# 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.<sup>1</sup> Subsequent investigations showed the formation of the *o*-, *m*-, and *p*-xylyl radicals from the corresponding xylenes and from dialkylbenzenes of the form  $\text{Me} \cdot \text{C}_{6}\text{H}_{4}\text{R}$  where R is ethyl or n-propyl.<sup>2</sup> 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.<sup>3</sup> 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.<sup>-1</sup> for the sharper bands and up to 20 cm.<sup>-1</sup> 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.

- <sup>2</sup> Bindley, Watts, and Walker, Trans. Faraday Soc., 1962, 58, 849.
- <sup>3</sup> Ray, *Řev. Sci. Instr.*, 1957, 28, 200.
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<sup>&</sup>lt;sup>1</sup> Bindley and Walker, Trans. Faraday Soc., 1962, 58, 217.

#### TABLE 1.

Comparative assignments for the radical from o-chlorotoluene with those for the o-xylyl radical<sup>2</sup> and those for o-xylene.<sup>4</sup> The wave-number differences are measured with respect to a (0,0) value of 21,027 cm.<sup>-1</sup> (vac.) of intensity 10.

Radical from o-chlorotoluene

Difference				o-Xvlvl radical	X laws
110m (0,0)					o-Aylene
band (cm. <sup>-1</sup> )	Intensity	Assignment †	Intensity	Assignment	Assignment
59	9	059(0)	8	059(0)	060(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	<b>2</b>	0735(0)	7	0735(0)	0736(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)			01054(0)
1097 *	<b>2</b>	0-1040-59(-2)			0 - 1054 - 60(+8)
		$0-735-2 \times 181(0)$			(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
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-xylyl<sup>2</sup> radical and those for m-xylene.<sup>4</sup> The wave-number differences are measured with respect to a (0,0) value of 21,182 cm<sup>-1</sup> (vac.) of intensity 10.

Radical from *m*-chlorotoluene

Difference m-Xylyl radical from (0,0)*m*-Xylene band (cm.-1) Intensity Assignment Intensity Assignment Assignment 48 2 0 - 48(0)0----86(0) 6 86 8 0 - 71(0)0 - 65(-5)154 0 - 154(0)0 - 129(0)0 - 110(0)4 6 -226(0) $\overline{2}$ 226 0-4 0 - 211(0)?0-226(+4)?684 1 0 - 684(0)?1 0 - 745(0)5 0 - 729(0)745 0 - 725(0)

### DISCUSSION

Of the frequency differences listed in Table 1, those of 735, 798, 1050, and 1275 cm.<sup>-1</sup> are close to frequencies obtained from infrared spectral analysis of o-chlorotoluene vapour.<sup>6</sup> The intervals 735, 1040, and 1275 cm.<sup>-1</sup> have been assigned as fundamentals. Fundamentals of 1031 + 5 (infrared),  $1029 \pm 10$  (Raman), and 1315 + 11 cm.<sup>-1</sup> (infrared) were found in the spectra of ortho-substituted benzenes by Randle and Whiffen.<sup>7</sup> 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.<sup>-1</sup> are close to those obtained from the infrared analysis of *m*-chlorotoluene vapour.<sup>6</sup> However, there is little precedence for the assignment of the 684 cm.<sup>-1</sup> 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.<sup>-1</sup>, the latter being fairly characteristic of meta-substituents.<sup>8</sup> 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 Sponer, J. Chem. Phys., 1952, 20, 1248.

Cooper and Sastri, J. Chem. Phys., 1952, 20, 607. Documentation of Molecular Spectroscopy, Butterworth's Scientific Publications.

<sup>7</sup> Randle and Whiffen, Molecular Spectroscopy Conference, Institute of Petroleum, London, 1954,

p.111

<sup>8</sup> Viswanath, Indian J. Phys., 1952, 26, 263.

