THE FLAME SPECTRA OF SOME AROMATIC COMPOUNDS.

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1. Introductory.

The study of the spectra of flames is of interest not only from the point of band-spectroscopy but also from the chemical standpoint as these throw light on the mechanism of combustion. In an earlier paper by the author,\(^1\) a band-system which had previously received little attention was fully described: it had appeared with great intensity in the inner cone of the flame of ethylene, burning in air in a Smithells' flame-separator. These bands were provisionally attributed to HCO mainly on three grounds:—

1. The separation of successive bands in their vibrational analysis did not show any relationship to any of the known separations in the spectra of \(\text{C}_2\), \(\text{CH}\) and \(\text{HO}\) which accompany the new bands in the ethylene flame, nor to those of \(\text{CO}\), or of formaldehyde.  
2. The constants in the formula representing the bands in question had a striking resemblance to those of the \(\beta\)-bands of \(\text{NO}\). If they were assumed to originate in \(\text{HCO}\), this similarity could be explained on Mecke's principle of isosterism.  
3. The presence and great intensity of the bands particularly in ethylene could be accounted for by supposing that in the process of combustion the \(\text{O}_2\) molecule entered the ethylene molecule and breaking the double bond in it formed two \(\text{HCO}\) groups—a conclusion important from the point of view of the mechanism of combustion. This supposition of the direct incorporation of the \(\text{O}_2\) molecule in a hydrocarbon molecule received additional support from a study of the spectra of other flames of aliphatic carbon compounds which the author had carried out in Professor A. Fowler's laboratory. Full details will be published in due course but the main facts may be referred to here briefly.

The inner cone of the flame of acetylene which has a triple bond gave the \(\text{HCO}\) bands though not with as great an intensity as with ethylene. The triple bond makes the molecule unstable and in consequence a great

intensity of the HCO bands could hardly be expected. The inner cone of the methane flame also yielded the HCO bands, somewhat faintly: the four bonds of carbon are satisfied and hence the entry of the O₂ molecule in methane would be difficult and thus but few HCO groups would be formed. The same reasoning applies to the explanation of the spectra of the inner cones of methyl chloride and acetaldehyde which exhibited the HCO bands. These four flames also showed the C₂, CH and HO bands in addition to the HCO bands referred to above.

The complete absence of the HCO bands from the spectra of the flames of formaldehyde, formic acid and methyl alcohol was also noticed and appeared to be significant. The C₂ bands were also absent from the spectra of the flames of formaldehyde, formic acid and methyl alcohol; the CH bands were present in the spectrum of methyl alcohol but not in that of formaldehyde or of formic acid. All these latter three flames exhibited the CO flame bands and the HO bands.

Since the investigation of the spectra of flames of aliphatic carbon compounds had thus proved to be of great interest, it was considered desirable to extend spectroscopic observations to flames of the aromatic series. Such an investigation has now been carried out by the author in Sir C. V. Raman's laboratory and the results are embodied in the present paper.

In this connection, the spectra of the flames of (1) benzene, (2) toluene, (3) phenol, (4) resorcinol, (5) pyrogallol, (6) benzaldehyde, (7) benzoic acid, (8) aniline, (9) nitrobenzene, (10) pyridine, and (11) diphenyl oxide, were studied.

Photographs of the spectra were taken with one of Hilger's small quartz spectrographs (E 31). The use of such an instrument, though of a small dispersion, results in a great saving of time which in the case of flames is a serious problem on account of the extreme faintness of their spectra and the difficulty of maintaining the flames for any length of time. All the bands occurring in their spectra are known, so that no measurements were necessary. Ilford's Golden Iso-Zenith plates were used.

2. Details of the Flame Technique.

In the cases of benzene and toluene, the two liquids were slightly warmed in a distilling flask and air under small pressure was bubbled through them by means of an electrical blower. The vapours were ignited on the top of a micro-burner. With its air-hole closed the flames were smoky and luminous with small greenish inner cones. On opening the air-hole, they became non-luminous and developed well-marked inner cones. No attempt towards the complete separation of the cones by means of a flame-separator was made because in the author's experiments with aliphatic
flames no advantage accrued by such separation as far as the spectra were concerned except in the case of ethylene.

