

THE ABSORPTION SPECTRA OF FURFURALDEHYDE AND BENZALDEHYDE IN THE VACUUM ULTRA-VIOLET.

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A previous publication¹ has described the spectroscopic effects of conjugating a C=C group with a C=O group by considering the spectra of acrolein, crotonaldehyde and mesityl oxide. The present paper continues that work by describing the spectra of furfuraldehyde and benzaldehyde.

The Spectrum of Furfuraldehyde.

The ultra-violet absorption of furan has been described by Price and Walsh.² The ultra-violet spectrum of furfuraldehyde was obtained by the use of a B.D.H. product of boiling-point 162°C.

Its most noticeable feature is the way the intensity of the bands below 2100 Å. in furan has here passed to a considerable extent into a prominent near ultra-violet system of maximum about 2600 Å.* The near ultra-violet spectrum has been studied in the vapour by Purvis³ and in solution by Getman⁴ and Hartley and Dobbie.⁵ Purvis in particular measured many of the bands of the 2600 Å. system. Furan has a similar but much weaker region of absorption around 2600 Å., also studied by Purvis.³

A second absorption region extends from about 2000 Å. to 1700 Å. The maximum is at about 1800 Å. and on the long wave-length side of this several diffuse bands are visible. The frequency differences of these bands are as shown in Table I.

Two main frequency differences seem to be involved—one of 887 cm.⁻¹ and one of about 230 cm.⁻¹.

¹ Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498.

² Price and Walsh, *Proc. Roy. Soc. A*, 1941, **179**, 201.

* Dr. W. C. Price informs me that this is also the case for vinyl furan. The spectra of furfuraldehyde and α vinyl furan are very closely similar, both having a region of strong absorption ($\log \epsilon \sim 4$) in the range 2750-2450 Å.

³ Purvis, *J. Chem. Soc.*, 1910, **97**, 1648.

⁴ Getman, *J. Physic. Chem.*, 1924, **28**, 397.

⁵ Hartley and Dobbie, *J. Chem. Soc.*, 1898, **73**, 598.

TABLE I—(cm.⁻¹).

50,055		
204		
50,259		
239		
50,498		887
246		
50,744		
50,942		
259		
51,201		
201		
51,402		

Around 1700 Å. is a short region of transparency, followed by diffuse bands from 1600 Å. onwards. These bands are obviously analogous to those of furan which start at the same wave-length: *i.e.* they are Rydberg in character. They show that the first π ionisation potential of furfural is probably not far different to that of furan. Probably the inductive effect of the C=O group (raising the ionisation potential) roughly compensates for the increased conjugation (lowering the ionisation potential) relative to furan.

No bands recognisable as due to the non-bonding electrons on the oxygen atom of the C=O group appear to be visible. This is in contrast to the benzaldehyde and acrolein spectra where the non-bonding oxygen electron bands are clearly recognisable and dominate the spectra to the exclusion of bands due to the π bonding electrons. The phenomenon in furfuraldehyde is probably connected with the tendency to "homocyclic" conjugation in furan:^{2, 6} the π C=C electrons are nearly equivalent to the lone pair on the oxygen atom of the ring. In general the appearance pressures of oxygen $2p_v$ lone pair Rydberg bands seem to be particularly low: in acrolein and benzaldehyde they are so strong that they hide the bands due to the π electrons of the chain or ring, but in furfuraldehyde the π electrons, being almost equivalent to the $2p_v$ ring lone pair electrons, have themselves very high transition probabilities.

The 2600 Å. region and the 1600 Å. bands are about equally strong: the 1800 Å. region is weaker. The 1600 Å. region is probably analogous to the region at the same wave-lengths in the furan spectrum.