# TABLE 3.

Comparative assignments for the radical from p-chlorotoluene with those for the p-xylyl radical <sup>2</sup> and those for p-xylene.<sup>5</sup> The wave-number differences are measured with respect to a (0,0) value of 21,733 cm.<sup>-1</sup> (vac.) of intensity 10. Radical from p-chlorotoluene

Difference				• V-ul-1 we disel	
from (0,0)				<i>p</i> -Ayiyi radical	p-Xylene
band $(cm.^{-1})$	Intensity	Assignment	Intensity	Assignment	Assignment
52	6	0 - 52(0)	9	0 - 51(0)	0 - 54(-1)
113	8	0-113(0)	1	089(0)	0 - 94(-2)
173	1	0173(0)	<b>2</b>	0 - 168(0)	0 - 192(0)
233	4	0 - 173 - 52(+8)	4	0 - 168 - 51(0)	0 - 192 - 54(-1)
		$0-2 \times 113(+7)$			$0-2 \times 94(0)$
326	1	0 - 326(0)	4	0 - 311(0)	
403	2	$0-2 \times 173-52(+5)$	<b>2</b>	$0-2 \times 168-51(-8)$	
<b>435</b>	1	0435(0)	7	0451(0)	0 - 458(0)
588	1	0 - 435 - 113 - 52(-12)			
<b>624</b>	1	0-624(0)	8	0640(0)	0 - 648(0)
682	3	0-624-52(+6)			0-648-54(+7)?
779	1	$0-435-2 \times 173(-2)$			
		0-624-113-52(-10)			
823	5	0823(0)	7	0832(0)	0 - 829(0)
875	<b>2</b>	0 - 823 - 52(0)	4	0 - 832 - 51(-7)	0 - 829 - 54(-1)
918	3	$0-823-2 \times 52(-9)$			-
953	<b>2</b>	0 - 624 - 326(+3)			
1078	3	$0-435-2 \times 326(-9)$	1	$0-451-2 \times 311(+1)$	
1137	1	0 - 823 - 326(-12)	<b>2</b>	0 - 832 - 311(-5)	
1188	1	0-1188(0)	1	0	0 - 1208(0)
1955	1.	$(0-2 \times 624(+7))$	5	$(0-2 \times 640(-3))$	
1200	1	10-1255(0)?	1	10-1255(0)?	
1413	1	$0-1188-2 \times 113(-1)$			
		0 - 1188 - 173 - 52(0)			
1442	1	0 - 823 - 624(-5)			0 - 829 - 640(-3)
1516	1	0 - 1188 - 326(+2)			

## Table 4.

Comparison of  $\omega''$  values (cm.<sup>-1</sup>) for *p*-chlorotoluene with those for the corresponding radical.

Radical	52	113	173	326		435	624			823		1188
p-Chlorotoluene	57	100		310	380		639	700	795	827		
Raman <sup>9</sup>				307	376		<b>634</b>	<b>692</b>	796	822	1090	

obtained. The lower state fundamentals employed are given in Table 4 with those used by Viswanath<sup>8</sup> to interpret part of the absorption spectrum of p-chlorotoluene.

It is concluded that the emitter of the spectrum is the p-chlorobenzyl radical.

Another fact which has to be accounted for in the discharge spectra of the chlorotoluenes is the emission of the V-spectrum which is characteristic of the presence of the benzyl radical. This could be caused by the presence of a monoalkylbenzene (e.g., toluene) as an impurity. However, neither infrared analysis nor gas chromatography detected a toluene impurity. Gas chromatography showed the presence of toluene in the discharge products. In the case of o-chlorotoluene it seems likely that the following decompositions occur in the discharge:



<sup>9</sup> Magat, 1936, "Numerical Data on Raman Effect," p. 77, cited by Viswanath.

A similar conclusion was reached by Porter and Wright <sup>10</sup> 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.

We are indebted to the D.S.I.R. for an apparatus grant and for an award (A. T. W.). We thank Mr. A. Clarke for technical assistance.

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<sup>10</sup> Porter and Wright, Trans. Faraday Soc., 1955, 51, 1469.