XCIX.—The "Uniform Movement" of Flame in Mixtures of Ethylene, Propylene, or Butylene with Air.

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THE uniform movement of flame, the first stage in its propagation from the open towards the closed end of a tube, provides the most convenient means for comparing the speeds of inflammation of various gas mixtures. This communication presents measurements of the speed of uniform movement of flame in the whole range of inflammable mixtures of air with ethylene, propylene, or butylene. The experiments were carried out in a horizontal tube of $2 \cdot 5$ cm. diameter, and the results are therefore directly comparable with those already obtained for carbon monoxide and the lower members of the paraffin series (Payman, J., 1919, **115**, 1446, 1454), for acetylene (Mason and Wheeler, *ibid.*, p. 578), and for hydrogen (Georgeson and Hartwell, J., 1927, 265). The limits of inflammability of the olefins named, in the conditions stated, were determined incidentally.

The apparatus and experimental procedure were similar to those described (J., 1927, 265). The use of a tube of transparent quartz, 2.5 cm. in diameter and 150 cm. long, and a quartz lens, enabled flame photographs to be taken over the whole inflammable range of each gas. The combustible gases, obtained commercially in cylinders, were purified by repeated liquefaction and fractional distillation. The butylene was a mixture, in approximately equal proportions, of Δ^{α} - and Δ^{β} -isomerides (W. L. Wood, private communication). Mixtures with air were prepared over mercury in iron gas-holders and, except when otherwise stated, the gases were roughly dried by passage over calcium chloride, and contained less than 0.1% of water vapour. A sample of each mixture was taken for analysis from the tube prior to ignition. The mixture was fired by passing a spirit-lamp flame, 2-3 cm. high, across the opened flanged end of the tube. Photographs were taken during the progress of the flames over a distance of 12.5-38.5 cm. from the point of ignition.

The values obtained from the photographic records are given in Table I. In each case, the first column contains the percentage (by vol.) of the hydrocarbon, and the second, the speed of uniform movement (in cm./sec.).

Fig. 1 shows the results as speed-percentage curves, together with the curves for the first five paraffin hydrocarbons. For the olefins

TABLE I.

The Speed of Uniform Movement of Flame in Mixtures. (Horizontal propagation in a tube 2.5 cm. in diameter.)

⁽i) Ethylene-air mixtures.

| C₂H₄, | | $C_{2}H_{4}$, | | $C_{2}H_{4}$, | |
|--------------|----------------|----------------|--|----------------|----------------------------|
| %. | Speed. | %. | Speed. | %. | Speed. |
| 3.26 | No propagation | | (112.7, 114.7, | 8.50 | 156.4 |
| 3.30 | 20.6 | 7.05 | 113.8, 156.1, | 8.75 | $141 \cdot 4, 143 \cdot 9$ |
| 3.34 | 23.4, 22.8 | | $163 \cdot 3, 160 \cdot 6$ | 9.01 | $131 \cdot 8$ |
| 3.36 | 25.8, 25.5 | T 04 | (164.8, 165.8, | 9.47 | 113.5 |
| 3.48 | 29.9, 28.9 | 1.24 | 168.4, 168.7 | 9.51 | 107.3 |
| $4 \cdot 14$ | 54.0, 54.8 | 7.27 | 165.0, 166.5 | 9.88 | 92.5, 91.5 |
| 4.33 | 61.0, 61.9 | 7.29 | 162.6, 166.5 | 10.25 | 73.2, 74.4 |
| 4.69 | 74.0, 73.3 | 7.31 | $162 \cdot 3, 163 \cdot 6$ | 11.20 | 47.2, 47.5 |
| 4.97 | 88.5, 87.5 | 7.42 | $165 \cdot 1, 167 \cdot 2$ | 12.10 | $35 \cdot 6, 36 \cdot 3$ |
| 5.07 | 92.1, 93.1 | T FO | ∫164.7, 165.7, | 12.95 | 30.1, 31.6 |
| 5.42 | 105.6 | 1.98 | 163.2 | 14.49 | $23 \cdot 6, 24 \cdot 0$ |
| 5.84 | 119.8, 121.0 | 7.61 | $161 \cdot 8, 163 \cdot 4$ | 14.66 | 22.7 |
| 6.39 | 143.7, 145.1 | 7.66 | $165 \cdot 2, 165 \cdot 8$ | 15.50 | 22.7 |
| 6.40 | 145.8 | 8.06 | $155 \cdot 1, 157 \cdot 3$ | 17.84 | 19.2 |
| 6.81 | 157.6, 155.8 | 8.11 | 162.5 | 18.06 | 18.4 |
| 6.88 | 159.4, 158.9 | 8.19 | $160 \cdot 2, 157 \cdot 2$ | 18.22 | 18.5 |
| 7.02 | 159.7, 153.6 | 8.32 | $\begin{cases} 151.6, 155.9, \\ 158.2 \end{cases}$ | 18.30 | No propagation |

