

ELECTRON IMPACT AND MOLECULAR DISSOCIATION—XIV

THE MASS SPECTRA OF PHTHALONITRILE AND VARIOUS PHTHALOCYANINES

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(Received 8 January 1964; in revised form 30 January 1964)

Abstract—The mass spectra of copper phthalocyanine and some chlorinated derivatives have been obtained employing a new method of sample introduction at high temperatures. The cracking patterns so obtained have been discussed.

COPPER phthalocyanine is known to sublime at 550°C.¹ The ion-source of the mass-spectrometer cannot produce ions from a compound which is involatile above 350°C. Certain modifications were made to overcome this limitation.² Essentially these consisted of building a heated probe which could vapourize the sample directly into the electron beam in the ionization chamber. The heat was supplied by a platinum filament which could be in contact with the sample or isolated from it by a glass wall. The former type of probe was employed during this work because intense local heat is possible and the temperature of the platinum filament responds very quickly to changes in the current passing through it. The mass spectrum of copper phthalocyanine can be obtained using both types of probe. The substituted derivatives, however, require more heat and attempting to supply this by heating through a glass wall results in melting of the probe. In cases where vapourization could occur the lack of temperature sensitivity of the pyrex probe caused very quick depletion of the sample. Only the very stable ions were of reasonable abundance and the information yielded was thus limited. The major ions of the spectrum of copper phthalocyanine thus obtained are shown in Table A column II.

Fragments containing copper or chlorine give ions corresponding to all combinations of isotopes. Table B has been included to facilitate recognition of these groups of ions by their abundance ratios. For convenience only the ion containing the most abundant isotopes, namely copper 63 and chlorine 35 is discussed. Neither phthalonitrile nor any of its chlorinated derivatives was present in any of the compounds studied.

(a) *Copper phthalocyanine*. This spectrum was obtained using the filament in contact with the compound under examination. Repeatedly scanning the mass range as the sample temperature was raised from the normal operating temperature to that of red-hot platinum gave the following result. Initially only ions of m/e 128 and below were obtained. As the overall temperature was raised ions were observed up to m/e 575. Further increase however resulted in only ions of m/e 128 and below again being recorded. Diagram I shows the molecule copper phthalocyanine and a proposed thermal depolymerization. As can be seen thermal depolymerization

¹ R. P. Linstead, *J. Chem. Soc.* 1020, 1035 (1934).

² H. C. Hill and R. I. Reed, *J. Sci. Instru.* 40, 259 (1963).

TABLE A. PERCENTAGE ABUNDANCE

m/e	I	II	III	IV	V	VI	VII
35				17.04	216.2	206.0	218.3
36				71.85	1075.	999.7	1072.
37				5.55	71.28	67.67	79.40
38				23.07	359.1	329.7	347.4
50	16.40		18.41	15.33	12.47	15.38	
50.5	0.70						
51	7.83		10.29	9.63	5.94	12.30	
52	2.79		5.14	5.18	3.56	7.69	
53	1.67		1.25		1.19	3.07	
61	1.42		1.71				
62	1.44		2.17				
63	2.14	27.30	29.23	40.74	16.63	5.38	8.30
64	4.62		11.52	5.37	51.48	15.38	1.25
65	1.07	11.40	11.85	17.04	7.72	2.31	3.60
73	1.43		2.11		10.69	2.38	
74	3.57		4.29	3.87	8.31	4.76	
75	12.86		16.43	13.99	14.61	19.22	
76	9.28		12.50	11.11	8.71	10.76	
77	6.87		5.87	5.92	2.37	5.76	
78	0.71		1.95	1.48			
79	2.85		0.60				
86	0.14		0.99	0.37		0.67	
87	0.14		1.32	0.74		0.98	
88	1.43		2.41	1.48		2.07	
98	0.71		1.05	1.11		3.07	
99	2.14		3.76	1.63	9.00	12.30	
100	3.57		6.27	4.07	8.31	15.38	1.62
101	25.71		25.74	19.26	2.01	42.29	3.57
102	2.85		6.27	3.70		7.69	0.71
103	1.21		9.90	6.66		3.07	
104			1.32			2.30	
127					2.97	14.61	7.00
128	100.0	8.40	100.0	100.0	8.91	100.0	8.75
129	8.57		15.01	11.85		16.91	
161					14.25	5.38	31.00
162					4.75	32.29	57.96
163					11.88	8.46	28.60
164					2.37	10.70	19.45
165					0.20	1.54	10.72
191		23.10	5.94	51.85			
193		10.50	2.64	21.22			
196					49.89	28.45	100.0
198					33.26	18.46	70.40
200					5.54	3.01	11.10
230					100.0		21.16
232					100.0		21.16
234					38.90		6.96
236					3.96		0.78
259					7.32	4.23	
261					12.67	4.99	
263					11.88	2.69	