The method of bubbling air through the substance was unsuitable for the production of the flames of the remaining compounds because some of them were solids and some had to be heated to a rather high temperature which resulted in their condensation at the micro-burner. Phenol, resorcinol, pyrogallol and benzoic acid were therefore melted in a wide pyrex tube one end of which was sealed and the other drawn to a narrow neck. An asbestos wick dipping in them was sufficient to give their flames. Similarly a continuous flame was obtained by using an asbestos wick with benzaldehyde, aniline, nitrobenzene and pyridine all of whom had to be slightly warmed up. No heating was necessary for diphenyl oxide.

The flames in all cases were extremely luminous and smoky, depositing a considerable amount of soot which was diminished by blowing air on the top part of the flames. Just at their bases, however, there were a few greenish spots, which when focussed on the slit of the spectroscope gave the spectra described below.

3. Description of the Spectra.

The HCO bands were obtained in the spectra of all the flames studied. They were of both the A and B types. As described in the paper on ethylene, the B bands appeared when its flame was modified, but in the aromatic flames they were given without any modification of the original flames. A similar appearance of the B bands in the natural state of a flame was found in the inner cones of ether and ethyl alcohol.

The intensity of the HCO bands, however, varies from flame to flame. They are fairly strong in toluene, phenol (Plate XIXb) and diphenyl oxide (Plate XXa) though not comparable with ethylene, and they are faint in the spectra of the remaining substances.

The inner cones of all compounds had the C₂, CH and HO bands.

4. Appearance of CN and NO Bands.

One interesting feature of the spectra of aromatic compounds was the occurrence of the CN bands and of the y bands of NO in the flames of aniline (Plate XXb), nitrobenzene and pyridine (Plate XXc). It had been previously noticed that they appeared in acetylene and this was explained on the supposition that the high temperature of the acetylene flame brought about the activation of atmospheric nitrogen. On the other hand, in the spectra of aniline, pyridine and nitrobenzene, the nitrogen forming a constituent part of their molecules was evidently responsible for the CN and NO bands. The CN bands were more intense than the NO bands and with their appearance the CH bands diminished in intensity.
5. Comparison of Aliphatic and Aromatic Flame-Spectra.

(1) Aromatic flames are far more smoky than aliphatics.

(2) All aromatic flames included in the present investigation gave the HCO bands which appeared only in some flames of the aliphatic series. Moreover, the HCO bands in the aromatic substances were of both the A and B types—no modification of the original flames was necessary for the appearance of the B bands. In aliphatic flames, only ether and ethyl alcohol yielded the B bands while burning naturally while the flame of ethylene had to be modified for their appearance.

(3) In the aliphatic compounds, there was a gradual variation of spectra from one substance to another. Thus formaldehyde and formic acid gave the HO and the CO flame bands; methyl alcohol had the HO and the CO flame bands and in addition those of CH. From these three flames, the HCO and the C₂ bands were absent. The HCO and the C₂ bands were however present in the spectrum of methane and also CH and HO, but not CO flame bands. In the aromatic flames, however, there is more uniformity, all flames giving the C₂, CH, HO and HCO bands.

### Table I.

<table>
<thead>
<tr>
<th>Nature of flame</th>
<th>C₂</th>
<th>CH</th>
<th>HO</th>
<th>HCO A and B</th>
<th>CN</th>
<th>γ bands of NO</th>
<th>Reference to plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (C₆H₆)</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>0.5</td>
<td></td>
<td></td>
<td>XIXa</td>
</tr>
<tr>
<td>Toluene (C₆H₅CH₃)</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol (C₆H₅OH)</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>0.9</td>
<td></td>
<td></td>
<td>XIXb</td>
</tr>
<tr>
<td>Resorcinol [C₆H₄(OH)₂]</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrogallol [C₆H₆(OH)₃]</td>
<td>1.8</td>
<td>3</td>
<td>2</td>
<td>0.3</td>
<td></td>
<td></td>
<td>XIXc</td>
</tr>
<tr>
<td>Benzoic acid (C₆H₅COOH)</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.6</td>
<td></td>
<td></td>
<td>XIXd</td>
</tr>
<tr>
<td>Benzoic acid (C₆H₅COOH)</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenyl oxide C₆H₅OC₆H₅</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.9</td>
<td></td>
<td></td>
<td>XIXe</td>
</tr>
<tr>
<td>Aniline (C₆H₅NH₂)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.2</td>
<td>0.3</td>
<td>4</td>
<td>2</td>
<td>XXa</td>
</tr>
<tr>
<td>Nitrobenzene (C₆H₅NO₂)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.2</td>
<td>0.3</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Pyridine (C₆H₅N)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.2</td>
<td>0.5</td>
<td>4</td>
<td>2</td>
<td>XXc</td>
</tr>
</tbody>
</table>
(4) In the CH₄ flame, the intensity of the C₂ bands was specially very susceptible to the oxygen supply; in C₆H₆ the intensity of the C₂ bands seemed independent of the quantity of oxygen mixed with it.