(ii) Propylene-air mixtures.

| | C ₂ H ₆ , | | C_3H_6 , | |
|--------------------------|---------------------------------|--|--|--|
| Speed. | %. | Speed. | %. | Speed. |
| (a) No propag- | 4.83 | 98.0, 98.9 | $5 \cdot 62$ | 94.0 |
| { ation | 4.95 | ∫ 101.0, 98.2, | 5.84 | 84.1, 90.8 |
| (b) 20.85 | | 1 99.6 | 6.01 | $82 \cdot 2, 82 \cdot 2$ |
| (28.4, 29.1, | 5.04 | 100.7, 99.6 | 6.31 | 73.3, 73.6 |
| 30.1 | 5.14 | 101.9, 100.9 | 6.40 | 65.5, 68.5 |
| 38.7, 38.8 | 5.24 | 100.0, 99.2 | 6.68 | 57.1, 57.8 |
| 51.9, 52.7 | 5.28 | 101.5, 102.0 | 7.10 | 39.9, 40.6 |
| 70.9, 68.8 | r 07 | ∫ 99·8, 99·1 | 7.46 | 31.8, 32.3 |
| 80.1, 81.9 | 5.37 | <u>)</u> 99∙3 | 7.56 | No propagation |
| $93 \cdot 1, 91 \cdot 0$ | 5.42 | 99.6, 99.0 | | 0 |
| | | $ \begin{array}{c} & C_{3}H_{6}, \\ Speed. & \%, \\ (a) No propag. & 4.83 \\ ation & 4.95 \\ (b) 20.85 & 5.04 \\ (b) 20.85 & 5.04 \\ 30.1 & 5.14 \\ 38.7, 38.8 & 5.24 \\ 51.9, 52.7 & 5.28 \\ 70.9, 68.8 & 5.37 \\ 80.1, 81.9 & 5.37 \\ 93.1, 91.0 & 5.42 \\ \end{array} $ | $ \begin{array}{c} & C_3H_6, \\ & \text{Speed.} & \%. & \text{Speed.} \\ & \%. & \text{Speed.} \\ & \text{(a) No propag-} & 4\cdot83 & 98\cdot0, 98\cdot9 \\ & \text{ation} & 4\cdot95 & \left\{ \begin{array}{c} 101\cdot0, & 98\cdot2, \\ 99\cdot6 \\ & 101\cdot0, & 98\cdot2, \\ 99\cdot6 \\ & 50\cdot1 & 5\cdot14 & 101\cdot9, 100\cdot9 \\ 38\cdot7, 38\cdot8 & 5\cdot24 & 100\cdot0, & 99\cdot2 \\ 51\cdot9, 52\cdot7 & 5\cdot28 & 101\cdot5, 102\cdot0 \\ 70\cdot9, 68\cdot8 & 5\cdot37 & \left\{ \begin{array}{c} 99\cdot8, & 99\cdot1 \\ 99\cdot3 \\ 99\cdot3, & 93\cdot1, & 91\cdot0 \\ 99\cdot4, & 99\cdot6, & 99\cdot0 \end{array} \right. \end{array} \right. $ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

(iii) Butylene-air mixtures.

| C ₄ H ₈ , | | CAH s, | | C₄H _s , | |
|---------------------------------|---------------------|--------|--------------------------------------|--------------------|-----------------|
| %. | Speed. | %. | Speed. | %. | Speed. |
| | ((a) No propag- | 3.65 | $92 \cdot 4, 93 \cdot 5$ | 4.65 | 81.0, 80.1 |
| 1.93 | { ation | 3.78 | $94 \cdot 5, 93 \cdot 5$ | 4.94 | 68·1, 69·3 |
| | (b) 18·9 | 3.91 | 99.0 | 5.25 | 53.7, 53.5 |
| $22 \cdot 2$ | `35 ·2, 33·0 | 3.94 | 96.9, 96.6 | 5.65 | 39.2, 39.2 |
| 2.64 | 53.5, 50.6 | 4.08 | 96.0, 98.2 | 5.96 | 32.5, 32.6 |
| 2.83 | 63.6 | 4.22 | $95 \cdot 7, 94 \cdot 6, 96 \cdot 6$ | 6.09 | Propagation for |
| 3.01 | 68.5, 68.1 | 4.60 | 83.3, 82.7 | | 55 cm. only |
| 3.35 | 81.4 79.6 83.1 | | , | | · |

