602. The Mercury Photo-sensitized Oxidation of Ethane and Methane.

By J. A. Gray.

The experiments were designed to reproduce, and thus verify, the now conventional peroxide mechanism used to explain the low-temperature oxidation of hydrocarbons and to isolate the predicted product. The results are consistent with the mechanism proposed, *viz.*,

$$Hg(^1S_0) + h\nu = Hg(^3P_1) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Hg(^3P_1) + RH = Hg(^1S_0) + R + H \quad . \quad . \quad . \quad (2)$$

$$R + O_2 = R{\cdot}O{\cdot}O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$R{\cdot}O{\cdot}O + RH = R{\cdot}O{\cdot}OH + R \quad . \quad . \quad . \quad . \quad (4)$$

where R represents C_2H_5 or CH_3. To prevent photochemical and thermal decomposition of the peroxide, a flow system was used at high rates of flow and low temperature (25°). The product condensable at $-80°$ from the oxidation of ethane was ethyl hydroperoxide in a high state of purity. Methane gave a product which was predominately methyl hydroperoxide, formaldehyde being absent, thus excluding the possibility of the reactions

$$CH_3 + O_2 = H{\cdot}CHO + OH \; (5)$$

and similar variants under the conditions of the present work and confirming that the suggested peroxide mechanism is operative.

The formation of hydroperoxides as intermediates has been postulated with increasing frequency during the last few years in order to obtain a reaction mechanism for the oxidation of organic compounds. Mulcahy (*Discuss. Faraday Soc.*, 1951, **10**, 259) has given a recent summary of the evidence for the formation of peroxides and extended the simplified theory of low-temperature oxidation as developed by Bardwell and Hinshelwood (*Proc. Roy. Soc.*, 1951, *A*, **207**, 461, 470) for hydrocarbons in the gas phase. As yet, however, experiments on gas-phase oxidations have not yielded peroxides in sufficient quantity or adequate purity to enable them to be isolated or identified, and there is still doubt as to the particular peroxide which is formed in a given set of circumstances in hydrocarbon combustion (Egerton, Emte, and Minkoff, *Discuss. Faraday Soc.*, 1951, **10**, 278). The object of the present investigation was to choose the oxidative conditions wherein a peroxide formed as an intermediate could survive and be recovered in a pure state for examination and identification. Photosensitized oxidation appeared to be the only satisfactory method, and ethane and methane were examined because of their position as the lowest members of the hydrocarbon series and because of the fundamental differences that have been suggested to explain their behaviour on oxidation: $C_2H_5 + O_2 = C_2H_5{\cdot}O{\cdot}O$ is not a difficult process to accept, but opinion has been more widely divided over the reaction $CH_3 + O_2$. Products suggested have been $H{\cdot}CHO + OH$ directly or through an intermediate energy-rich $CH_3{\cdot}O{\cdot}O$ molecule (Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689; Norrish, *Rev. Inst. franç. Pétrole Ann. Combust. Liq.*, 1949, **4**, 288; Chamberlain and Walsh, *ibid.*, p. 301), $CH_3{\cdot}O_2$ (Raley, Porter, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1951, **73**, 15), $HCO + H_2O$ (Marcotte and Noyes, *Discuss. Faraday Soc.*, 1951, **10**, 236), and it was hoped that the present work would enable this point to be settled for the particular conditions which had been chosen.

EXPERIMENTAL

Commercial ethane, methane, and oxygen were used without further purification. The apparatus was similar to that used by Volman (*J. Chem. Physics*, 1946, **14**, 709), the arrangement being shown in Fig. 1. A metered hydrocarbon–oxygen mixture was dried by passage over Anhydrone and then passed over a number of mercury surfaces which were kept at 100° by water boiling under reflux. Two traps immersed in the water-thermostat acted as desaturators before the gas passed into the quartz spiral which surrounded the arc. The low-pressure mercury arc (type T/M5/369) was supplied by Messrs. Thermal Syndicate Ltd., and operated at 110 ma. from 1000 v A.C. Emission is unreversed at 2537 Å and, by running the arc immersed in the thermostat and cooling the electrodes with a flow of compressed air, pressure broadening was reduced to a minimum and 1849-Å radiation was unlikely to reach the reaction spiral. The latter consisted of 6 turns of 9-mm. quartz tubing, the total volume being aprox. 92 c.c. The trap which followed the spiral was cooled on the outside by solid carbon dioxide–ethanol, and the centre tube was warmed by a jet of air. The annular space of approx. 1·5 mm. was found to be very efficient in condensing small quantities of product from a large volume of gas at rapid flow rates. At the end of an experiment this trap was isolated and residual hydrocarbon and oxygen were pumped off. The product was then subjected to fractionation under vacuum and was finally collected in a small tube which could be detached from the apparatus for weighing and for examination of the product.