For helping in the discussion of the results, the spectra of the flames investigated are quantitatively characterised in Table I. The figures refer to the eye estimates of the intensities of the various bands occurring in the individual flames.

6. Discussion.

The existence of the HCO bands in all the aromatic compounds investigated may reasonably be explained as due to the double bond in them and the decomposition of oxygenated molecules formed by the direct incorporation of the O₂ molecule in the benzene ring. The O₂ molecule must be assumed to enter the ring at one of the double bonds as in ethylene.

![Chemical structure](image)

Important light on the combustion of benzene is thrown by the spectrum of pyridine. Its spectrum includes the CN and NO bands, the intensity of the CN bands being greater than that of NO or CH. The breaking up of the benzene ring seems to take place at the N atom.

![Chemical structure](image)

The NO bands may be formed by the oxidation of N in the ring or the subsequent reaction of CN with the atmospheric oxygen. The rupture of the ring at N producing CN seems a more favoured reaction than the simple oxidation of N forming NO because of the great intensity of the CN bands compared with NO.

If it be supposed that the oxidation of benzene proceeds through the successive formation of hydroxyl groups, as might happen according to "the hydroxylation theory" of combustion, spectra of C₆H₆, C₆H₅OH, C₆H₄(OH)₂ and C₆H₃(OH)₃ should differ from one another but the observed spectra show
that the spectrum of pyrogallol with three (OH) groups is not different from that of benzene with no (OH) group at all. Hence the hypothesis of successive formations of (OH) groups does not seem to work well in the benzene oxidation.

A complete scheme for the combustion of benzene cannot yet be given because little information about the subsequent reactions between the free radicals like CH, HO, C₂, CN, NO, etc., is available.

In conclusion the author wishes to express his sincere thanks to Sir C. V. Raman for his kind permission to work in his laboratory. The author is also grateful to him for the grant of a scholarship.

7. Summary.

The author's previous investigation of the spectrum of the flame of ethylene burning in a Smithells' flame-separator proved to be of great interest because it led to the appearance with great intensity of a band system which had hitherto received little attention. There were reasons to believe that it was due to HCO. One of the arguments in favour of HCO as the emitter of this band system was that the O₂ molecule might be supposed to be directly incorporated in the ethylene molecule and breaking the double bond formed two HCO groups, thus accounting for the great intensity of the HCO bands particularly in ethylene. This hypothesis of the direct incorporation of the O₂ molecule received additional support from the study of the spectra of other aliphatic carbon compounds.

A similar investigation of the aromatic flames was undertaken and the results of a study of the spectra of eleven flames are given in the paper.

The bands attributed to HCO were also found to occur in the spectra of the flames of benzene and other aromatic compounds. Their appearance in the aromatic flames has been explained as due to the double bond of the benzene ring and the breaking up of oxygenated molecules formed by the direct incorporation of the O₂ molecule.

The spectra of aliphatic and aromatic flames are compared. There is a gradual variation in the spectra of the flames of aliphatic series, while there is more uniformity in the spectra of benzene and its related compounds.

Considerable light on the mechanism of combustion of benzene is thrown by the spectra for pyridine, aniline and nitrobenzene in which flames the CN bands and the γ bands of NO appeared. The rupture of the ring seems to take place at the N atom.

A tentative scheme for the combustion of benzene is given; it is however incomplete for want of knowledge of subsequent reactions between free radicals like CH, O₂, CN, NO, etc. But the hypothesis of the direct incorporation of the O₂ molecule explains the spectroscopic observations better than that of successive formation of hydroxyl groups.
W. M. Vaidya.  


\[ \lambda \rightarrow 3064 \quad 3872 \quad 4315 \quad 4737 \]

\[ a \]

\[ b \]

\[ c \]

\[ d \]