This Week's Citation Classic

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Knox J H. A new mechanism for the low temperature oxidation of hydrocarbons in the gas phase. *Combust. Flame* **9**:297-310, 1965.
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The gas phase oxidation of an alkane (C_2-C_5) produces the conjugate alkene as the major product in the temperature range 300-400°C. Involvement of this alkene is crucial to the subsequent progress of the reaction and enables initially formed HO_2 radicals to be converted to the much more reactive OH radicals. [The *SCI*® indicates that this paper has been cited in over 100 publications since 1965, making it the most-cited paper ever published in this journal.]

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"The new mechanism for low temperature oxidation of alkanes proposed in this paper arose out of investigations which started under R.G.W. Norrish in 1947, when I went up to Cambridge to study for my PhD degree. We used a flow system to study the 'cool-flame oxidation of propane,' condensing out liquid products at -80°C and collecting uncondensed gaseous products in a bulb. The products were analysed by standard volumetric methods or by the then current gas handling techniques.[1] Both methods were laborious, time-consuming, insensitive, and relatively unselective. The objective of this work, to put it bluntly, was to substantiate the 'aldehyde theory' proposed by Norrish[2] and to discredit the rival 'peroxide theory.'[3] Unfortunately, things did not work out quite as hoped! Neither theory showed much correlation with reality. Higher aldehydes, which Norrish proposed were the key autocatalytic agents, were minor products, and the 'peroxides,' favoured by the rival school, were mainly condensation products of H_2O_2 and aldehydes, probably formed in the cold trap.

"It was clear that no real progress could be made with the analytical methods then in existence. Something radically new was required, and gas chromatography (GC) provided the answer. On my appointment to a lectureship in Edinburgh, I applied GC to study the mechanism of the isothermal combustion of hydrocarbons between 300 and 400°C.[4] A key discovery was soon made.[5] At alkene conversions below about one percent, the major products (> 80 percent) from oxidation of ethane, propane, and isobutane were always the alkenes having the same number of C-atoms as the parent alkane. Oxygenated products, while formed in parallel, were always present in very small quantities relative to the alkene. If any product was responsible for the autocatalysis of alkane combustion it was most likely to be alkene. It was also shown that carbonyl compounds were the primary products of oxidation of the alkenes[6] so the main steps in the combustion of an alkane, HABH, were:

$$HABH + O_2 \longrightarrow AB + H_2O_2$$
$$AB + O_2 \longrightarrow AO + BO$$

(AB = alkene; AO, BO = aldehyde or ketone)

"It was further established that the composition of the oxygenated products were strongly dependent on the nature of the walls of the reaction vessel[6] and therefore that the elaborate attempts which were being made around 1965 to explain their formation by homogeneous unimolecular reactions of peroxy radicals (HABOO) were misconceived.

"The paper assembles these ideas. HO_2 radicals are first formed by hydrogen abstraction by oxygen from alkyl radicals HAB.

$$HAB + O_2 \longrightarrow AB + HO_2$$

It is proposed that these then react mainly by addition to AB followed by further addition of oxygen, reaction with a second HO_2 radical, and final homogeneous decomposition of the diperoxide HOOABOOH to give the carbonyl compounds AO and BO. The main steps are then:

$$AB \xrightarrow{+HO_2} ABOOH \xrightarrow{+O_2} OOABOOH \xrightarrow{+HO_2}$$
$$\longrightarrow HOOABOOH + O_2$$
$$\longrightarrow HO + AO + BO + OH$$

"In this way HO_2 radicals are converted to OH radicals which can abstract H atoms and propagate oxidation chains via the alkene as intermediate.

"The wide citation of this paper probably arises because it gives a clear and concise account of a mechanism of alkane combustion based upon detailed chemical analysis, which explained all the major features of these complex reactions as known in 1965. Furthermore, its conclusions are still broadly valid today."

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4. **Falconer J W & Knox J H.** The high-temperature oxidation of propane. *Proc. Roy. Soc. A* **250**:493-513, 1959.
5. **Knox J H.** Some features of the oxidation of propane and ethane at 318°C. *Trans. Faraday Soc.* **55**:1362-74, 1959.
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