Results.—1. *Ethane.* All experiments were carried out at a total gas pressure of 1 atm. This relatively high pressure eliminated unwanted side-reactions and prevented the quenching of excited mercury by the reaction products.

Trial experiments with a 50 : 50 C_2H_6–O_2 mixture suggested that at 25° conversion was very low, that the condensable product was mainly peroxide, and that ozone was also present, the formation of which was presumably initiated by the reaction

$$Hg(^3P_1) + O_2 = HgO + O \quad . \quad . \quad (6)$$

In reducing the effect of ozone to a minimum it was found that a 90 : 10 C_2H_6–O_2 mixture gave the optimum results, *i.e.*, a relatively pure product with no diminution of yield and with little or no ozone formation. Mercuric oxide was still found in the annular trap, but if ozone were formed it had no effect on the nature of the product, which appeared to be ethyl hydroperoxide. Further reduction of the oxygen to 5% hardly affected the yield or nature of the product. High flow rates had to be used to avoid photochemical decomposition of the peroxide, the total flow being 10—15 c.c./sec. On reducing this rate, aldehydes were detected in the carbon dioxide trap. An increase in flow rate did not affect the nature or amount of product, but of course the conversion was lower.

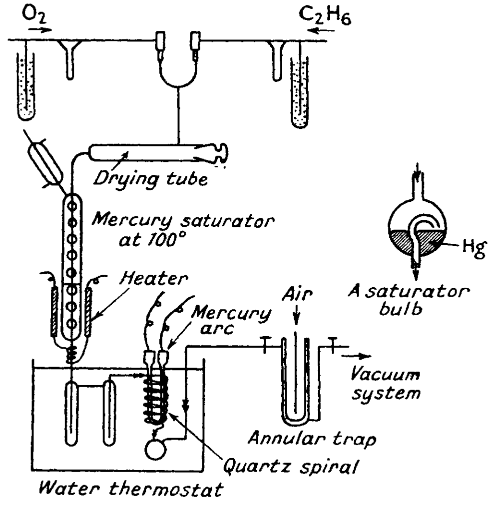


FIG. 1. *Experimental arrangement.*

Because of the unstable nature of the lower alkyl peroxides and the difficulty of finding suitable reagents to differentiate between them, the product was examined and identified by a variety of methods, namely, by titration, carbon and hydrogen analysis, micro-b. p., refractive index, vapour pressure, infra-red absorption, and polarography. On fractionation and melting it appeared to consist of a single compound (Found : C, 39·2; H, 9·7. Calc. for $C_2H_6O_2$: C, 38·7; H, 9·7%). The micro-b. p. was approx. 90—91°, extrapolation of the vapour-pressure measurements of Egerton, Emte, and Minkoff (*loc. cit.*) giving 95°; n_D^{20} was 1·388 as against their value of 1·380. Iodine liberation was 101—103% of theory; it was carried out by weighing about 0·1 g. of product, making it up to a known volume, adding glacial acetic acid and sodium hydrogen carbonate to a portion, and keeping it in the dark in a loosely stoppered bottle for 10 minutes. Saturated potassium iodide solution was added, and after standing in the dark for a further 15 minutes, the solution was diluted and titrated with 0·1N-sodium thiosulphate, with starch as indicator. Trial experiments showed that this method, which is basically the same as that of Harris (*Proc. Roy. Soc.*, 1939, *A*, **173**, 126), gave reproducible results.

Polarographic examination was best carried out in 0·1N-lithium chloride solution (Stern and Polak, *Acta Physicochim.*, 1939, **11**, 797). A Cambridge polarograph was used, and hydrogen was bubbled through the solution under examination for 2 minutes to eliminate the oxygen wave. The reduction potential of the product was found to be 0·25—0·3 v, which is the same as that given by Stern and Polak for $C_2H_5{\cdot}O{\cdot}OH$ and is well removed from the value of 0·5 v quoted by the same authors for $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$. Aldehydes were absent.

