841. *Absorption and Emission Spectra of Aromatic Radicals. Part II.* Electronic Absorption Spectra of Radicals obtained on Photolysis of Dialkylbenzenes.*

By T. F. BINDLEY, A. T. WATTS, and S. WALKER.

Absorption spectra in the 3200—3300 Å region have been obtained from dialkylbenzene radicals produced by the photolysis of *o*-, *m*-, and *p*-dialkylbenzenes in a rigid medium at $-196°$. The following types of radical have been identified: $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}$, $R{\cdot}C_6H_4{\cdot}CHMe{\cdot}$, and $R{\cdot}C_6H_4{\cdot}CMe_2{\cdot}$, where R is a straight- or branched-chain alkyl group.

NORMAN and PORTER [1] have shown that the free radicals produced on photolysis of certain aromatic substances trapped in a rigid medium at low temperature may be stabilized sufficiently for their electronic absorption spectra to be recorded. From the absorption spectrum of the radical from *p*-xylene they suggested that p-$C_6H_4Me{\cdot}CH_2{\cdot}$ was the probable radical. This work was later extended by Porter and Strachan,[2] and for photolysis of *o*-, *m*-, and *p*-xylene a similar type of radical was proposed.

Systematic identification of radicals from monoalkylbenzenes has been achieved; for example, photolysis of toluene yields the benzyl radical, and radicals such as $C_6H_4Me{\cdot}CH_2{\cdot}$ from the xylenes have been identified mainly by analogy.[2] The object of the present work is a more detailed study of the radicals produced on photolysis of dialkylbenzenes.

EXPERIMENTAL AND RESULTS

The apparatus was similar to that of Norman and Porter,[1] but the cell was 2·5 cm. long. The spectra were recorded by means of a medium quartz spectrograph. For wavelength calibration iron arc lines were superimposed, and the wavelengths of the bands were determined when feasible from microdensitometer traces. Band-maxima values are recorded in the Tables. Some of the bands were rather broad but, in general, the accuracy of the band maxima is $\sim\pm 3$ Å. The relative intensities were obtained mainly by visual estimation on a 1 : 10 scale.

Dialkylbenzenes were supplied by British Petroleum Ltd. and, apart from a minute trace of aldehyde, were very pure. The impurity was removed by refluxing the compound over sodium wire for 3—4 hr., then fractionating it from fresh sodium wire.

The purification of the solvents and the experimental technique were similar to those used by Porter and Strachan.[2]

Results.—The monoalkylbenzenes and the radicals which they yield on photolysis have absorption band systems at about 2660 and 3200 Å (Table 1), respectively. The xylenes have corresponding bands (Table 1) at about 2700 and 3225 Å.

The absorption of the radicals produced on photolysis of the dialkylbenzenes is recorded in Table 2.

Table 1 shows that replacing hydrogen of the methyl group of toluene by methyl shifts the

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* Part I, Watts and Walker, preceding paper.

[1] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.

[2] Porter and Strachan, *Trans. Faraday Soc.*, 1958, **54**, 1595.

TABLE 1.

Comparison of (O,O)-absorption band of parent molecule with the radical band furthermost to the red.

Parent molecule (vapour)	(O,O) band (Å)	Radical (in solid solution)	Furthermost red radical band (Å)	
			E.P.A.§	M.I. ¶
C_6H_6	2624·6 *	—		
PhMe	2667·5 *	$Ph{\cdot}CH_2{\cdot}$	3187	3178
PhEt	2664·3 *	Ph·CHMe·	3222	
$PhPr^i$	2658·7 *	$Ph{\cdot}CMe_2{\cdot}$	3242	
$PhBu^t$	2655·2 *	,,	3242	
o-$C_6H_4Me_2$	2680·4 †	o-$C_6H_4Me{\cdot}CH_2{\cdot}$	3230	3226
m-$C_6H_4Me_2$	2706·0 †	m-$C_6H_4Me{\cdot}CH_2{\cdot}$	3230	
p-$C_6H_4Me_2$	2722·3 ‡	p-$C_6H_4Me{\cdot}CH_2{\cdot}$	3230	3222

* Matsen, Robertson, and Chuoke, *Chem. Rev.*, 1947, **41**, 273. † Cooper and Sponer, *J. Chem. Phys.*, 1952, **20**, 1248. ‡ Cooper and Sastri, *ibid.*, p. 607. § Ref. 2; E.P.A. is 5 : 5 : 2 ether–isopentane–ethanol.

¶ This work; M.I. is 2 : 3 methylcyclohexane–isopentane.

TABLE 2.

