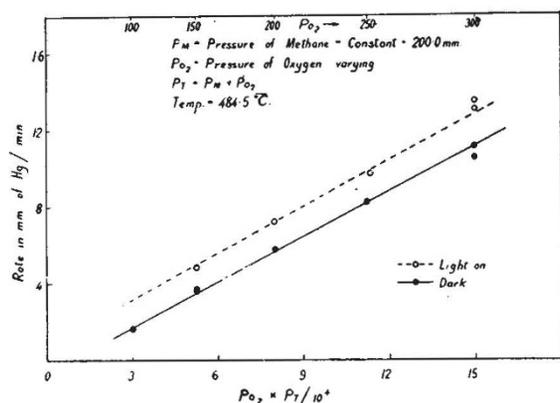


Fig. 5. Effect of light on the slow oxidation of methane; oxygen varying

With heavier hydrocarbons the characteristics of degenerate branching are similarly observed, and we believe that the heavier aldehydes which are first produced are similarly responsible for the delayed branching reaction. On this basis it is possible to build a self-consistent mechanism of a pattern resembling the simpler reactions treated here<sup>6</sup>. It is significant that light readily accelerates the oxidation of butane, and the shapes of the curves in the dark and in the light suggest different end points; it is probable that the phenomenon will be found to be general for hydrocarbons.

This photochemical effect provides a new experimental approach to the study of the reaction kinetics of combustion, and cannot fail to be revealing.

<sup>1</sup> Semenov, *Z. phys. Chem.*, 11B, 464 (1930); *Phys. Z. d. Sowjetunion*, 1, 546 (1932); "Chemical Kinetics and Chain Reactions", 68 (Oxford, 1935).

<sup>2</sup> Bone, Haffner and Rance, *Proc. Roy. Soc., A*, 143, 16 (1933).

<sup>3</sup> Harding and Norrish, *Nature*, 163, 797 (1949).

<sup>4</sup> Norrish and Foord, *Proc. Roy. Soc., A*, 157, 503 (1936).

<sup>5</sup> Axford and Norrish, *Proc. Roy. Soc., A*, 192, 518 (1948).

<sup>6</sup> Norrish, communication to the Centre National de la Recherche Scientifique, Paris, 1948 (in course of publication).

<sup>7</sup> Herzberg and Franz, *Z. Phys.*, 76, 720 (1932). Gradstein, *Z. phys. Chem.*, B, 22, 384 (1933).

## OPTICAL PROPERTIES OF SOLID THIN FILMS

A MOST successful international colloquium on the optical properties of solid thin films was held at Marseille during the week April 19-23 under the auspices of the Centre National de la Recherche Scientifique. Some forty-four physicists attended by invitation, and, of these, twenty-five contributed papers. There was, of course, a strong contingent from France, including, among others, P. Jacquinot, M. Perrot and P. Rouard. From Great Britain contributions were read by K. M. Greenland, O. S. Heavens, H. Kuhn and S. Tolansky. The United States were represented by B. H. Billings, N. W. Scott, J. Strong and A. F. Turner, the Netherlands by P. van Alphen and B. Blaisse, Italy by M. Ballerini, Switzerland by M. Schaetti and Czechoslovakia by A. Vasecek.

The conference was well organised by Prof. P. Rouard, director of the physical laboratory in the University of Marseille, and was characterized by smooth, efficient working and excellent programme

planning. This meeting was held in a provincial university as part of deliberate policy of the Centre National de la Recherche Scientifique, which is arranging a series of international conferences in French provincial university centres. The choice of Marseille for this particular subject of optical properties of thin films was a happy one indeed; for it was there, at the beginning of this century, that Fabry laid the foundation of the very subject under discussion, and it was there, too, under his inspiration that the branch of classical optics associated with the names of Fabry, Buisson, Macé de Lepinay and others was created. Indeed, the visitors all derived considerable pleasure from an exhibition of the original apparatus used by these masters of experimental optics, and were much moved, too, by listening to a recording of the voice of Fabry.

Although a considerable number of papers were read (many contributors read several: for example, the writer contributed five), these all crystallized into four fairly distinct groups: (a) determination of optical properties and thickness of thin metal or dielectric films; (b) the principles and applications of multiple-beam interferometry; (c) preparation of interferometric wave-length filters and discussion of their characteristics; (d) improving the optical properties of surfaces by deposition of multiple films with alternate low and high refractive indices.

The conference opened with a session of theoretical papers on the properties of single and multiple thin films, and then plunged into its main work, which consisted of formal papers on experimental aspects connected with the properties and optics of thin films. Occasionally the conference assumed the character of informal discussions on experimental techniques, yet all were agreed that these informal exchanges constituted one of the most valuable features of the whole conference. For it is a fact that success with experimental interferometry, or with those other branches of applied optics which involve surface deposition of films, depends largely upon minor details of personal techniques which are not easily publishable, and are, indeed, often even difficult to describe. For example, a most lively discussion ensued simply on the question of the best method of cleaning a glass surface which is to accept a film by deposition by vacuum evaporation. There were perhaps ten speakers, with the inevitable result that perhaps ten distinctly different techniques were described; but all had one thing in common, namely, final cleaning by ions with a gas discharge. It appears that any reasonable method of cleaning is satisfactory provided the glow discharge is the final cleansing agent.

Many striking and novel optical results were described, and it is anticipated that all the papers contributed will be published together in some form. Such a collection will make a notable contribution to a subject rapidly becoming of considerable importance to technical optics, particularly those fields concerned with either reduction or enhancement of reflectivities of surfaces. The conference was an unqualified scientific success and equally successful socially, thanks largely to Prof. Rouard. The visitors will long remember the magnificent hospitality of their French colleagues. A visit was paid to the astronomical observatory at St. Michel, the visit being of mutual benefit to visitors and residents, for the astronomers there were glad to welcome so much expert opinion on the problems associated with the coating of the mirrors of their reflector telescopes.