A COMPARISON OF THE BANDS IN THE LABORATORY EMISSION SPECTRUM OF m-HYDROXYBENZ4LDEHYDE AND THE CO*BANDS IN COMET TAIL SPECTRA

A GREAT deal of experimental work has been devoted to the study of emission spectra of

benzaldehyde and its derivatives¹⁻⁴. The present note reports an unusual band system due to *m*-hydroxybenzaldehyde. The spectrum was photographed on a Q-24 medium quartz and a Fuess glass spectrograph using* the experimental procedure described in earlier works¹⁻⁴. Figure 1 shows the

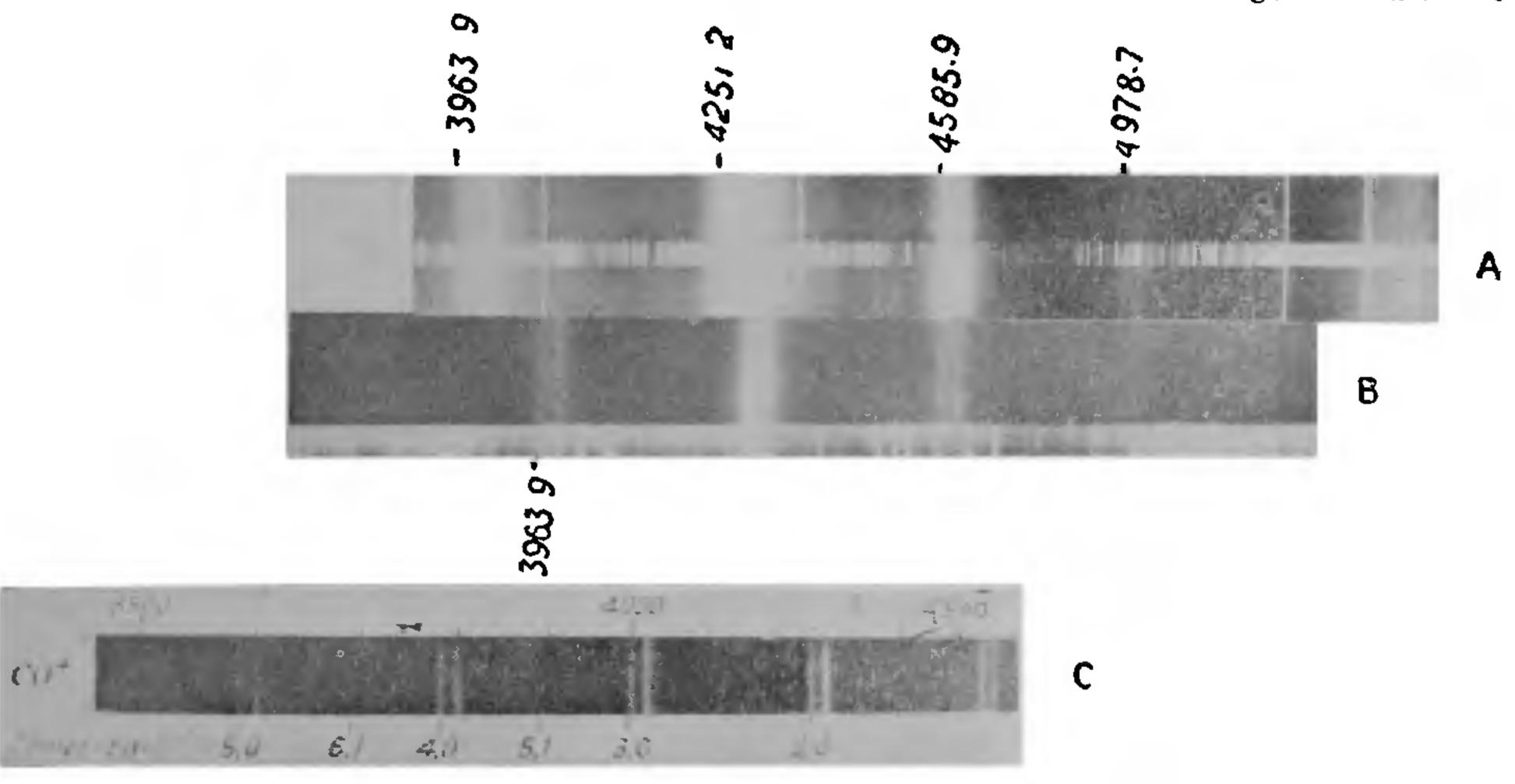


Fig. 1. Emission spectrum of m-OH benzaldehyde. A: in Fuss glass spectrograph; B: in Medium quartz spectrograph and C: Comet tail band taken from reference 5.

