

441. Emission Spectra of Radicals from Dimethylnaphthalenes.

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Electronic emission spectra have been obtained in the 5800—6600 Å region from the decomposition products of seven dimethylnaphthalenes, and radicals of the form $\text{CH}_3\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot$ have been detected.

PREVIOUS work has indicated that the benzyl radical is produced from mild discharges through n-alkylbenzenes.¹ In addition, an examination of the emission spectra from 14 dialkyl-substituted benzenes in a Tesla discharge showed that radicals² of the form *o*-, *m*-, and *p*- $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot$ are formed from compounds of the type *o*-, *m*-, and *p*- $\text{CH}_3\cdot\text{C}_6\text{H}_4\text{R}$, where R = H, or n-alkyl.

This Paper is concerned with extending the work to the examination of the spectra of the radicals formed from the dimethylnaphthalenes.

EXPERIMENTAL

Some compounds were kindly supplied by B.P. Ltd. and by Imperial Chemical Industries Limited. The others were obtained commercially. Purification was effected by fractional distillation in a column of the type described by Ray³ or by recrystallisation in a suitable solvent.

The work proved to be very much more difficult than that on the substituted benzenes mainly because of the lower volatility of the naphthalenes and the amount of vapour being fairly critical. This was overcome by use of a furnace situated beneath the discharge tube and an external heating coil wound around the sample container. The surrounding of the windows of the tube was also heated electrically. In all other respects the technique was identical to that of the earlier work.

A Hilger F/4 spectrograph was used to record the spectra on Ilford long range spectrum or Astra III plates. Exposure times varied between 1 and 7 hr.

RESULTS

The spectra obtained consisted of 4—6 bands which were generally diffuse. Where possible the wavelengths of the bands were determined from a microdensitometer trace. The accuracy of the measurements is about ± 15 or even ± 20 cm.⁻¹ for the most diffuse bands. The emission spectra data are listed in Table 1 with vibrational frequency assignments.

¹ Watts and Walker, *J.*, 1962, 4233.

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

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

TABLE 1.

Emission spectra from a discharge through dimethylnaphthalenes and tentative assignment of vibrational frequencies (cm. ⁻¹).							
Wave-number (vac.)	In-tensity	Difference from (0,0) band	Assignment	Wave-number (vac.)	In-tensity	Difference from (0,0) band	Assignment
<i>Radical from 1,2-dimethylnaphthalene</i>				<i>Radical from 1,7-dimethylnaphthalene</i>			
17,011	10	0	(0,0) band	17,080 *	2	412	0 + 412
16,546	8	465	0 - 465	16,648	10	0	(0,0)
16,086	3	925	0 - 925	16,216	7	432	0 - 432
15,645	7	1366	0 - 1366	15,744 *	2	904	0 - 904
<i>Radical from 1,3-dimethylnaphthalene</i>				<i>Radical from 2,3-dimethylnaphthalene</i>			
17,207 *	1	447	0 + 447	16,828	10	0	(0,0)
17,031 *	2	271	0 + 271	16,732 *	1	96	0 - 96
16,760	10	0	(0,0)	16,378	6	450	0 - 450
16,242	5	518	0 - 518	15,894	2	934	0 - 934
15,793 *	2	967	0 - 967	15,440	8	1388	0 - 1388
15,452	7	1308	0 - 1308	<i>Radical from 2,6-dimethylnaphthalene</i>			
<i>Radical from 1,5-dimethylnaphthalene</i>				16,816	5	0	(0,0)
16,774	10	0	(0,0)	16,392	3	424	0 - 424
16,579 *	1	195	0 - 190	16,047 *	1	767	0 - 767
16,254	10	520	0 - 520	15,404	10	1412	0 - 1412
16,073 *	2	701	{0 - 701?				
15,793 *	2	981	{0 - 520 - 190?				
15,488	8	1286	{0 - 981				
			{0 - 522 - 4 × 190?				
			{0 - 1286				
<i>Radical from 1,6-dimethylnaphthalene</i>							
17,031	4	382	0 + 382				
16,648	10	0	(0,0)				
16,229	7	419	0 - 419				
15,476	2	1172	0 - 1172?				
15,319	8	1329	0 - 1329				

* Band centre estimated visually.

DISCUSSION

Characteristic vibrational frequencies of disubstituted naphthalenes have been listed in Table 2 with a view to determining the positions of the (0,0) bands and assignments of vibrational frequencies of the radicals from the dimethylnaphthalenes. Work on both the monoalkyl-¹ and dialkyl-substituted² benzene radicals had shown that on the whole there was good correspondence between the vibrational frequencies of the radical and that of the parent molecule.

It may be expected that the ground-state vibrational frequencies (ω'') obtained by the phosphorescence method would link up with those determined by the discharge method; likewise, the ω' values obtained from the latter may show some correspondence with those from ultraviolet absorption in a rigid glass at 77°K, even though different electronic states are involved. Thus, from Table 2 characteristic ground-state frequencies may be of the order: 500, 780, 950, 1100, 1370, and 1540 cm.⁻¹ The frequency about 500 cm.⁻¹ is of particular interest as it is a characteristic carbon skeletal motion and is found in mono-substituents of naphthalene, for example:

α -D 510 (ref. 4), α -Me 515 (ref. 5), α -F 526, α -Cl 515, α -Br 511 cm.⁻¹ (ref. 6)

β -D 509 (ref. 4), β -Me 521 (ref. 5), β -F 464, β -Cl 516, β -Br 519 cm.⁻¹ (ref. 6)

Furthermore, it may be correlated with the total symmetric vibration of 512 cm.⁻¹ in the naphthalene molecule.⁵ The corresponding frequency in the excited electronic state

⁴ Goubeau, Luther, Feldmann, and Brandes, *Chem. Ber.*, 1953, **86**, 214.

