CCXXIX.—*The Light Emission from the Phosphorescent Flames of Ether, Acetaldehyde, Propaldehyde, and Hexane.*

By Harry Julius Emeléus.

In 1882 (J., **41**, 363), W. H. Perkin, senr., showed that when a mixture of air with the vapour of ether or one of a number of other organic substances was allowed to impinge on a heated copper ball, a very faintly luminous bluish flame played round the surface, provided that the latter was not quite hot enough to cause normal ignition. Interest in this phenomenon was revived by the discovery that substances giving such a flame have a tendency to promote "knocking" when used as motor fuels, whilst many "anti-knocks" inhibit the flames. The chemical changes were first studied by Perkin (*loc. cit.*), who recognised that little carbon dioxide was formed. Callendar found that in the combustion of a hexane–air mixture at 300°, 67% of the product consisted of "aldehydes," the other products being carbon monoxide and dioxide, hydrogen, ethylene, unsaturated substances, water, acids, and tar. Later, Mardles and his co-workers published similar analyses of the reaction products from ethyl ether, acetaldehyde, amylene, and hexane (J., 1928, 812; *Trans. Faraday Soc.*, 1928, **24**, 574), and Berl, Heise, and Winnacker isolated acraldehyde from the oxidation products of hexane (*Z. physikal. Chem.*, 1928, **139**, 453). The nature of the light emission from these flames attracted little attention; indeed, it was not clear whether the normal flame spectrum was to be expected, whether the different flames would give different spectra, or whether all would give some new spectrum characteristic of the phosphorescent combustion, just as the Swan bands and water bands characterise the hot flames. The spectrum of the phosphorescent ether flame has already been described (Emeléus, J., 1926, 2948), and this investigation is an extension of that observation.

The Spectra of the Phosphorescent Flames of Acetaldehyde, Propaldehyde, and Hexane.

Acetaldehyde and propaldehyde were redistilled from material supplied by the British Drug Houses, and boiled at 20—22° and 67—69° respectively. The *n*-hexane, prepared by fractionating commercial hexane in a 5-ft. column filled with copper turnings, boiled at 68·8—69·0°. The liquids and air used were all undried. The apparatus and method used in photographing the above spectra were the same as those used for ether (Emeléus, *loc. cit.*). A small Hilger quartz spectrograph and a large-aperture quartz instrument were used (Emeléus and Purcell, J., 1927, 788). Exposures in the first case varied from 150 to 250 hours, and from 20 to 80 hours for the faster instrument. Approximate temperature measurements were made by inserting the bulb of a small thermometer in the luminous zone. The temperatures recorded were for acetaldehyde 220—250°, for propaldehyde 290—310°, and for hexane 300—360°. In each case the luminosity first became noticeable in the form of pulses as the silica tube AB (Fig. 2, *loc. cit.*) was gradually heated, and then gave place to a steady bluish-white glow. At higher temperatures intermittent flashes of blue flame passed down the tube. These were visible in daylight, and were taken to indicate the beginning of normal ignition. The steady glow was observed over a temperature range of approximately 100°, and could be maintained without difficulty during the long periods needed to give satisfactory photographs. The nature of the flame did not appear to depend on conditions (*e.g.*, it was not appreciably altered by cooling the bubblers containing hexane in ice), but the composition of the vapour–air mixture was not controlled.

The phosphorescent flames of acetaldehyde, propaldehyde, and hexane all gave the same band spectrum, consisting of a series of bands degraded towards the red between 5000—3360 Å. The plates were measured and also compared directly, and the spectrum was proved to be identical with that previously described for the phosphorescent ether flame. The wave-lengths of the band heads for the latter have already been recorded (*loc. cit.*). There was no indication of other band systems.

As far as has been ascertained, this spectrum does not correspond with any hitherto recorded system associated with carbon. An attempt was made to excite it by passing a discharge through a stream of acetaldehyde vapour at a pressure just high enough to maintain a discharge, external electrodes being used, but this gave no indication of the bands. There is a certain correspondence with the " blue bands " described by Marsh in the Tesla spectra of a number of organic substances (J., 1923, **123**, 2147), but this is not sufficient to establish the identity. The problem of associating the light emission with some definite stage of the reaction is one which is made more difficult by the fact that the end products afford but little indication of the intermediate stages. One possibility, however, appeared to warrant further investigation : " aldehydes " are known to be among the reaction products in each case. Now the phosphorescent flame of acetaldehyde itself gave the characteristic glow spectrum, and it was thought that in the phosphorescent flames of ether, propaldehyde, and hexane, acetaldehyde might be formed as an intermediate. It was first shown that acetaldehyde was not completely oxidised in its phosphorescent flame. The reaction products of the other three flames were then examined for acetaldehyde by Stock's method of vacuum fractionation (*Ber.*, 1914, **47**, 154; 1917, **50**, 989; 1918, **51**, 983).

