The Effect of Oxygen on the Ionic Reactions in γ-Irradiated Methane–Propane Mixtures

By P. G. CLAY* and A. A. SIDDIQI

(*Department of Chemical Engineering and Chemical Technology, Imperial College, London, S.W.*7)

Summary Methane oxidation products react with the ionic precursors of ethane in irradiated methane–oxygen–propane systems.

AUSLOOS and LIAS[1] observed an apparent competition between propane and oxygen for the ionic precursors of ethane in irradiated methane. Subsequent mass spectrometric studies by Munson and Field[2] confirmed Ausloos' suggestion that the ions CH_5^+ and $C_2H_5^+$ were reactive towards propane but showed them to be unreactive towards oxygen. Munson suggested that the observed effect of oxygen in decreasing the ionic $G(C_2H_6)$ could be explained by the participation of water and other methane oxidation products in the ionic reactions. Thus a competition between propane and water for the ions would be set up:

$$\begin{aligned} CH_5^+ + H_2O &\rightarrow CH_4 + H_3O^+ \\ CH_5^+ + C_3H_8 &\rightarrow 2CH_4 + C_2H_5^+ \\ C_2H_5^+ + H_2O &\rightarrow C_2H_4 + H_3O^+ \\ C_2H_5^+ + C_3H_8 &\rightarrow C_2H_6 + C_3H_7^+ \end{aligned}$$

Similar competitions might be expected with other oxidation products.

In a study of the system methane–oxygen–propane we have obtained results supporting the conclusions of Munson. Table 1 shows the effect of varying $[O_2]$ and $[C_3H_8]$ on $G(C_2H_6)$ in systems irradiated to a constant dose of 3·3 × 10^{16} ev $ml.^{-1}$. It can be seen that for any given $[C_3H_8]$ there is essentially no effect of $[O_2]$ between 0·2—2%. On the other hand, $G(C_2H_6)$ increases with $[C_3H_8]$ from 0·2 in the absence of propane to 3·1 in the presence of propane at 0·4%.

TABLE 1

γ-Radiolysis of CH_4–O_2–C_3H_8 *mixtures: the dependence of* $G(C_2H_6)$ *on* $[O_2]$ *and* $[C_3H_8]$ (*total dose* 3·3 × 10^{16} ev $ml.^{-1}$)

$[C_3H_8]\%$	$[O_2]\%$	$G(C_2H_6)$
0·01	0·20	0·90
0·01	2·00	0·95
0·02	0·20	1·00
0·02	2·00	1·00
0·05	0·20	2·00
0·05	2·00	2·10
0·25	1·00	3·00
0·25	2·00	3·05
0·40	2·00	3·10

When the system was studied in more detail by examining dose against yield plots the results in the Figure were obtained. At $[C_3H_8]$ = 0·025% the plot is curved from the lowest measurable yield of ethane whereas at the intermediate concentration the rate of formation of ethane is initially linear. At $[C_3H_8]$ = 1·0% the rate of formation of ethane is linear up to the highest dose used. The Figure also shows that in the case of the mixture containing 0·1% propane the rate of formation of ethylene increased from *G ca.* 0·5 at low dose to *G ca.* 1 at the highest dose.

These results demonstrate that there is no direct competition, in the concentration range used, between propane and oxygen for the ionic precursors of ethane (the methyl radical route to ethane is of course scavenged by oxygen). The results do, however, support the belief that the oxidation products (H_2O, CH_3OH, C_2H_5OH, CH_3OOH, *etc.*) can compete for the CH_5^+ and $C_2H_5^+$ ions with a consequent reduction in $G(C_2H_6)$ as the radiolysis proceeds and the oxidation products build up to concentrations at which they can compete with added propane. The increasing rate of formation of ethylene as the radiolysis proceeds is also in accord with this view since this is a measure of the extent of the reaction of $C_2H_5^+$ with H_2O or other proton-accepting oxidation products.

TABLE 2

γ-Radiolysis of CH_4–O_2 (2%)–C_3H_8 (0·025%) *mixtures: effect of methane oxidation products on* $G(C_2H_6)$ (*total dose* 2·0 × 10^{19} ev $ml.^{-1}$)

Oxidation products added (molecules × 10^{-18})	$G(C_2H_6)$
0·57	1·0
1·07	0·72
2·24	0·43
4·55	0·08

Composition of oxidation products: $G(CH_3OOH)$ = 3·7; $G(CH_3OH)$ = 1·0; $G(C_2H_5OH)$ = 0·24; $G(HCHO)$ = 0·3.

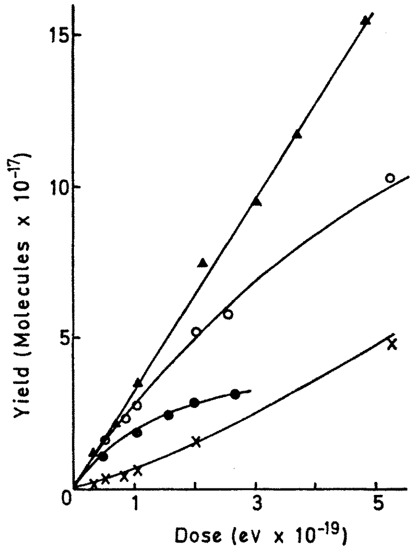

FIGURE. *γ-Radiolysis of* CH_4–O_2 (2%)–C_3H_8 *mixtures* (*atmospheric pressure; vessel vol.* 600 ml.): *dose yield plots for* C_2H_6 *at different* C_3H_8 *contents* (●) 0·025%; (○) 0·1%; (▲) 1%; (×) C_2H_4 *yield at* 0·1%.

Further evidence for the role of the oxidation products in reducing $G(C_2H_6)$ was obtained by irradiating CH_4–O_2 (2%) mixtures for varying times, trapping out the condensable products, adding them to a fresh CH_4–O_2 (2%)–C_3H_8 (0·025%) mixture and re-irradiating to a constant dose of 2×10^{16} ev ml.$^{-1}$. As Table 2 shows, the yield of ethane was increasingly reduced as the amounts of oxidation products added were increased.

In these experiments we have been unable to distinguish between the relative effects of the different oxidation products. In particular, although water is suspected to be an oxidation product we have been unable to detect it as the probable yields lie below the present limits of our gas chromatography apparatus. Both methanol and ethanol have high proton affinities and are presumably capable of being involved in proton-transfer reactions with CH_5^+ and $C_2H_5^+$. The behaviour of the major oxidation product methyl hydroperoxide in this respect is not known.

Oxygen has been widely used as a radical scavenger in hydrocarbon radiolysis and it seems probable that effects due to the accumulation of oxidation products may also be important in systems other than the one reported here.

The irradiations were carried out with γ-radiation from a 17,000 Ci cobalt source. The gas mixtures, at room temp. and pressure, were contained in cylindrical borosilicate glass vessels of about 600 ml. volume. Analyses were carried out by gas chromatography on a column of di-2-ethyl hexyl sebacate (2½% on silica gel) using a flame ionisation detector.

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[1] P. Ausloos, S. G. Lias, and R. Gorden, jun., *J. Chem. Phys.*, 1963, **39**, 3341.

[2] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, 1965, **87**, 4242.