Absorption wavelengths (Å) and relative intensities (in parentheses) of radicals produced on photolysis of dialkylbenzenes in 2 : 3 methylcyclohexane–isopentane at −196°.

	o-Isomer	*m*-Isomer	*p*-Isomer		*o*-Isomer	*m*-Isomer	*p*-Isomer
$C_6H_4Me_2$	3226	—	3222	$C_6H_4Et_2$	3306(10)	3303(10)	3295(2) *
C_6H_4MeEt	3297(7) *				3278(3) *	3257(8)	3247(10)
	3245(10) *			$C_6H_4Pr^i_2$	—	3300 *	3300(2) *
	3220(2) *	3223	—				3245(10)
$C_6H_4MePr^n$	3305(3) *	3223	3220(10) *	C_6H_4EtBu	—	3290(10) *	3305(1) *
	3247(10)		3100(1) *			3245(10) *	3250(10) *
$C_6H_4MePr^i$	—	3218	3219				

* These wavelengths are medium quartz internal scale readings; the unmarked values were obtained from microdensitometer traces.

wavelength of the (O,O)-band progressively towards the violet by ∼4 Å. This offers a means of identifying the radical providing the (O,O)-band position can be ascertained.

It was shown in Part I that for the benzyl radical the (O,O)-band is the one nearest the red (4635 Å). This band is shifted by ∼160 Å to the red compared with the gas value. For the ultraviolet transition the difference between the values for the solid solution (band furthest to the red) and for the gas is also of this order (∼125 Å). Further, if this band at 3178 Å (in methylcyclohexane–iso-pentane) is taken to be the (O,O)-band, then the other three bands [3] (at 3125, 3078, and 3039 Å) could be accounted for within the limits of experimental error by vibrational frequencies of the same order as those obtained for the visible emission system of the benzyl radical and the ultraviolet-emission system of toluene, the two sets of values being roughly of the same order. Hence, it seems likely that the furthermost red band of the ultraviolet-absorption system is the (O,O)-band.

DISCUSSION

Photolysis of the monoalkylbenzenes [2] has shown that the following types of decomposition may occur: $PhMe \longrightarrow Ph{\cdot}CH_2{\cdot} + H{\cdot}$; $PhPr^i \longrightarrow Ph{\cdot}CMe_2{\cdot} + H{\cdot}$; $PhBu^t \longrightarrow Ph{\cdot}CMe_2{\cdot} + Me{\cdot}$. Significant red shifts are observed on proceeding from $Ph{\cdot}CH_2{\cdot}$ to Ph·CHMe· (35 Å) to $Ph{\cdot}CMe_2{\cdot}$ (a further 20 Å). The different spectra obtained on photolysis of the C_6H_4RR' may be explained similarly. For example, it seems from Table 2 that a furthermost red band at 3220—3230 Å which typified the decompositions, $C_6H_4Me_2 \longrightarrow C_6H_4Me{\cdot}CH_2$ (*o, m, p*) indicates the decompositions m-$C_6H_4MeR \longrightarrow m$-$C_6H_4R{\cdot}CH_2{\cdot} + H{\cdot}$ when R = Et, Pr^n, or Pr^i, and also $C_6H_4MePr^i \longrightarrow C_6H_4Pr^i{\cdot}CH_2{\cdot} + H{\cdot}$ when R = *m*- or *p*-Pr^i. When R = R′, as in diethylbenzene, then the decomposition would be $C_6H_4Et_2 \longrightarrow C_6H_4Et{\cdot}CHMe{\cdot} + H{\cdot}$, and of the two bands obtained for each of these radicals the only feasible candidate for the (O,O)-band is that in the region 3300 Å, since the wavelength values of the extreme red bands for 2-, 3-, and 4-methylbenzyl

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[3] Porter and Strachan, *Spectrochim. Acta*, 1958, **12**, 299.

radicals are so similar. If this value is taken to be characteristic of the $C_6H_4R{\cdot}CHMe{\cdot}$ radical, then we have o-$C_6H_4MeEt \longrightarrow o$-$C_6H_4Me{\cdot}CHMe{\cdot} + H{\cdot}$. On comparison of the results for *o*-, *m*-, and *p*-propyltoluene the following decompositions appear to take place: o-$C_6H_4MePr^n \longrightarrow o$-$C_6H_4Me{\cdot}CHEt{\cdot} + H{\cdot}$, and *m*- or p-$C_6H_4MePr^n \longrightarrow C_6H_4Pr^n{\cdot}CH_2{\cdot} + H{\cdot}$. It thus seems that fission of either side-chain may occur. This is borne out by the results for *o*-ethyltoluene where the wavelength data suggest that radicals $C_6H_4Me{\cdot}CHMe{\cdot}$ and $C_6H_4Et{\cdot}CH_2{\cdot}$ may both be produced. The radicals from the *m*- and *p*-di-isopropylbenzenes also give bands in the 3300 Å region: the decomposition therefore produces radicals $C_6H_4Pr^i{\cdot}CMe_2{\cdot}$. That this value is not significantly greater than that for m-$C_6H_4Et{\cdot}CHMe{\cdot}$ may be explained if the red shift from $-CHMe{\cdot}$ to $-CMe_2{\cdot}$ is counterbalanced by the violet shift from $-Et$ to $-Pr^i$.

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School of Chemistry, College of Technology,
The Newarke, Leicester.

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