Investigation of the Reaction Products.

The following determinations of the vapour pressures of acetaldehyde, ether, and propaldehyde at low temperatures were made for subsequent use in identifying these substances during the fractionation. The same pair of pentane-filled thermometers was used throughout this work. Values for hexane are given in Landolt–Bornstein's tables.

Acetaldehyde.

Temp.	−97°	−74°	−59°	−48°	−37°	−23°	−14°	0°
V. p. (mm.)	3	7·5	19	33	59	103	171	337

Ether.

Temp.	−65°	−54°	−94°	−34°	−26°	−19°	−14°	−8°	0°
V. p. (mm.)	2	5	9·5	21	37	55	77	114	190

Propaldehyde.

Temp.	−55°	−39°	−27°	0°
V. p. (mm.)	7	16	29	133

Three experiments were carried out to determine if acetaldehyde vapour was completely oxidised. An air stream from a cylinder was divided and measured by two calibrated flow-meters. That through one passed through acetaldehyde in a weighed bubbler, cooled in ice. From the readings of the flow-meters and the loss in weight of the bubbler, the mean composition of the gas mixture was calculated. The vapour–air mixture passed through a heated tube of Jena combustion glass (30 cm. long, 1 cm. internal diameter), the furnace temperature being recorded by a thermometer attached to the outside of the tube. The reaction product was collected in three **U**-tubes, the first of which was cooled in ice, whilst the others were immersed in liquid air. The third **U**-tube was fused on to the vacuum fractionation apparatus already described (Emeléus, J., 1928, 1944). When a sufficient quantity of the reaction product had collected, the flow-meters were sealed off, and the whole apparatus (including the fractionation apparatus) was evacuated. The reaction product was then distilled into the fractionation apparatus.

The method of splitting up the mixture for the purpose of isolating acetaldehyde, if present, was to distil off in vacuum a series of fractions at gradually increasing temperatures, so chosen that the vapour pressure of the mixture was always 1—3 mm. The lowest distillation temperature employed was − 130° to − 120°, at which carbon dioxide and similar products were completely removed, whilst acetaldehyde was non-volatile. The low-temperature baths were made by cooling an ether–alcohol mixture (2 : 1 by vol.) with liquid air. The **U**-tube E (Fig. 2, J., 1928, 1944) was immersed in liquid air, and in the high vacuum there was a rapid distillation from D (containing the mixture) to E, which was continued as long as appreciable quantities of condensate formed in E. The connecting valve V′ (Fig. 2, *loc. cit.*) was then closed, the vapour pressure of the condensate in E recorded at suitable temperatures for purposes of identification, and the volume measured, after which the fraction was stored. The temperature of the bath round D was now raised until the vapour pressure was again 1—3 mm., a second fraction was distilled off and examined, and so on. Difficulty arose when the mixture to be fractionated became solid, in that volatile material was held back until the melting point was reached. This was partly overcome by melting the solid prior to distillation, and then recooling it to the distillation temperature. In this way most of the volatile material was evolved and not appreciably reabsorbed. The alternative method of fractional condensation was not employed. In some cases certain fractions were recombined and refractionated to obtain a better separation.

In each of the three experiments with acetaldehyde it was possible by the above method to isolate fairly pure unchanged acetaldehyde. Details of the first of these experiments are given below as being typical of these and subsequent separations.

Combustion of Acetaldehyde, I.

Temp. = 240° ± 2°. Concentration = 10% by vol.
Wt. of acetaldehyde oxidised = 1·37 g.

The reaction product was divided into the following fractions :

	Temp.	Time.	Vol. of distillate.
(1)	−118° to −104°	45 mins.	225 c.c. (gas)
(2)	− 98° to − 80°	55 ,,	6·0 ,,
(3)	− 80° to − 70°	55 ,,	8·5 ,,
(4)	Residue	—	1·30 c.c. (liquid)

Vapour-pressure measurements. The vapour pressure determinations made with the above fractions were as follows :

(2)	−60°, 24 mm.; −36°, 47 mm.; −25°, 73 mm.; −16°, 112 mm.
(3)	−63°, 55 mm.; −42°, 70 mm.
Residue	−29°, 22 mm.

Fraction (1), which distilled at a temperature below that at which acetaldehyde was appreciably volatile (about − 95°), contained carbon dioxide and other similarly volatile products, and was not further examined.