Vapour-pressure measurements on the product confirmed that of the two most probable compositions, *i.e.*, $C_2H_5{\cdot}O{\cdot}OH$ pure, or containing an equimolar mixture of $C_2H_5{\cdot}O{\cdot}OC_2H_5$ and H_2O_2, the former was the only possible one. The vapour pressure at −16° and 0° coincided exactly with that reported by Egerton, Emte, and Minkoff (*loc. cit.*) for $C_2H_5{\cdot}O{\cdot}O{\cdot}H$, being 1·5 and 4·7 mm., respectively, in contrast with 28·4 and 63·1 mm. for $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$.

The published data on the absorption spectra of the lower alkyl peroxides are scanty. Egerton, Harris, and Young (*Trans. Faraday Soc.*, 1948, **44**, 745) have re-examined the ultra-violet absorption spectra of peroxides but the method cannot be used for the positive identification of an unknown. The infra-red absorption of $C_2H_5{\cdot}O{\cdot}OH$ does not appear to be recorded in the literature but Dr. G. J. Minkoff has kindly made available his unpublished collection of infra-red absorption spectra of organic peroxides, including that of $C_2H_5{\cdot}O{\cdot}OH$ in solution. He has described the double-beam instrument which he used (*Fuel*, 1950, **39**, 228).

The infra-red absorption of the liquid product was examined on a Grubb-Parsons single-beam instrument with a rock-salt prism and A.C. amplification; the spectrum obtained was nearly identical with that obtained by Minkoff for $C_2H_5{\cdot}O{\cdot}OH$, due allowance being made for the different conditions obtaining. In contrast to the absorption of $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$ were noticed: (*a*) the absence of an intense band at ~880 cm.$^{-1}$ found by Minkoff and tentatively attributed by Leadbeater (*Compt. rend.*, 1950, **230**, 829) to the RO–OR linkage, and (*b*) the presence of a band at 783 cm.$^{-1}$ and strong general absorption below about 900 cm.$^{-1}$ which were not given by diethyl peroxide. No detectable amount of ethanol was present.

Thus there seems to be little doubt that the main product of the photosensitized oxidation of ethane at 25° and under the conditions described is ethyl hydroperoxide, in agreement with the reaction mechanism proposed:

$$Hg(^1S_0) + h\nu = Hg(^3P_1) \qquad \ldots\ldots\ldots \qquad (1)$$

$$Hg(^3P_1) + C_2H_6 = Hg(^1S_0) + C_2H_5 + H \qquad \ldots\ldots \qquad (7)$$

$$C_2H_5 + O_2 = C_2H_5{\cdot}O{\cdot}O \qquad \ldots\ldots\ldots \qquad (8)$$

$$C_2H_5{\cdot}O{\cdot}O + C_2H_6 = C_2H_5{\cdot}O{\cdot}OH + C_2H_5 \qquad \ldots\ldots \qquad (9)$$

A chain-ending reaction has not been proposed in this qualitative study as it has not been possible to make accurate kinetic measurements. The limit set on the conversion by the high flow rates makes the detection of non-condensable products extremely difficult. An attempt was made to build up the concentration of these products by using a circulating system which incorporated a diaphragm-operated mercury-piston type pump, but the flow rates obtainable were not sufficient to prevent photolysis of the peroxide, formaldehyde and a higher aldehyde being detected in the product. Even in the case of the normal flow system, when the temperature of the thermostat was raised to 50° aldehyde was detected in the product by the polarographic method but formaldehyde was absent. This indicated that heterogeneous thermal decomposition of the peroxide was commencing. An approximate calculation of the quantum yield of $C_2H_5{\cdot}O{\cdot}OH$ formation based on the known 2537-Å emission of the arc indicates that very short chains are involved.

The rate of production of $C_2H_5{\cdot}O{\cdot}OH$ is shown in the table, where, owing to variations in pumping, etc., the weight of product refers to the maximum obtained and not to the mean of several runs.

The variation of yield with reaction conditions.

Run	Conditions		$C_2H_5{\cdot}O{\cdot}OH$ produced, g./h.	
6A/94	90 : 10 C_2H_6–O_2	25°	0·012	
6A/93	,,	40	0·036	Product contained approx. 7% of $CH_3{\cdot}CHO$
6A/101	,,	50	0·039	
6A/107	95 : 5 C_2H_6–O_2	25	0·014	

