CCCXCIV.—*The Spectra of the Phosphorescent Flames of Carbon Disulphide and Ether.*

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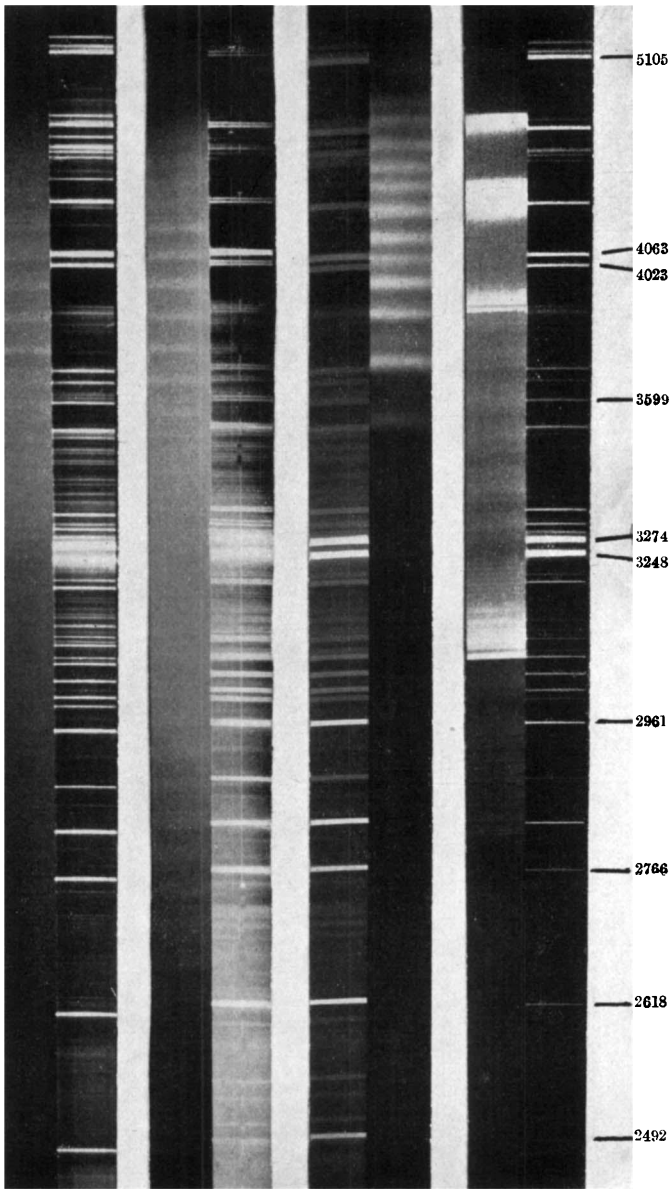
WHEN a combustible mixture containing carbon disulphide or ether is maintained at a temperature somewhat below the ignition point, a feebly luminous and relatively cool flame is produced, which is termed the *phosphorescent flame* by analogy with the well-known glow of phosphorus. This mode of combustion of ether was studied by Perkin (J., 1882, **41**, 363), who found that little carbon dioxide was formed and that aldehydes could be isolated. The phosphorescent flame of carbon disulphide was investigated by Dixon and Russell (J., 1899, **75**, 600) and by Dixon (*Rec. trav. chim.*, 1925, **44**, 305), and the partial nature of the oxidation was again demonstrated by the isolation of carbon monosulphide. The spectra of these flames have now been studied and compared with those of the substances burning normally.

A Hilger quartz spectrograph (size E. 6), for the loan of which the author is indebted to the Air Ministry, was used. Although this instrument has a small dispersion for wave-lengths greater than 3000 Å.U., it is rapid in action, and therefore well suited for the very feeble light sources examined.

Spectra of the Phosphorescent and Normal Flames of Carbon Disulphide.

Carbon disulphide was purified by distillation from paraffin wax and stored in contact with mercury. A transparent silica tube (15 cm. long and 1·4 cm. internal diameter), open at both ends, was heated electrically over the upper 5 cm. of its length by a winding of resistance wire; it was clamped vertically with the heated zone opposite the slit of the spectrograph, and a slow stream of nitrogen saturated with carbon disulphide was passed upwards through it from a jet. By adjusting the heating current the phosphorescent

FIG. 1.



a. *Carbon disulphide, normal flame spectrum—8 seconds.* b. *Carbon disulphide, phosphorescent flame spectrum—80 hours.* c. *Ether, phosphorescent flame spectrum—180 hours.* d. *Ether, normal flame spectrum—8 hours. Copper-arc reference spectra.*

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flame was produced, its temperature varying between 180° and 250°. Exposures of 40—250 hours were made on rapid plates, a copper-arc reference spectrum being superposed in every case. Photographs of the normal flame spectrum were obtained by burning nitrogen saturated with the vapour at a jet in an atmosphere enriched with oxygen.

The phosphorescent flame gave a band spectrum which shows certain differences from that of the normal flame. The bands were degraded towards the red, extending from 4530—3400 Å.U., and from 3100—2480 Å.U. Between these two groups the spectrum appeared to be continuous. The violet edges * of the bands in the first group were measured in the usual way. Those of shorter wave-length were measured by superposing an accurately divided scale on an enlargement, the latter values being checked on the negative by a wave-length scale. In Table I, the wave-length of the violet edge and the estimated relative intensity of each band are given; it is considered that the maximum error in the observations is 10 Å.U. above 3000 Å.U., and 5 Å.U. below.

