Electronic Emission Spectra of α- and β-Napthyl Methyl Radicals

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Emission spectra have been recorded in the 5550-6850 Å region from the decomposition products of five monoalkyl-naphthalenes in a discharge. The spectra have been attributed to α- and β-naphthyl methyl radicals.

The benzyl radical is formed when the vapours of n-alkylbenzenes are subjected to a mild electric discharge.[1] Radicals from dialkylbenzenes produced in an identical manner showed a similar decomposition pattern, one side-chain only undergoing fission.[2] The present paper contains the results obtained by extending the work to some α- and β-monoalkyl naphthalene derivatives.

EXPERIMENTAL

Purification of the compounds was effected by fractional distillation in a column of the type described by Ray; [3] it was difficult mainly because of the lower volatility of the naphthalenes, the appearance of the bands in the discharge being critically dependent on the amount of vapour present. This was overcome by the 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.[1, 2]

A Hilger F/4 spectrograph was used to record the spectra on Ilford Long Range Spectrum or Astra III plates, exposure times varying between 1 and 6½ h.

RESULTS

The spectra from all the alkylnaphthalenes were similar, consisting of sets of diffuse bands. Where possible the wavelengths of the bands were determined from a microdensitometer trace, the accuracy of the measurements being probably about ± 10 cm^{-1}.

Identical band spectra were recorded from discharges through 1-methylnaphthalene and 1-ethylnaphthalene, and were attributed to a common radical. The analysis assumes that the (0,0) band is at 16593 cm^{-1} and that the vibrational frequencies involved are not very different from those found in the spectra of the parent molecule.

The spectrum recorded from the 1-isopropyl-naphthalene discharge was much fainter than that from the methyl- and ethyl-compounds, although the exposure time was 6½ h. The spectrum was too faint to yield a satisfactory microdensitometer trace and approximate band positions were 5890, 6065, 6225, 6400, 6450 and 6850 Å.

Identical spectra were obtained from mild discharges through 2-methylnaphthalene and 2-ethylnaphthalene, and resembled the spectrum from the corresponding 1-substituted compounds but were slightly displaced to the red. A vibrational analysis is given in table 2 based on a (0,0) band of 17017 cm^{-1}.

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TABLE 1.—VISIBLE EMISSION SPECTRUM FROM A DISCHARGE THROUGH 1-METHYL- AND 1-ETHYL-NAPHTHALENE AND ASSIGNMENT OF VIBRATIONAL FREQUENCIES (cm^{-1})

wave-number (vac.)	intensity	difference from (0,0) band	assignment *
17916 †	1	1323	$0+3\times443(-6)$
17820 †	1	1227	$0+680+4\times141(-17)$
17663 †	2	1070	$0+3\times443-258(-1)$
17570 †	2	979	$0+680+2\times141(-11)$
17478 †	2	885	$0+2\times443(-1)$
17192 †	2	599	$0+443+141(+15)$
17031	10	438	$0+443(-5)$
16732	1	139	$0+141(-2)$
16593	8	0	(0,0)
16335	1	258	0-258
16060	4	533	0-533
15657	7	936	0-946(−10)
15380	1	1213	0-946-258(+9)
15010	1	1583	0-1583

* The number in brackets is the experimental wave number minus the calculated one.
† band centre estimated visually.

TABLE 2.—VISIBLE EMISSION SPECTRUM FROM A DISCHARGE THROUGH 2-METHYL- AND 2-ETHYL-NAPHTHALENE AND TENTATIVE ASSIGNMENT OF VIBRATIONAL FREQUENCIES (cm^{-1})

wave-number (vac.)	intensity	difference from (0,0) band	assignment
17017	10	0	(0,0)
16579	5	438	0-438
16073	2	944	0-944
15932 *	1	1085	0-1085 ?
15843 *	1	1174	0-1174
15621	8	1396	0-1396
15500	4	1517	0-1517 ? 0-1085-438 ?

* band centre estimated visually.

DISCUSSION

In order to determine the positions of the (0,0) bands and assign the vibrational frequencies for the radicals from the α- and β-compounds it is assumed that the vibration frequencies of the radical are closely similar to the ω' and ω'' of the parent molecule. These data are given in tables 3 and 4, and the ω'' values in the former are compared with those of naphthalene. One would expect that the ω'' values from the phosphorescence spectrum of the parent molecule would be of similar magnitudes to those obtained for the radical in the discharge; likewise, that the ω' values from the latter would show some correspondence with those from ultra-violet absorption spectra of the parent molecules in a rigid glass at 77°K, even though different excited electronic states are involved. Thus, characteristic frequencies for α-substituents from discharge spectra may be of the order:

ω'	435	710		
ω''	515		1375	1575

A reasonable analysis of the bands in table 1 may be obtained only by choosing the band at 16593 cm^{-1} as a (0,0) together with upper state vibrational frequencies of 443 and 680 cm^{-1} and lower state values of 533, 946 and 1583 cm^{-1}. The ω' frequency of 443 cm^{-1} is particularly striking in that it corresponds with the most intense band and has two characteristic overtones. In addition, the ω'' values of 533 and 1583 cm^{-1} are fundamentals and the 946 cm^{-1} has its parallel in α-chloronaphthalene. On the whole, the fundamental frequencies obtained for this compound and also for α-fluoronaphthalene correspond well with that of the radical,

TABLE 3.—GROUND-STATE VIBRATIONAL FREQUENCIES OF α- AND β-NAPHTHALENE COMPOUNDS OBTAINED BY FLUORESCENCE, PHOSPHORESCENCE AND RAMAN METHODS AND COMPARISON WITH RELEVANT NAPHTHALENE FREQUENCIES

naphthalene derivatives					naphthalene	
D (Raman [6])	CH_3 (Raman [4])	F (phosphorescence [5] at 77°K)	Cl (phosphorescence [5] at 77°K)	Br (phosphorescence [5] at 77°K)	(vapour fluorescence [7])	(Raman [4])
			α-SUBSTITUENTS			
		224	222	176		
				304		
510	515	526	515	511	512	512
				731	764	
			954			
				1055	1025	
1148		1153	1159			1148
1377	1374	1378	1368	1363	1380	1379
1571	1582	1576	1565	1559		1579
			β-SUBSTITUENTS			
			281	276		
509	521	464	516	519		512
		768	863	812		
		948				
		1173				
1376	1383	1390	1386	1376		1379
1572	1577	1586	1624	1574		1579

TABLE 4.—EXCITED STATE VIBRATIONAL FREQUENCIES OF NAPHTHALENE AND α- AND β-NAPHTHALENE COMPOUNDS OBTAINED BY THE ULTRA-VIOLET ABSORPTION METHOD EMPLOYING A RIGID GLASS AT 77°K

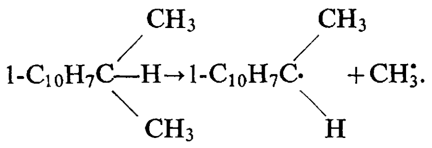
naphthalene derivatives					
F [9]	Cl [9]	Br [9]	I [9]	CH_3 [8]	naphthalene [8]
			α-SUBSTITUENTS		
433	444	420	428		430
	488		495		
679	707	760	710		710
		934			910
1010	1027				
		1186			
	1464				
			β-SUBSTITUENTS		
455	495		472	430	430
721	720		716	710	710
972				960	910
	1025		1005		
1419	1418		1418	1410	

and a ω' $\sim$680 cm^{-1}, which is involved in the α-F- and α-Cl-analyses, has been assumed for the radical.

From the analysis given in table 1 it is likely that the emitter is a monosubstituted naphthalene radical. On account of the shift (to the red) shown by the spectrum obtained with α-isopropyl naphthalene it is possible that the fission is analogous to that indicated for toluene and isopropyl benzene.[10] Thus, the decompositions are probably:

$$\text{1-C}_{10}\text{H}_7\text{CH}_3 \rightarrow \text{1-C}_{10}\text{H}_7\text{CH}_2^{\bullet} + \text{H}^{\bullet}$$

$$\text{1-C}_{10}\text{H}_7\text{CH}_2\text{CH}_3 \rightarrow \text{1-C}_{10}\text{H}_7\text{CH}_2^{\bullet} + \text{CH}_3^{\bullet}$$



$$\text{1-C}_{10}\text{H}_7\text{C}\begin{matrix}\diagup \text{CH}_3\\ \text{—H}\\ \diagdown \text{CH}_3\end{matrix} \rightarrow \text{1-C}_{10}\text{H}_7\text{C}^{\bullet}\begin{matrix}\diagup \text{CH}_3\\ \\ \diagdown \text{H}\end{matrix} + \text{CH}_3^{\bullet}.$$

Unfortunately, the β-radical gives only half the number of bands compared with the α-, and consequently the analysis becomes less certain.

Two analyses of the band system seem feasible based on (0,0) bands of 17017 cm^{-1} and 16579 cm^{-1}, and the fundamentals involved in the analysis are listed below and compared with those of β-fluoronaphthalene.

		fundamentals (cm^{-1})					
	ω'	ω''					
(0,0) band of 17017 cm^{-1}		438		944	1174	1396	1517?
(0,0) band of 16579 cm^{-1}	438	506	736	958			
β-fluoronaphthalene	455	464	768	948	1173	1390	1586

The band at 17017 cm^{-1} has been preferred as the (0,0) since it leads to a greater correspondence of the resulting vibrational frequencies with those of β-fluoronaphthalene. The comparison has been made between the vibrational frequencies of β-fluoronaphthalene and the radical because the frequencies of the benzyl radical correspond more closely with those of fluorobenzene than with the frequencies of the other halogenobenzenes.[10]

In conclusion, a decomposition process analogous to that for the α-methyl- and α-ethyl- may be proposed for the β-methyl- and β-ethyl-naphthalene compounds.

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