The 2600 Å. region may be the 2600 Å. region of furan made more intense by the loss of symmetry in furfuraldehyde; but with more probability one may tentatively assign the $N \rightarrow V_1$ transition of the π electrons of furfuraldehyde to the 2600 Å. region † (the increased conjugation causing this to be moved to long wave-lengths relative to furan, as with benzaldehyde relative to benzene, in spite of the C=O group taking negative charge out of the ring). The intensity (footnote, p. 62) is that of a fully allowed transition, supporting the $N \rightarrow V_1$ assignment. Further assignment of the furfuraldehyde absorption regions is at present too speculative. One would expect a transition of the type $N \rightarrow A$ ‡ to occur between 3000 and 4000 Å., but no such absorption has been reported.

The Spectrum of Benzaldehyde.

Benzaldehyde has a weak region of absorption around 3200 Å.^{7, 8} Strong absorption begins with an elaborate band system around 2800 Å. This region can be seen on the extreme left-hand side of the photograph (Plate 1); it is presumably analogous to the benzene 2600 Å. region. The bands in it have been reported by Purvis and McClelland.⁹ A second, stronger, region stretches from 2400 Å. to about 2250 Å. At high pressures it spreads chiefly to short wave-lengths. Its maximum is at about 2330 Å. and on the long wave-length side of this several diffuse bands can be seen. The frequency differences of these bands are as shown in Table II. Two main frequencies seem to be involved, one $\sim 765 \text{ cm.}^{-1}$ and the other $\sim 215 \text{ cm.}^{-1}$.

A region of transparency occurs from 2250 Å. to a sharp limit at 2000 Å. Thence very strong diffuse absorption extends to about 1850 Å. The maximum is at about 1940 Å. This absorption is by far the strongest in the whole spectrum and presumably corresponds to the benzene 1790 Å. peak.¹⁰ A short region of transparency follows this strong absorption.

⁶ Mulliken, *J. Chem. Physics*, 1939, **7**, 339.

† The $N \rightarrow V_1$ transition will be stronger in furfuraldehyde than in furan because the addition of a C=O group gives the molecule some *s-trans* nature.

‡ See ref.¹.

⁷ Bielecki and Henri, *Ber.*, 1914, **47**, 1690.

⁸ Morton and Stubbs, *J. Chem. Soc.*, 1940, 1347.

⁹ Purvis and McClelland, *ibid.*, 1913, **103**, 1088.

¹⁰ Walsh, *results in course of publication*.

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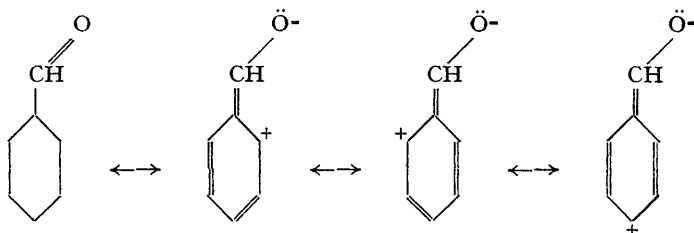
Then from 1800 to 1600 Å. several rather diffuse bands occur. The strongest of these is a doublet of which the first member lies at 1685 Å. Benzaldehyde is obviously to be compared with acrolein: both molecules have a C=O group conjugated with a C=C group. The 1685 Å. doublet agrees very closely in position and appearance with the 1640 Å. doublet of acrolein. Indeed, all the benzaldehyde bands from 1800 to 1600 Å. have obvious analogies in the acrolein spectrum. They are uniformly shifted about 800 cm.⁻¹ to the red relative to acrolein. We may therefore interpret the bands below 1800 Å. in benzaldehyde as due to the non-bonding $2p$, oxygen electrons and, probably, the ionisation potential of these electrons

TABLE II.—(cm.⁻¹).

41,090		41,514		42,279	
207		765		219	
41,297		42,279		42,498	
217					
41,514					
226					
41,740					
207					
41,947					

is a little less than the acrolein value of 10.06 v. It is a considerable simplification that the various regions of the benzaldehyde spectrum can be picked out with confidence as separately analogous to the various benzene or carbonyl regions.