Fractions (2) and (3) were combined and refractionated, giving the following fractions :

	Temp.	Time.	Vol. of distillate.
(1A)	−94° to −90°	70 mins.	2·45 c.c.
(2A)	−90° to −85°	10 ,,	8·64 ,,
(3A)	Residue	—	1·80 ,,

The total volume of (2) and (3) was 14·5 c.c., whereas that of (1A), (2A), and (3A) was only 12·9 c.c. Similar losses of material were found to take place throughout this work and were attributed to polymerisation : after a series of distillations the U-tubes frequently contained small amounts of gum-like products.

The vapour-pressure measurements for the above fractions were as follows :

(1A)	−80°, 34 mm.
(2A)	−45°, 43 mm.; −37°, 50 mm.; −26°, 83 mm.; −21°, 106 mm.; −18°, 123 mm.
(3A)	−65°, 6 mm.; −55°, 11 mm.; −38°, 27 mm.

The values for (2A) lie just below the curve for pure acetaldehyde. The process of purification of the acetaldehyde was not carried beyond this point. The results of the other two experiments with acetaldehyde were of a similar nature, showing incomplete oxidation of the aldehyde, and all three are summarised below.

	Temp.	Wt. of aldehyde used, g.	Mixture strength.	Unchanged aldehyde, % (app.).
I	240°	1·37	10%	2
II	280—290	2·84	20	1
III	300	5·95	48	15

Results for Propaldehyde, Hexane, and Ether.—The observations with these substances were made in exactly the same manner. Three experiments with propaldehyde were carried out under the following conditions :

	Mixture strength, % by vol.	C_3H_6O used, g.	Temp.
I	27	1·13	260—270°
II	19	3·38	225
III	19 *	1·08	200

* Oxygen used instead of air.

In each of these experiments unchanged propaldehyde was isolated, but there was no acetaldehyde present in the oxidation product. A similar negative result was obtained in two experiments on the oxidation of hexane, although unchanged hexane was again isolated. The conditions of these experiments were as follows: Mixture strength, (1) 16%, (2) 14% by vol.; wt. of hexane used, (1) 2·51 g., (2) 4·57 g.; temp., (1) 300° ± 5°, (2) 370° ± 5°.

Two experiments were next made with ether, and in both cases acetaldehyde was definitely isolated. The conditions were as follows :

(1) Mixture strength, not recorded; temp., 250—270°; 0·40 c.c. of impure acetaldehyde isolated.

(2) Mixture strength, 55% by vol.; wt. of ether used, 3·54 g.; temp., 270°. In experiment (2), 0·33 c.c. of a liquid, with a vapour-pressure curve corresponding closely with that of acetaldehyde, was obtained; moreover, the fractions on each side of this (vol. = 0·72 c.c.) had vapour pressures near those of acetaldehyde, of which they contained a considerable proportion. The total quantity of acetaldehyde was estimated to be of the order of 10% of the weight of ether burned; and *ca.* 10% of the ether remained unoxidised and was separated from the reaction product.

These results leave little doubt as to the formation of acetaldehyde in the combustion of ether, but not in that of hexane and propaldehyde. Possibly the extension of the investigation to a wider range of concentrations and temperatures would have given positive results for the last-named substances also, or acetaldehyde may have been formed as an intermediate and then completely oxidised; an alternative is that it played no essential part in the luminous oxidation of hexane and propaldehyde. The following facts favour the latter view. The formulæ of the substances, as ordinarily written, show that, whereas acetaldehyde is a probable oxidation product of ethyl ether, there is no obvious reason why it should be formed in the incomplete oxidation of either of the other two substances. Mardles (*loc. cit.*), moreover, found that in the oxidation of hexane, lead tetraethyl and ethyl alcohol had a marked inhibiting action on the glow and chemical change, whereas in the oxidation of acetaldehyde their action was slight. At present, therefore, the evidence appears to indicate that acetaldehyde is not an essential intermediate concerned with the light emission in these reactions.

This subject still presents many unsolved difficulties. One of these is the question of the origin of the light emission. It is also quite unknown whether the light emission in these flames is a secondary and somewhat accidental effect, or whether the molecules which radiate are in any way connected with the "active" molecules and the "peroxides," the existence of which has been postulated in connexion with the mechanism of the reaction.

A further interesting point is the speculation that other flames of this type (*e.g.*, the phosphorescent flames of paraffin wax, turpentine, and amylene) will all be found to give this same spectrum, which may indeed prove to be characteristic of this type of combustion of carbon compounds.

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