TABLE A (cont)

m/e	I	II	III	IV	V	VI	VII
264					76.82		
265					*	0.38	
266					105.3		
268					49.89		
270					13.46		
272					1.01		
287.5		29.40	3.63	40.74		6.92	
288.5		13.65	2.64	25.87		3.92	
293					11.68		1.98
295					24.95		5.95
297					23.76		7.15
299					12.27		4.37
301					4.75		1.98
303.5				} Unresolved 0.37			
304.5							
305.5							
321.5						4.99	
322.5						5.38	
323.5						2.30	
324.5						0.38	
344					1.98		
336					2.77		
338					4.36		
340					2.18		
342					0.80		
355.5						3.46	
356.5						6.15	
357.5						4.99	
358.5						1.92	
359.5						0.38	
360.5						—	
389.5						2.30	0.70
390.5						4.99	1.30
391.5						5.77	1.50
392					3.76		
392.5						3.07	1.00
393.5						1.15	0.30
394					9.70		
394.5						0.36	—
395.5							
396					10.89		
398					8.91		
400					4.36		
402					1.98		
423.5							0.5
424.5							1.40
425.5							1.90
426.5							1.50
427.5							0.80
428.5							0.30
429.5							—
430.5							—

* obscured by adjacent peaks

TABLE A (contd)

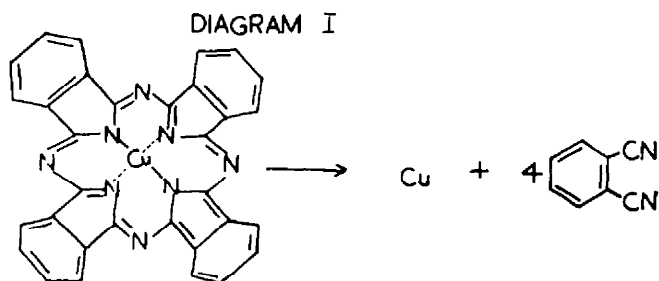
m/e	I	II	III	IV	V	VI	VII
431.5							—
432.5							—
575		100.0	5.28	100.0		23.01	
577			2.97	56.35		13.84	
609				11.11		10.76	
611				8.75		8.46	
613				1.51		1.54	
643						39.27	
645				2.22		45.37	
647				Unresolved		23.07	
649						9.22	
677						6.92	
679						11.53	
681						5.76	
683						3.04	
685						1.54	
711						34.60	
713						47.68	
715						33.84	
717						16.15	
719						3.85	
721						—	
745						3.07 Unresolved	
747							
749							
751							
753							
755							
757							
779						7.69	
781						11.54	
783						12.30	
785						8.46	0.8
787						3.85	Unresolved
789						0.77	
791						—	
793						—	
813							Unresolved
829							
847							1.3
849							3.5
851							4.6
853							3.8
855						4.61	2.0
857						Unresolved	0.8
859							
861							—
863							—
865							—
881							Unresolved
901							

I = phthalonitrile, II = copper phthalocyanine, III = copper phthalocyanine, IV = copper monochlorophthalocyanine, V = copper dodecachlorophthalocyanine, VI = copper 3:6 hexachlorophthalocyanine, VII = copper 3:6 octachlorophthalocyanine.