2. *Methane.* The product of the photosensitized oxidation of methane, carried out under the conditions already described for ethane, was examined by similar methods and appeared to be mainly $CH_3{\cdot}O{\cdot}OH$. Properties were as follows: n_D^{20} 1·374; micro-b. p. 88—89° (Egerton, Emte, and Minkoff give 1·364 and 86°) (Found: C, 29·1; H, 9·6. Calc. for CH_4O_2: C, 25·0; H, 8·3%). Its polarographic behaviour was the same as that reported by Stern and Polak (*loc. cit.*) for $CH_3{\cdot}O{\cdot}OH$, and aldehydes were absent. It was undoubtedly peroxidic in nature, but iodine liberation was only 60% of theory, and although a low result is often to be expected, it is probable that an impurity was present. This might be $CH_3{\cdot}O{\cdot}OCH_3$, $CH_3{\cdot}OH$, and/or H_2O_2. The infra-red absorption spectrum was in fair agreement with that of the $CH_3{\cdot}O{\cdot}OH$ spectrum provided by Minkoff, but the possibility of the presence of up to 30% of $CH_3{\cdot}OH$ could not be excluded. The absorption spectrum of $CH_3{\cdot}O{\cdot}O{\cdot}CH_3$ was not available and $CH_3{\cdot}O{\cdot}OH$ could not be differentiated from H_2O_2 on the polarograph.

Although the composition of the whole of the product is not known with certainty, the significant conclusion to be drawn is that it contained at least 50% of methyl hydroperoxide but no formaldehyde. Trace amounts of formaldehyde were detected in the carbon dioxide trap when it was washed out with water after a run, and may have been produced from the decomposition of peroxide in the presence of mercury even at −80° or during vacuum distillation. The maximum yield of product was 0·0129 g./h. at 40° and 0·0106 g./h. at 25°.

DISCUSSION

Ethane.—It appears that the peroxide mechanism applied to the photosensitized oxidation of ethane gives a prediction which has been fulfilled by experiment. A variant which might have been applied to the mechanism, *viz.*, $C_2H_5{\cdot}O{\cdot}O + C_2H_6 = C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5 + H$, does not take place to any significant extent under the conditions of the present work. The absence of detectable amounts of water or hydrogen peroxide in the product indicates that at the temperatures used hydrogen atoms are not removed by way of $H + O_2 = HO_2{}^* \longrightarrow H_2O$ or H_2O_2, and that radical recombination or abstraction of hydrogen from ethane is of greater importance. Both radicals being comparatively stable, a possible chain-ending step is the reaction $C_2H_5{\cdot}O{\cdot}O + HO_2 = C_2H_5{\cdot}O{\cdot}OH + O_2$.

The course of the reaction is in general similar to that obtaining in the photochemical oxidation of olefins (Bateman and Gee, *Proc. Roy. Soc.*, 1949, *A*, **195**, 376). Reaction (7) is that expected from the findings of Steacie and his co-workers ("Atomic and Free Radical Reactions," Reinhold Publ. Corpn., N.Y., 1946), although it is at variance with the conclusions of Nalbandyan, who has investigated the photosensitized oxidation of ethane (*Compt. rend. U.R.S.S.*, 1949, **66**, 413) and of methane (*ibid.*, 1948, **60**, 607). He concludes from the $H{\cdot}CHO/CH_3{\cdot}CHO$ ratio in his product, with a flow-system at 300°, that of the two reactions

$$C_2H_6 + Hg(^3P_1) = CH_3 + CH_3 + Hg(^1S_0) \quad . \quad . \quad . \quad . \quad (10)$$

$$C_2H_6 + Hg(^3P_1) = C_2H_5 + H + Hg(^1S_0) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the former is the faster. This was not the finding of Bywater and Steacie (*J. Chem. Physics*, 1951, **19**, 326) who found the reverse to hold, and may easily be explained by the homogeneous decomposition of the hydroperoxide :

$$C_2H_5{\cdot}O{\cdot}OH = C_2H_5{\cdot}O + OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$C_2H_5{\cdot}O = CH_3 + H{\cdot}CHO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$C_2H_5{\cdot}O = H + CH_3{\cdot}CHO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

It has been found (Gray, Thesis, London, 1950) that ethoxy-radicals generated by the photolysis of ethyl nitrate can decompose by the two alternative methods; the bond dissociation energies were calculated to be 11 kcal. for (12) and 13 kcal. for (13). Estimated activation energies were 21 and 23 kcal., respectively.

