Atomic Hydrogen Flames

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A NUMBER of gas-phase chemiluminescent reactions at low pressure attributed to atomic hydrogen appear in the literature.[1] Recently one of these, the reaction between atomic hydrogen and acetylene, has been shown to be "dark," the formerly observed C_2, C_3, and CH emissions being due to oxygen atoms originating from water vapour present in the discharge used to produce hydrogen atoms.[2] Since it is now possible to make hydrogen atoms without the use of water as catalyst or wall poison, these atomic flames have been re-examined.

The apparatus was similar to that previously described.[2] Atomic hydrogen was produced by a 2450-Mc. electrodeless discharge in a 95% He : 5% H_2 mixture which had passed through two liquid-nitrogen cold traps. The walls of the discharge tube, light horn, and spherical Pyrex reaction vessel were poisoned against hydrogen atom recombination with dimethyldichlorosilane. Fuel vapours were carried by helium from a cold trap at known temperature. The gases were supplied by Air Products Ltd.: hydrogen, < 1 p.p.m. of oxygen, < 200 p.p.m. of nitrogen; helium, $< 0{\cdot}7$ p.p.m. of oxygen, < 6 p.p.m. of nitrogen; nitrogen, < 10 p.p.m. of oxygen, < 1 p.p.m. of hydrogen. Reagents were Hopkin and Williams Spectrosol grade, except for trichloroethylene (Surgical), formaldehyde (Analar) and glyoxal (G.P.R.). The discharge was carefully shielded and the background against which a flame was viewed was matt black. Pressures in the flame zone were in the range 0·1 — 5 torr.

When dry atomic hydrogen was added to carbon suboxide,[3] methanol, ethanol, formaldehyde, or glyoxal no flame was observed, even with the

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[1] A. G. Gaydon, "Spectroscopy of Flames," Chapman and Hall, London, 1957, p. 256.
[2] K. D. Bayes and R. E. W. Jansson, *Proc. Roy. Soc.*, 1962, *A*, **282**, 275.
[3] K. D. Bayes and R. E. W. Jansson, unpublished work.

dark-adapted eye. Faint orange chemiluminescence was observed with chloroform, carbon tetrachloride, and trichloroethylene, and brighter, yellower, chemiluminescence with bromoform. 5-Hour exposures of pre-sensitised Kodak I.R.E.R. and Ilford Long Range plates on a Hilger Medium Quartz spectrograph showed 17 bands of the CN red system, and the (0,0) and (0,1) bands of the CN violet system. In addition the bromoform flame showed the (1,0) violet band. No other bands could be detected. Flames of the halogenated hydrocarbons reacting with the products of a nitrogen discharge emitted all the above CN bands and many others in the red system; these reactions have been discussed in detail by Bayes.[4] The weak CN emission observed above, therefore, must have been due to the 200 p.p.m. impurity of nitrogen in the hydrogen. Purer hydrogen was not readily available.

When the helium–hydrogen mixture was untrapped the flames of the halogenated hydrocarbons showed the emissions listed by Gaydon. Under these conditions the other fuels did not give rise to chemiluminescence. However, except for glyoxal, flames were apparent when the wall poison had been removed and wet hydrogen, or water vapour, was passed through the discharge. With glyoxal any emission was less obvious than the candoluminescence due to hydrogen atom recombination on the pyrex surfaces. Since the flames were weak, and a Beck 10° hand spectroscope showed them to be qualitatively the same as described by Gaydon, no attempt was made to photograph them. By analogy with the previous work,[2] and from comparison of the published tables of reactions of the same fuel with products of water, atomic oxygen and (wet) atomic hydrogen,[1] these flames are probably initiated by oxygen atoms.

Carbon disulphide showed a dim blue flame with dry atomic hydrogen. Spectra taken with a 0·5 m. Ebert grating monchromator and E.M.I. 9558 B photomultiplier showed only S_2 bands superimposed on a continuum in the region 2900 — 6000 Å. Although Pyrex nominally cuts-off at 3200 Å, a signal was detectable down to 2900 Å in the second order of the grating (blazed for 5000 Å, 1st order). When the hydrogen–helium mixture was untrapped the total intensity increased by about 20% for the same flow conditions and all the bands became more prominent, but the biggest change was the noticeable increase in total intensity in the region 2900 — 3600 Å. A flame of oxygen atoms (from an oxygen — helium discharge) reacting with carbon disulphide under comparable conditions showed a relatively intense continuum, which could not be resolved, apparently peaking in just this region. The greater part of the increase, therefore, may be ascribed to the side reaction $O + CS_2$. Gaydon and Wolfhard[5] have shown that with (moist) hydrogen bands of S_2 with high values of v^1, lying in the range 2800 — 3000 Å, appear to be relatively more intense than in the S_2 emission from an atmospheric carbon disulphide flame.[6] The bands lie within the pyrex absorption region, and only a few were observed in low intensity, but the (8,1), (7,1) and (6,1) bands stayed about the same, while the (0,9) and (0,10) bands at λλ 3939 and 4046 increased four times in intensity when the traps were removed. This suggests that with dry hydrogen bands of high v^1 will be even more abnormally intense than Gaydon and Wolfhard have found; work will be extended to the quartz region when greater detector sensitivity is available.

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[4] K. D. Bayes, *Canad. J. Chem.*, 1961, **39**, 1074.

[5] A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc.*, 1952, *A*, **213**, 366.

[6] A. Fowler and W. M. Vaidya, *Proc. Roy. Soc.*, 1931, *A*, **132**, 310.