TABLE I

Bands observed in m-OH benzaldehyde and the bands in the tail CO system

Present system			Comet tail system			
Tentative assignment	Wavenumber cnr-1	Wavelength Å	Intensity	Wavelength Å	Intensity	Assignment
0-0	26895	3707·1 3718·2	vw	3707·4 3724·9	9	Q_1 Q_2
0–1680	25227	3963·9 3989·1	vs	3957·0 3977·7	7 4	$\mathbf{P_{a}}$ $\mathbf{P_{1}}$
0-2 × 1680	23524	4251·2 4280·2	VS	4252·4 4274·3	iò	Q_2 Q_1
		4485·9 4505·2	vw	45i8	3	$R_{\mathbf{x}}$
0-3 × 1680	21805	4585·9 4625·4	S	4565·8 4539·0	8	R_1
		4978 · 7 5018 · 4	S	5039 · 7 5072 · 1	3	R ₁ R ₂
		5437·3 5473·0	vw	5461·4 5499·9	6	R ₁ R ₂
		5960-0 5998-2	w	5970 6015	Ü	${f R_i}$

s = strong, vs = very strong, w = weak and vw = very weak.

emission spectrum of the molecule. The spectrum of the comet tail band CO+ is given for a direct comparison.

The conspicuous feature of the spectrum is its striking similarity with the comet tail band system due to CO-5.67. It does not bear any resemblance with the emission spectra of benzaldehyde or its derivatives. Measurements however show that the present band system does not coincide with the comet tail system or the Johnson-Baldet system. Like the comet tail system the present system also consists of double headed bands but the bands are more diffuse. For comparison the bands in the comet tail system of CO- can be correlated with the bands of the present system. This is shown in Table I. The present system appears to be a CO+ system shifted to the lower energy side.

It may be noted that the present emission spectrum is tentatively analysed on the basis of a 0,0 band at 3718 A with a carbonyl stretching band (v == 1680 cm⁻¹) superposed on it. This type of analysis has been made on the emission spectra of identical molecules. However, from the striking similarity between the bands of CO+ and the present band system we infer that the present band system may not actually belong to the molecule under investigation but corresponds to some intermediate molecule or radical formed as a result of dissociation, occurring in the process of discharge. It may further be added that there is also a similarity in the process of excitation of the two systems. The comet tail system in the laboratory was observed in the discharge tube containing helium with a trace of CO while the present system was observed in the discharge tube containing m-hydroxybenzaldehyde with flowing vapour of benzene.

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FRIEDEL-CRAFTS ALKYLATION OF AROMATIC HYDROCARBONS WITH THE LACTONE OF 2-HYDROXYCYCLOPENTANEACETIC ACID

THE AlCla-catalysed alkylation of aroma ic hydrocarbons with simple unsubstituted alicyclic lactones like the lactone of trans 2-hydroxycyclohexaneacetic acid was studied by Phillips and Chatterjee¹ who observed that the reaction was attended with extensive rearrangement leading to the formation of a small amount of the expected trans 2-aryleyclohexaneacetic acid together with a large amount of the rearranged product consisting of trans 4-arylcyclohexaneacetic zcid and the 3-aryl isomer of unknown stereochemistry. The reaction was interpreted as going through the carbonium ion formed by the action of the Lewis acid on the lactone followed by a series of 1, 2 shifts and electrophilic attack on the arenes. The observation by Friedman² that the alkylation of aromatics by branched chain cycloolefines like methyl cyclohexene in the presence of Lewis acid catalyst leads to the formation of a large amount of the secondary alkylate but very little of the tertiary alkylate led Chatterjee and Bhattacharyya³ to investigate the cationic nuclear alkylation of aromatics with the lactone of 4-methyl-2-hydroxycyclohexaneacetic acid. Those investigators is clated 2-aryl- and 3-arylcyclohexaneacetic acids to the exclusion of the 4-aryl isomer, the former components being successfully converted to poly yelic compounds by way of cyclisation, reduction and dehydrogenation. The facile rearrangement in the cyclohexane system is quite common and in order to see if similar rearrangement of the carbonium ion in the cyclopentane system can also take place, the lactone of cyclopentanol-2acetic acid (I) has been prepared and the AlCl₃-catalysed alkylation of benzene with this lactone has been investigated.

The lactone (I) has been prepared from 2-carbetho xycyclopentanone by condersing the sodio derivative with ethyl chloroacetate followed by hydrolysis

^{*} The experiment was performed at the spectroscopy laboratory of B.H.U., Varanasi.

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