Methane.—Of greatest interest in the photosensitized oxidation of methane at temperatures up to 50° is that the two variants on the peroxide mechanism, *viz.*,

$$CH_3 + O_2 = H{\cdot}CHO + OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$CH_3 + O_2 = H{\cdot}CO + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

are quite definitely excluded. This result is not unexpected, for neither (5) nor (14) involves simple reaction steps, both requiring drastic rearrangement of inter-atomic linkages. The initial step (Steacie, *op. cit.*)

$$CH_4 + Hg(^3P_1) = CH_3 + H + Hg(^1S_0) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

being assumed, the impurities in the product indicate that there is a possibility that

$$CH_3 + O_2 = CH_3O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

is followed by

$$CH_3{\cdot}O{\cdot}O + CH_4 = CH_3{\cdot}O{\cdot}O{\cdot}CH_3 + H \quad . \quad . \quad . \quad . \quad . \quad (17)$$

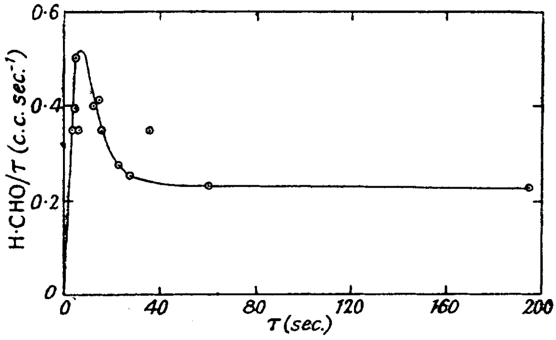
in addition to

$$CH_3{\cdot}O{\cdot}O + CH_4 = CH_3{\cdot}O{\cdot}OH + CH_3 \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The product may undergo further heterogeneous decomposition even in the carbon dioxide trap, particularly in the inevitable presence of mercury before the separation by vacuum fractionation.

Nalbandyan has used equation (5) to interpret his results on the photosensitized oxidation of methane. However, it is considered that the peroxide mechanism may equally well be applied to explain his results. If $CH_3{\cdot}O{\cdot}OH$ is an intermediate, then the quantum yield of formaldehyde should be zero at infinitely rapid flow rate, should rise rapidly to a maximum with decomposition of $CH_3{\cdot}O{\cdot}OH$, and then fall off quasi-exponentially at longer contact time, to a value dependent on the proportion of oxygen in the reactants, owing to thermal and photochemical oxidation of formaldehyde itself. In Fig. 2, $H{\cdot}CHO/\tau$ is plotted against τ from values given by Nalbandyan (*loc. cit.*, 1948) for H·CHO (total H·CHO produced, in c.c.) and τ (time of residence in the illuminated zone, in sec.) in runs carried out at 400° on equal volumes of reacting material. It will be seen that a curve of the shape described above for $CH_3{\cdot}O{\cdot}OH$ as an intermediate fits the experimental data with only one major deviation, whereas a curve representing monotonic decay of formaldehyde from a positive intercept on the $H{\cdot}CHO/\tau$ axis would involve a considerable amount of scatter.

FIG. 2.



Thus it is possible that even at 400° the thermal oxidation of methane proceeds in a manner which can be explained on the assumption of an intermediate hydroperoxide with subsequent oxidation of its decomposition products :

$$CH_3 + O_2 = CH_3{\cdot}O{\cdot}O \tag{16}$$

$$CH_3{\cdot}O{\cdot}O + CH_4 = CH_3{\cdot}O{\cdot}OH + CH_3 \tag{18}$$

$$CH_3{\cdot}O{\cdot}OH = CH_3{\cdot}O + OH \tag{19}$$

$$CH_3{\cdot}O = H{\cdot}CHO + H \tag{20}$$

$$H{\cdot}CHO + O_2 \longrightarrow \text{Products}$$

$$CH_3{\cdot}O{\cdot}OH + O_2 \longrightarrow \text{Products}$$

Reaction (16) is also supported by the work of Raley, Porter, Rust, and Vaughan (*loc. cit.*) who caused oxygen to react with methyl radicals produced from the thermal decomposition of di-*tert.*-butyl peroxide. In their case the CH_3O_2 radicals were in high concentration and did not abstract a hydrogen atom from di-*tert.*-butyl peroxide and disproportionation occurred : $CH_3O_2 + CH_3O_2 = 2CH_3O + O_2$. It may be that a similar process in the present work leads to the formation of methanol by the reaction $CH_3O + CH_4 = CH_3{\cdot}OH + CH_3$, as investigations on the photolysis of methyl nitrite (Gray, *op. cit.*) indicate that the CH_3O radical may be comparatively stable up to temperatures of well above 100°.

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IMPERIAL CHEMICAL INDUSTRIES LIMITED, ALKALI DIVISION,
RESEARCH DEPARTMENT, WINNINGTON, NORTHWICH, CHESHIRE. [*Received, April 4th*, 1952.]