TABLE I.

Wave-lengths of the violet edges of bands in the spectrum of the phosphorescent flame of carbon disulphide.

λ.	λ.	λ.	λ.	λ.	λ.
4530 (3)	4040 (8)	3550 (5)	2910 (4)	2765 (2)	2605 (2)
4440 (4)	3940 (10)	3500 (5)	2890 (1)	2730 (5)	2590 (3)
4350 (4)	3830 (7)	3410 (4)	2865 (5)	2715 (2)	2575 (3)
4310 (1)	3730 (7)	3100 (5)	2850 (2)	2700 (4)	2540 (2)
4250 (5)	3680 (2)	3045 (5)	2820 (5)	2680 (1)	2510 (1)
4190 (2)	3640 (6)	2995 (5)	2800 (2)	2655 (4)	2485 (1)
4150 (8)	3590 (5)	2955 (5)	2780 (4)	2620 (2)	

The spectrum of the normal carbon disulphide flame has been only incompletely described, perhaps owing to the heavy continuous background (compare Kayser, "Handbüch d. Spectroscopie," Vol. 6), but the present measurements establish its identity with that of the phosphorescent flame between 4530—3400 Å.U. A group of closely-spaced bands occurring between 3400—2900 Å.U. was not observed in the low-temperature flame. These, however, may have become merged in the continuous background. The bands below 3100 Å.U. were much less intense in the hot flame than in the glow, as illustrated by photographs *a* and *b* (Fig. 1). The former is a short exposure (8 secs.) of the normal flame spectrum, no bands being visible below 3400 Å.U. In the latter, which is an

* The violet edges are utilised in these measurements, both because they are sharp and because they are probably very close to the head of the band.

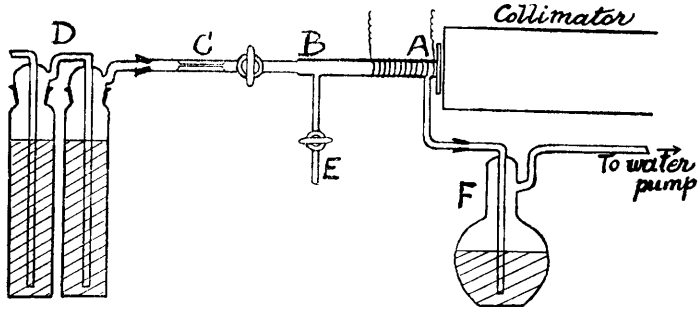
80-hour exposure of the phosphorescent flame spectrum, the group between 3100—2480 Å.U. is very little less intense than that above 3400 Å.U. A similar intensity variation was observed in the flame spectra of phosphorus and some of its compounds under various conditions (Emeléus, J., 1925, **127**, 1362).

Spectra of the Normal and Phosphorescent Flames of Ether.

Ether (B.P., pure for anæsthesia) was used without further treatment. The apparatus for producing the phosphorescent flame is shown in Fig. 2.

The tube AB (3·5 mm. internal diameter) had a quartz window cemented to the ground end A, and was heated electrically over a distance of 5 cm. from it by an external winding of resistance wire. The bubblers, *D*, containing ether, and the wash bottle, *F*, containing water, were connected by ground joints, no lubricant being used

FIG. 2.



either on these or on the taps. The capillary, *C*, was inserted to prevent the passage of a flame back into *D*. A stream of air saturated with ether vapour was drawn through the heated tube, the temperature of which was adjusted so that a phosphorescent flame resulted. Its brightness was increased on admitting a slow stream of air at *E*. By arranging *AB* in alinement with the collimator slit, satisfactory negatives were obtained in 180—250 hours, a moderately wide slit and rapid plates being used. The spectrum of the blue zone at the base of the normal hot ether flame was also photographed.

The phosphorescent ether flame gave a band spectrum, of which (*c*) is an enlargement (180 hours' exposure). The violet edges of the bands, which were degraded towards the red, were measured, the wave-lengths and estimated relative intensities being given in Table II. Owing to the indefinite nature of the edge, and the low dispersion, an error of 5—10 Å.U. may occur in certain cases.

TABLE II.

Wave-lengths of the violet edges of bands in the spectrum of the phosphorescent ether flame.

λ.	λ.	λ.	λ.	λ.
4930 (1)	4550 (7)	4210 (8)	3940 (9)	3670 (8)
4785 (3)	4425 (7)	4115 (8)	3840 (8)	3520 (4)
4675 (5)	4345 (7)	4040 (5)	3745 (3)	3385 (2)

Examination of the corresponding wave-numbers shows the existence of nearly constant differences, indicating that this spectrum has a normal structure. Certain of the heads correspond with sulphur bands, but no sulphur could be detected analytically, nor were the bands in question observed with long exposures of the normal ether flame. Since the spectra differ in general appearance, the coincidence was regarded as fortuitous.

The light from the low-temperature ether flame gives a totally different spectrum from that of the ordinary flame, of which (*d*) is an enlargement (8 hours' exposure). The latter is the well-known hydrocarbon flame spectrum, showing the " water bands " and the " Swan bands " prominently. It is concluded that the incomplete combustion (compare Perkin, *loc. cit.*) is the cause of the different light emission. No previous description of this spectrum can be traced.

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