

440. *Electronic Emission Spectra of Radicals from Chlorotoluenes.*

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Visible emission spectra have been recorded from mild electrical discharges through the vapours of the chlorotoluenes. Evidence has been obtained for the formation of chlorobenzyl radicals.

It has been confirmed that benzyl radicals are formed when n-alkylbenzenes are passed through a mild electric discharge.¹ Subsequent investigations showed the formation of the *o*-, *m*-, and *p*-xylyl radicals from the corresponding xylenes and from dialkylbenzenes of the form Me·C₆H₄R where R is ethyl or n-propyl.² The present work is an examination of the radicals from *o*-, *m*-, and *p*-chlorotoluenes.

EXPERIMENTAL AND RESULTS

The three compounds studied were available commercially and were purified by careful fractionation in an efficient column of the type described by Ray.³ The middle third of the desired fraction was used.

A description of the experimental technique has been given previously. Spectra were recorded on Ilford Zenith plates by means of a Hilger F/4 spectrograph.

Emission spectra were obtained in the 4400—5100 Å region, and vibrational frequency assignments are given in Tables 1—3 (the error in the determined frequencies being 5—10 cm.⁻¹ for the sharper bands and up to 20 cm.⁻¹ for the diffuse bands).

Many of the bands recorded in each spectrum belong to the *V*-spectrum. Maxima of the other bands, not assigned to the benzyl radical, are listed in Tables 1—3, and a comparison of the vibrational frequency assignments made with those of the corresponding xylyl radical and xylene.

¹ Bindley and Walker, *Trans. Faraday Soc.*, 1962, **58**, 217.

² Bindley, Watts, and Walker, *Trans. Faraday Soc.*, 1962, **58**, 849.

³ Ray, *Rev. Sci. Instr.*, 1957, **28**, 200.

TABLE 1.

Comparative assignments for the radical from *o*-chlorotoluene with those for the *o*-xylyl radical² and those for *o*-xylene.⁴ The wave-number differences are measured with respect to a (0,0) value of 21,027 cm.⁻¹ (vac.) of intensity 10.

Radical from <i>o</i> -chlorotoluene			<i>o</i> -Xylyl radical			<i>o</i> -Xylene
Difference from (0,0) band (cm. ⁻¹)	Intensity	Assignment †	Intensity	Assignment	Assignment	Assignment
59	9	0—59(0)	8	0—59(0)		0—60(0)
119	9	0—119(0)	8	0—117(-3)		0—131(0)
181	7	0—181(0)	5	0—181(0)		
		0—119—59(+3)		0—117—59(+5)		0—131—60(-2)
680	3					
735	2	0—735(0)	7	0—735(0)		0—736(0)
798	1	0—735—59(+4)	5	0—735—59(+1)		0—736—60(+1)
910	1	0—735—181(-6)	1	0—735—181(-1)		
		0—735—119—59(-3)		0—735—117—59(+4)		0—736—131—60(-2)
1050 *	1	0—1040(+10)				0—1054(0)
1097 *	2	0—1040—59(-2)				0—1054—60(+8)
		0—735—2 × 181(0)				
1275 *	1	0—1275(0)?				0—1222(-11)

* Band centre estimated visually. † The figure in parentheses is the experimental wave-number minus the calculated one.

TABLE 2.

Comparative assignments for the radical from *m*-chlorotoluene with those for the *m*-xylyl² radical and those for *m*-xylene.⁴ The wave-number differences are measured with respect to a (0,0) value of 21,182 cm.⁻¹ (vac.) of intensity 10.

Radical from <i>m</i> -chlorotoluene			<i>m</i> -Xylyl radical		<i>m</i> -Xylene
Difference from (0,0) band (cm. ⁻¹)	Intensity	Assignment	Intensity	Assignment	Assignment
48	2	0—48(0)			
86	6	0—86(0)	8	0—71(0)	0—65(-5)
154	4	0—154(0)	6	0—129(0)	0—110(0)
226	2	0—226(0)	4	0—211(0)?	0—226(+4)?
684	1	0—684(0)?			
745	1	0—745(0)	5	0—729(0)	0—725(0)

DISCUSSION

Of the frequency differences listed in Table 1, those of 735, 798, 1050, and 1275 cm.⁻¹ are close to frequencies obtained from infrared spectral analysis of *o*-chlorotoluene vapour.⁶ The intervals 735, 1040, and 1275 cm.⁻¹ have been assigned as fundamentals. Fundamentals of 1031 ± 5 (infrared), 1029 ± 10 (Raman), and 1315 + 11 cm.⁻¹ (infrared) were found in the spectra of *ortho*-substituted benzenes by Randle and Whiffen.⁷ It is concluded that the emitter is close in structure to *o*-chlorotoluene and by analogy with the formation of the *o*-xylyl radical from *o*-xylene may be taken to be the *o*-chlorobenzyl radical.

The discharge through *m*-chlorotoluene gave a spectrum similar to that from *o*-chlorotoluene but displaced to the violet. The frequency differences 684 and 745 cm.⁻¹ are close to those obtained from the infrared analysis of *m*-chlorotoluene vapour.⁶ However, there is little precedence for the assignment of the 684 cm.⁻¹ as a fundamental in this type of spectra and the guiding features in the identification of the *m*-chlorobenzyl radical are the intervals 226 and 745 cm.⁻¹, the latter being fairly characteristic of *meta*-substituents.⁸ Thus, it would seem that the *m*-chlorobenzyl radical is the emitter.

An analysis of all the frequency differences from the *p*-chlorotoluene discharge was

⁴ Cooper and Spomer, *J. Chem. Phys.*, 1952, **20**, 1248.

⁵ Cooper and Sastri, *J. Chem. Phys.*, 1952, **20**, 607.

⁶ Documentation of Molecular Spectroscopy, Butterworth's Scientific Publications.

⁷ Randle and Whiffen, Molecular Spectroscopy Conference, Institute of Petroleum, London, 1954, p. 111

⁸ Viswanath, *Indian J. Phys.*, 1952, **26**, 263.

A similar conclusion was reached by Porter and Wright¹⁰ for the photochemical dissociation of *o*-chlorotoluene vapour. It was shown that migration of a hydrogen atom from the side-chain to the ring may occur to form the benzyl radical from the less stable *o*-tolyl radical. In the case of the *m*- and the *p*-tolyl radicals, these probably abstract a hydrogen atom from a parent molecule to form toluene which subsequently decomposes to the benzyl radical.

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¹⁰ Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.