⁵ Luther and Hampel, *Z. phys. Chem.*, 1954, **202**, 390.

⁶ Ferguson, *J.*, 1954, 304.

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TABLE 2.

Excited electronic state and ground-state vibrational frequencies (ω' and ω'' , respectively) in cm^{-1} of disubstituted naphthalenes obtained by phosphorescence⁷ (at 77°K), Raman methods,⁴ and ultraviolet absorption⁸ in a rigid glass (at 77°K).

Compound	Method	Ground-state fundamentals			
1,5-Dideutero-	Phosphorescence	500	1112	1386	1541
1,5-Dibromo-	Phosphorescence	494	1126	1366	1536
2,6-Dibromo-	Phosphorescence	504	796	986	1066
1-Deutero-2-methyl-	Raman	445	516	766	944
2-Deutero-1-methyl-	Raman	448	517	940	1379
1-Deutero-2-ethyl-	Raman	460		943	1377
1-Deutero-4-ethyl-	Raman	479	516	949	1376
1-Deutero-4-methyl-	Raman	474	519	974	1372
		Excited-state fundamentals			
2,6-Dimethyl-	Ultraviolet	490	710	900	1420

resulting from ultraviolet absorption studies⁶ in a rigid glass at 77°K has the following range of values:

$$\alpha\text{-F } 433, \alpha\text{-Cl } 444, \alpha\text{-Br } 420, \alpha\text{-I } 428 \text{ cm}^{-1}$$

$$\beta\text{-F } 455, \beta\text{-Cl } 495, \beta\text{-I } 472 \text{ cm}^{-1},$$

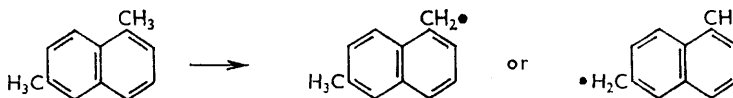
and the value of naphthalene⁶ itself is 455 cm^{-1} .

Another relevant feature to the vibrational frequency assignments in the radicals is the intensity of the (0,0) band. As regards the discharge spectra from the benzyl and *o*-, *m*-, and *p*-xylyl radicals the (0,0) band was the most intense,² and this is also the case for the ultraviolet absorption spectrum⁷ of 2,6-dimethylnaphthalene in 3-methylpentane glass at 77°K. In the phosphorescence work on the monosubstituted and disubstituted naphthalenes the (0,0) is one of the most intense.⁸ It follows that if a vibrational frequency analysis—based on fundamentals which are of the order of those in the disubstituted naphthalenes—is carried out, then it is preferable that the emergent (0,0) band should be one of the most intense. As Table 1 shows, this proves to be the case since the (0,0) bands are in six cases the most intense. The most characteristic ground-state fundamental is one of the order 450—500 cm^{-1} , and in the case of the 1, 3-, 1,6-, and 1,7-radicals the corresponding $\omega' \sim 380\text{—}450 \text{ cm}^{-1}$ is observed.

From these reasonably successful analyses on seven systems it follows that the emitters contain naphthalene ring systems. By analogy with the *n*-dialkylbenzene decompositions under similar discharge conditions it would seem that the breakdown is of the type:



For the symmetrically substituted radicals from 1,5-, 2,3-, and 2,6-dimethylnaphthalenes the identity of such an emitter is straightforward. However, for the 1,2-, 1,3-, 1,6-, and 1,7-isomers there are two possible fission products, as shown.



Bearing in mind the quoted accuracy in the vibrational frequencies determination a certain pattern in the vibrational frequencies appears to exist. If the frequencies of the 2,3- and 2,6-radicals may be taken as characterising a $\beta\text{-CH}_2 \cdot$ radical and that of the 1,5-radical as typical of an $\alpha\text{-CH}_2 \cdot$, then the radicals may be classified as in Table 3.

This determination of the $\alpha\text{-CH}_2 \cdot$ and $\beta\text{-CH}_2 \cdot$ positions must be regarded as somewhat speculative for the 1,3-, 1,6-, 1,7-, and 1,2-radicals; also there is no reliable precedent

⁷ McConnell and Tunnicliff, *J. Chem. Phys.*, 1955, **23**, 927.

⁸ Ferguson, Iredale, and Taylor, *J.*, 1954, 3160.

TABLE 3.

Tentative classification of radicals based on vibrational frequency similarities.

Substituent positions	α -CH ₂ • radicals				
	ω'	ω''			
1,3	447	518		967	1308
1,5		520	701	981	1286
	β -CH ₂ • radicals				
2,3		450		934	1388
2,6		424	767		1412
1,6	382	419			1329
1,7	412	432		904	1333
1,2		465		925	1366
					1547

regarding such variability in the vibrational frequency values in the limited number of polyatomic free radicals previously examined. Nevertheless, it would seem that a definite difference does exist between the α - and β -radicals, particularly for the total symmetric frequency in the 420—520 cm.⁻¹ region. One difference between the α -CH₂• and β -CH₂• radicals is the close proximity of the *peri*-hydrogen in the former radical and its possible steric effect on the degree of planarity of the CH₂• group and the consequent extent of conjugation of the unpaired electron with the π -electrons of the ring.

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