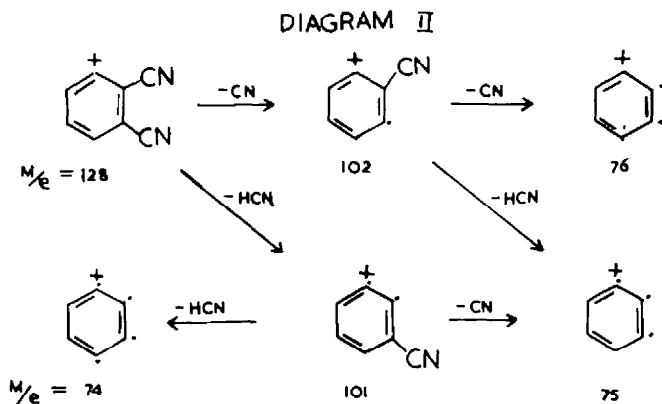
TABLE B

Empirical formula	m/e fragment	Isotope abundance ratio	Fragment plus copper	Isotope abundance ratio
$C_8H_4N_2$	128		191	7
			193	3
$C_8H_3N_2Cl^{85}$	162	3	225	21
$C_8H_3N_2Cl^{87}$	164	1	227	16
			229	3
$C_8H_2N_2Cl_2^{85}$	196	9	259	63
$C_8H_2N_2Cl^{85}Cl^{87}$	198	6	261	69
$C_8H_2N_2Cl_2^{87}$	220	1	263	25
			265	3
$C_8HN_2Cl_3^{85}$	230	27	293	189
$C_8HN_2Cl_2^{85}Cl^{87}$	232	27	295	270
$C_8HN_2Cl^{85}Cl_2^{87}$	234	9	297	148
$C_8HN_2Cl_3^{87}$	236	1	299	34
			301	3
$C_8N_2Cl_4^{85}$	264	81		
$C_8N_2Cl_3^{85}Cl^{87}$	266	108		
$C_8N_2Cl_2^{85}Cl_2^{87}$	268	54		
$C_8N_2Cl^{85}Cl_3^{87}$	270	12		
$C_8N_2Cl_4^{87}$	272	1		

would yield the stable phthalonitrile molecule. The explanation of the above observations is as follows. The hot filament depolymerizes the molecules near it and the phthalonitrile thus produced becomes ionized and fragmented. General increase allows evaporation of the copper phthalocyanine and normal fragmentation of this molecule occurs yielding ions up to m/e 575. Further heating causes complete depolymerization yielding only ions up to m/e 128. The spectrum shown in Table A column III is one scan in which ions up to m/e 575 were recorded. The spectrum of phthalonitrile was obtained and is shown in column I. Comparison between this spectrum and the spectrum of copper phthalocyanine below m/e 128 shows good agreement and confirms that m/e 128 is some resonance form of phthalonitrile. Diagram II shows the breakdown of phthalonitrile. The ion at m/e 191 is 63 mass units above m/e 128 and the abundance ratio of the ions m/e 191 and 193 is 7:3, suggesting that



it is the quarter phthalocyanine nucleus plus one copper atom. (Natural abundance ratio $\text{Cu}^{63}:\text{Cu}^{65}$ is 7:3). Ions at m/e 63 and 65 ratio 7:3 also confirms the presence of copper in the parent molecule. The parent ions singly and doubly charged are present at m/e 575 and m/e 287.5 respectively and the isotope peaks present with them correspond to one copper atom. However, the isotope ratios are not in good agreement owing to the limited resolving power and the high m/e values. The unusual stability of the copper phthalocyanine molecule is demonstrated by the exceedingly large abundance of the parent ions in the spectrum shown in column II and mentioned previously. The only difference between the thermal and electron impact induced dissociations is that a copper atom is combined with one quarter of the phthalocyanine nucleus in the latter case.



(b) *Copper 3,6 octachlorophthalocyanine*. From the mass spectrum of this compound shown in Table A, column VII it can be seen that the hexa, hepta and nonachloro derivatives are present as impurities. The parent ion is at m/e 847, $\text{Cu}^{63}\text{C}_{32}\text{H}_8\text{N}_8\text{Cl}_8^{35}$ and a doubly charged parent ion occurs at m/e 423.5. The base peak at m/e 196 is in a group the abundance ratio of which confirms the presence of two chlorine atoms. This suggests that this ion is a dichlorinated phthalonitrile. The position of the substituents cannot be deduced. Loss of chlorine is observed to a small extent. m/e 259 and its associated peaks correspond to the addition of a copper atom to the above fragment. The other ions are chlorinated phthalonitrile fragments derived from the impurities; e.g. m/e 162, monochlorophthalonitrile and m/e 230 trichlorophthalonitrile. Copper ions are also observed at m/e 63 and 65. The ions at m/e 35, 36, 37 and 38 were so large that to normalize the spectrum with respect to them would have been pointless. They correspond to chlorine and hydrogen chloride which are formed by thermal decomposition of the halogenated copper phthalocyanine under high vacuum.