The benzaldehyde bands are shifted to long wave-lengths not only relative to acrolein but also to acetaldehyde.¹¹ This shift shows that there is a greater negative charge on the oxygen atom in benzaldehyde than in acetaldehyde. This is in agreement with the *m*-directing power of the CHO group. The removal of electrons from the benzene ring to the oxygen atom can be portrayed by the resonance structures:



The positive charge on the ring, alone, would raise the ionisation potential of the benzene π electrons. The benzene 1790 Å. peak (which is Rydberg in type¹⁰), however, is shifted not to short but to long wave-lengths in benzaldehyde. The explanation must be that conjugation of the C=O with the ring causes the first bonding energy level of the π electrons to be raised. This raising of the initial energy level more than compensates for the decrease of negative charge in the ring and so the benzene spectrum is shifted not to short but to long wave-lengths. The effect is present wherever a side chain is conjugated with the ring. Thus phenyl cyanide, phenyl ethylene and phenyl acetylene all show a shift to long wave-lengths relative to benzene.¹⁰

There is no region in the benzaldehyde spectrum obviously comparable with the benzene 1980 Å. region. A similar absence is noticeable in the spectra of phenyl ethylene, phenyl acetylene and phenyl cyanide: that is, the "step-out" on the long wave-length side of the benzene 1790 Å. peak

¹¹ Walsh, *Proc. Roy. Soc. A. In press.*

is not present when the side chain conjugates with the ring. It is probable that the benzaldehyde 2350 Å. region corresponds to the benzene 1980 Å. transition and that the extra conjugation due to the C=O group pushes the transition so far to long wave-lengths that it becomes separated from the benzaldehyde 1940 Å. (Rydberg) peak of absorption.* Absorption around 2350 Å. also appears in the spectra of phenyl acetylene and phenyl ethylene. That such conjugation is important is known from the probable reduction in ionisation potential of the $2p_y$ oxygen electrons and of the first π ionisation potential of the benzene ring. The vibrational structure of the 2350 Å. region appears similar to that of the 1980 Å. region in benzene and the corresponding regions in monochlor benzene and *o*-dichlor benzene. The region has also much the same intensity relation to the 1940 Å. peak as the 1980 Å. region of benzene to the 1790 Å. peak.

McMurry¹² has identified the 2800 Å. region of benzaldehyde as $N \rightarrow V_1$. It is probable that this is the benzene 2600 Å. transition (*cf.* Morton and Stubbs⁸) increased in strength by the decreased symmetry of the molecule. Both the 2800 Å. and 2350 Å. regions are $N \rightarrow V_1$ in type. The bands of the 2800 Å. benzaldehyde system have a strong similarity in appearance to systems at about the same wave-length found in the spectra of a large number of benzene derivatives and all analogous to the benzene 2600 Å. absorption.¹⁰

The 3200 Å. region is probably $N \rightarrow A$ in type. The 2800 Å. region is shifted to the *violet* in acetophenone (relative to benzaldehyde).⁷ This is similar to the way certain regions of the styrene spectrum are shifted to the violet in 1-methyl, 1-phenyl, ethylene;¹⁰ the cause in both cases being probably due to steric hindrance of conjugation.

Below 1600 Å. benzaldehyde is almost transparent, until strong C—C absorption begins to set in about 1300 Å.

Summary.

The spectra of furfuraldehyde and benzaldehyde have been photographed in the vacuum ultra-violet. Furfuraldehyde shows absorption in the region 2000–1700 Å. and again below 1600 Å. The bands below 1600 Å. are very similar to those of furan. This is in contrast to benzaldehyde, whose bands below 1800 Å. are similar not to the benzene spectrum but to the acrolein and acetaldehyde spectra. These benzaldehyde bands are due to the excitation of the $2p_y$ lone pair electrons on the oxygen atom. At longer wave-lengths benzaldehyde shows absorption corresponding to the absorption regions found in benzene.

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* In certain molecules, *e.g.* *p*-hydroxy benzoic acid and *p*-amino benzoic acid, the "1980 Å." and "2600 Å." regions of benzene become fused.⁸ The "1980 Å." region moves much further to longer wave-lengths than does the "2600 Å." region.

¹² McMurry, *J. Chem. Phys.*, 1941, 9, 241.