as well as for the paraffins the mixtures of maximum speed of uniform movement contain less air than is required for complete combustion. For paraffin hydrocarbons, this has been attributed to the influence of mass action (Payman, J., 1920, **117**, 48), and the same explanation may be adopted for the olefins.



Table II shows the limits of inflammability in a horizontal glass tube, 2.5 cm. in diameter and 150 cm. long, and also the composition and speed of uniform movement of the maximum speed mixture of each hydrocarbon.

TABLE II.

| | maximum speed | | | | | |
|---------------|------------------|--------|-------------------------|-------------|--------------|--|
| | Lim | its of | mix | | | |
| | inflammability : | | | Theoretical | | |
| | hydrocarbon, %. | | · | Speed of | for complete | |
| | | | Hydro- | uniform | combustion : | |
| | Lower | Upper | carbon, | movement | hydrocarbon, | |
| | limit. | limit. | %. | (cm./sec.). | %. | |
| Ethylene-air | 3.30 | 18.25 | 7.3 - 7.7 | 166 | 6.51 | |
| Propylene-air | 2.58 | 7.50 | 5.0 - 5.3 | 101 | 4.44 | |
| Butylene-air | 1.93 | 6.0 | $3 \cdot 9 - 4 \cdot 1$ | 98 | 3.36 | |
| - | | | | | | |

A peculiarity of the ethylene-air curve is the flattening towards the upper limit.

Chapman (J., 1921, 119, 1677) has given measurements of the speed of uniform movement of flame in ethylene-air mixtures. His results are from 14 to 28% lower than ours. In the course of attempts to explain the difference we found : (i) that the speeds of flame in mixtures of ethylene and air saturated with water vapour

at laboratory temperature were only slightly lower than the speeds in mixtures roughly dried by passage over calcium chloride; (ii) that ethylene, prepared in the laboratory by Newth's method (J., 1901, **79**, 915) and purified by condensation of alcohol and ether vapours in vessels cooled by solid carbon dioxide and ether, gave the same flame speeds as those recorded in Table I; (iii) that the speed of uniform movement of ethylene-air mixtures was not affected by variations in length of the explosion tube.

It seemed that the cause of the difference might be found in the methods of registering the flame speeds, for Chapman had recorded automatically the time interval between the fusion of successive screen wires, whereas we had used the photographic method. The latter is now regarded as the more trustworthy, for screen wires are obstacles in the path of the flame, and, moreover, they record only the mean speed of flame between one wire and the next. We therefore fitted a tube with screen wires and made measurements by both methods simultaneously, over the same length of tube. The speed measurements agreed with one another, but were some 3-4 cm./sec. higher than corresponding figures in Table I, a result which the photographs explained by showing a small increase in flame speed near the wires, which presumably function as small constrictions in the tube. So far as we could discover, therefore, the differences between Chapman's figures and ours are not attributable to an error in either method of measurement of flame speeds.

A clue to an explanation was provided by the flame speed of the 7.05% ethylene-air mixture, which was found to be either 114 or 160 cm./sec., approximately. The lower speed was obtained when the ground-glass cap at the firing end of the tube was removed in such a manner as to cause mechanical disturbance of the mixture. Low flame speeds were also regularly induced by firing the mixture while the tube was still "ringing" after a rather sharp blow; in these circumstances speeds of 110-120 cm./sec. were obtained with a maximum speed mixture instead of the normal speed of 166 cm./sec. Mason and Wheeler (J., 1920, 117, 1233) observed a similar effect in the upward propagation of flame in certain methane-air mixtures, and attributed the effect to resonance. We are inclined, therefore, to explain the comparative slowness of Chapman's flames as being due to the incidence of resonance during part of their progress between the screen wires. The photographic registration of flame speeds prevents such an effect from being overlooked.

The upper limit of ethylene in air was found to be 18.25%. At about 14% of ethylene, the colour of the flame changed from bluish-green (below 14%) to yellow (14-18%), and carbon was liberated.

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