(c) *Copper dodecachlorophthalocyanine*. The spectrum is shown in Table A, column V. Neither parent ion singly or doubly charged was present in this spectrum. This is expected due to the amount of substitution in the molecule which requires a higher temperature for volatilization. This facilitates depolymerization. However, the ion at m/e 292, $\text{Cu}^{63}\text{C}_8\text{H}_2\text{N}_2\text{Cl}_3^{35}$ suggests that electron induced dissociation is occurring. The ion at m/e 230 $\text{C}_8\text{H}_2\text{N}_2\text{Cl}_3^{35}$, the trichlorophthalonitrile is the base

peak of the spectrum. The other major ions correspond to di- and tetrachlorophthalonitrile. Steric blocking occurs during chlorination of copper phthalocyanine and hence many different isomers and derivatives will be produced. The name dodeca is used here because this particular compound has been chlorinated until the analysis was consistent with twelve chlorine atoms per molecule. Depolymerization gives the chlorinated quarters of the phthalocyanine nucleus as discussed above. The ions at m/e 35, 36, 37, 38 are also abnormally abundant in this spectrum. The ions at m/e 63 and 65 are very small since depolymerization is the most prominent process.

(d) *Copper 3, 6 hexachlorophthalocyanine.* The spectrum is shown in Table A, column VI. Impurities can be seen in it ranging from copper phthalocyanine to the octachloro derivative. Basically this compound is made by combining three dichlorophthalonitrile molecules one phthalonitrile and a copper salt. However, impurities of mono and trichlorophthalonitrile are present in the dichlorophthalonitrile and a range of compounds is produced, the even chlorine content derivatives being the most abundant. In the case of low abundance ions the broad band containing all the isotope contributions is given under one value of percentage abundance since the ions cannot be resolved with certainty as discussed earlier. Ions which are separated well are listed and the presence of the ions due to very small isotope contributions is inferred in the tables as shown.

The value of each isotope contribution is calculated from the expression $(ACu^{63} + BCu^{65})^m(CCl^{35} + DCl^{37})^m$ where A, B and C, D are the isotope ratios and m and n are the number of atoms of Cu and Cl present respectively. For six chlorine atoms and one copper atom present in a molecule eight are produced and their ratios are found from the above expression using $Cu^{63}:Cu^{65}$ as 7:3 and $Cl^{35}:Cl^{37}$ as 3:1, to be 5103:12393:12879:7425:2565:531:61:3. As can be seen the abundance of the last two ions is so small that they could not be measured. The ions of m/e 575 to 847 correspond to the parent molecular ions of the range of chlorinated copper phthalocyanine molecules present. That these ions are parent molecular ions is indicated by comparison with the spectrum of the octachloro derivative (VII) which shows no ready loss of chlorine from the molecular ion. Doubly charged ions corresponding to the more abundant parent molecular ions are observed. The ions m/e 128, m/e 162, m/e 196 are all abundant ions and a very small ion occurs corresponding to $Cu^{63}C_8H_2N_2Cl_2^{35}$.

The very abundant ions m/e 35, 36, 37, 38 occur here also and show that thermal decomposition is occurring. Loss of chlorine is occurring to a small extent from the substituted phthalonitrile fragments and from the parent ions. Beynon *et al.* obtained the spectrum of copper tetrachlorophthalocyanine using their M.S.8 double focusing instrument,³ and they discuss the loss of chlorine and hydrogen chloride from the parent ion. The lack of resolving power of our instrument does not allow us to draw conclusions about the behaviour of the parent ions.

(e) *Copper monochlorophthalocyanine.* The spectrum is shown in Table A, column IV. Parent ions are present here corresponding to copper phthalocyanine and its mono and dichloro derivatives. The molecule of copper phthalocyanine is known to be abnormally stable but the monochloro derivative is known to thermally decompose under vacuum to yield chlorine and hydrogen chloride.¹ The comparative abundances of the parent ions m/e 575 and m/e 609 and the fact that no appreciable

³ J. H. Beynon, R. A. Saunders and A. E. Williams, *Appl. Spectroscopy* 17, 63 (1963).

ion occurs at m/e 162 and m/e 225 confirm this. The abundances of m/e 35, 36, 37, 38 are also very large and the copper peaks at m/e 63 and m/e 65 are present.

The general conclusion about this technique is therefore that ions in the spectra have been produced by three processes.

- (a) Electron impact induced dissociation,
- (b) Thermal depolymerization,
- (c) Thermal decomposition.

To recognise any pure copper phthalocyanine the only ions necessary are the parent ion and the phthalonitriles derived from it by depolymerization.

EXPERIMENTAL

The measurements were made with a Metropolitan-Vickers Ltd. M.S.2 Mass Spectrometer, the spectra being recorded on a N.E.P. 1050 UV Recorder. The special technique involved has been discussed.

Acknowledgements—We wish to acknowledge with thanks the generous assistance and provision of materials by members of Imperial Chemical Industries Ltd., Blackley, Manchester, during the course of this work, and also the interest shown in it by Professor R. A. Raphael, F.R.S.