LETTERS TO THE EDITORS

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Role of Formaldehyde in the Oxidation of Ethylene

AT temperatures above 300° C. the reaction of oxygen with methane or ethylene shows the induction period and exponential development of the reaction rate with time, which are two of the characteristics of chain reactions that proceed by degenerate branching, that is, reactions in which the chains are initiated by the subsequent reaction of a fairly stable intermediate produced in the primary reaction process. To substantiate this hypothesis, it is clearly important to discover the nature of the intermediate by which the chains characteristic of degenerate branching are initiated.

Norrish and Foord[1] have concluded from a study of the kinetics of the oxidation of methane that formaldehyde is the important intermediate in this reaction. Since more detailed information on the oxidation of formaldehyde has become available[2], we have developed and applied a more detailed scheme[3] to interpret both the previously observed kinetics of the oxidation of methane and also the results we have obtained from our recent work on the oxidation of ethylene. We find that the concentration of formaldehyde in a reacting mixture of ethylene and oxygen develops to a maximum as the maximum rate is attained, and that the maximum concentration is proportional to the ethylene concentration. These are two examples of the behaviour that would be expected of the intermediate that gives rise to degenerate branching.

We also find that the activation energy (E_A) of the ethylene oxidation varies smoothly from 26 kcal. below 400° C. to 53 kcal. at 550° C., and furthermore that throughout this range of temperatures all the characteristics of degenerate branching are preserved without discontinuity.

The chief contribution to the activation energy must be from the degenerate branching reaction by which chains are initiated from the unstable intermediate ; for the primary initiation process is insignificant as soon as the reaction begins to develop, and the reactions between radicals and molecules which propagate the chains have of necessity activation energies much smaller than the activation energies of reactions which start new chains. If, therefore, the degenerate branching process is identical with that by which the intermediate produces chains in its own oxidation, the activation energy of the latter should vary in like manner to that of the ethylene oxidation in the same temperature-range.

In confirmation of this, we find that while the energy of activation of the oxidation of formaldehyde in the range 300–370° C. is c. 21 kcal. as observed by previous workers, it rises with increase in temperature to a value of 39 kcal. in the range 450–470° C., at which temperature the activation energy of the ethylene oxidation is 42 kcal. These measurements were made by a comparison of the initial reaction velocities at different temperatures, but could not be extended above 470° C. because the reaction became self-heating. Measurements of the ignition limits, however, in the region 500–550° C. indicate that the activation energy exceeds 40 kcal., though

there is some uncertainty by how much because of our lack of knowledge of the precise order of the reaction in this range.

We regard this parallel trend in the activation energies of the two reactions as strong support for our theory that formaldehyde is the agent by which degenerate branching takes place in the oxidation of ethylene. It indicates further that there are two mechanisms of chain initiation in the oxidation of formaldehyde. In the low temperature-range, the reaction, suggested by Axford and Norrish[2],

$$HCHO + O_2 = (HCOOOH) = HCOOH + O,$$

which is approximately thermoneutral[4], is consistent with an overall activation energy of 21 kcal. In the high temperature-range, the reaction may be

$$HCHO + O_2 = HCO + HO_2$$
$$\searrow$$
$$H + CO$$
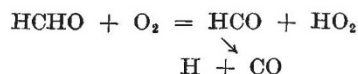
The energy-change of this reaction cannot as yet be stated unequivocally, but as a rough estimate, if the reaction $H + O_2 = HO_2$ is 50 kcal. exothermic[5], then the reaction is c. 50 kcal. endothermic. Since the energy of activation must be at least as great as the endothermicity, we may conclude that this could be the initiation reaction at temperatures above 500° C.

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[1] Norrish and Foord, *Proc. Roy. Soc.*, A, **157**, 503 (1936).
[2] Axford and Norrish, *Proc. Roy. Soc.*, A, **192**, 518 (1948).
[3] (*a*) Norrish, Com. to the Centre National de la Recherche Scientifique, Paris, 1948 (in course of publication). (*b*) Harding and Norrish, "Oxidation of Ethylene" (in course of publication).
[4] Data from Bichowsky and Rossini, "Thermochemistry of Chemical Substances" (Reinhold Publishing Corporation, New York, 1936).
[5] Bray, *J. Amer. Chem. Soc.*, **60**, 82 (1938).

Radioactive Diisopropyl Fluorophosphonate

DI*iso*PROPYL fluorophosphonate containing labelled phosphorus (P^{32}) has recently been prepared in this Laboratory. Phosphorus (of the order of 1 gm.) containing P^{32} was converted into phosphorus trichloride. This small-scale conversion presented considerable initial difficulties, the most serious feature being the facile production of phosphorus pentachloride ; most reliable descriptions of the preparation of phosphorus trichloride are on a basis of 200 gm. of phosphorus[1]. A communication to the *Journal of the Chemical Society* will give details of the methods employed to overcome these difficulties.

The active trichloride was converted into diisopropyl hydrogen phosphite, and thence through the chlorophosphonate to the fluorophosphonate, using the general principles as set forth by Saunders *et al.*[2].

$$3ROH + PCl_3 \longrightarrow \underset{\underset{OR}{|}}{\overset{\overset{OH}{|}}{P}} - OR + RCl + 2HCl \xrightarrow{Cl_2}$$

$$O = \underset{\underset{OR}{|}}{\overset{\overset{Cl}{|}}{P}} - OR \xrightarrow{NaF} O = \underset{\underset{OR}{|}}{\overset{\overset{F}{|}}{P}} - OR$$