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Absorption spectrum of the HCCO radical

S L N G KRISHNAMACHARI and R VENKATASUBRAMANIAN
Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Abstract. In the flash-photolysis of oxazole and isoxazole, new transient absorption bands are observed in the region 3080–3670 Å. Vibrational analysis of these bands showed that they can be arranged into two electronic systems with their origin bands at 3333·60 Å and 3667·01 Å. Based on the experimental conditions under which the bands are produced and on the analysis of their vibrational and gross-rotational structure, these bands are assigned to a new carrier, the HCCO free radical.

Keywords. HCCO radical optical absorption spectrum; oxazole/isoxazole flash-photolysis.

1. Introduction

As a part of our general programme of the spectroscopic studies on the transient species produced in the flash photolysis of organic compounds, we have recently investigated a series of five-membered heterocyclic ring compounds. Studies carried out with thiophene (C_4H_4S) and selenophene (C_4H_4Se) have yielded the spectra of two new free radicals, HCCS and HCCSe (Krishnamachari and Venkitachalam 1978, 1979; Krishnamachari and Ramsay 1981; Krishnamachari and Venkatasubramanian 1983). In order to obtain the spectrum of the corresponding HCCO radical, flash-photolysis experiments were conducted with oxygen containing ring compounds, *viz* furan (C_4H_4O), oxazole and isoxazole (C_3H_3NO). While no transient species were observed with furan (presumably due to the absence of photodecomposition with the radiation employed) several new transient absorption bands were observed with oxazole and isoxazole. The new absorption features observed with both these compounds consist of three groups of bands lying in the regions 2500–3050, 3080–3400 and 3400–3670 Å. As shown below the latter two groups of bands could be assigned to the HCCO radical.

2. Experimental

To obtain the absorption spectra of the transient species, the flash-photolysis apparatus, described earlier has been used (Krishnamachari 1974). Spectra were recorded with an absorption path length of 16 m using the multiple reflection mirror set-up. At an interval of 5 μsec between the photolysis and monitoring flashes the intensity of the absorption bands was maximum. Chemically pure samples of oxazole and isoxazole (M/s. Sigma Chemicals and M/s. Fluka Chemicals) were further purified by repeated cycles of freezing at liquid nitrogen temperature, pumping and thawing. Spectra were studied under different pressure conditions, *i.e.* with isoxazole and oxazole pressures varying from 0·1 to 5 torr and dilution with argon about 10 to 100 times. Maximum intensity for the bands was observed when a mixture of 2 torr of isoxazole and 50 torr of argon was used. Iron hollow cathode lines were employed for wavelength calibration and the measurements made on a Jarrel-Ash photoelectric comparator; the wavelengths of the sharp bands are accurate up to 0·01 Å.

3. Results

The flash photolysis of both isoxazole and oxazole showed the transient absorption spectra due to known free radical species CH (4300 and 3900 Å systems), HCO (bands in the region 5200–6500 Å) and CN (3880 Å, violet system). In addition, several new transient absorption bands in the region 2500–3700 Å were also obtained which could not be identified with any known species. Based on the structure of these bands, they could be classified into three distinct groups lying in the regions 2500–3050; 3080–3400 and 3400–3670 Å. Of these the one lying on the shorter wavelength side *i.e.* the 2500–3050 group, was also observed in the flash photolysis of thiazole (C_3H_3NS) but was absent in the flash photolysis of thiophene (C_4H_4S). These bands were assigned to an excited species of HCN, the triplet HCN or isomeric HNC (Krishnamachari and Venkatasubramanian 1984). The remaining two groups are discussed here. The data on these bands are given in tables 1 and 2. Spectrograms of these bands, obtained in the flash-photolysis of isoxazole-argon mixture are shown in figures 1a and b. The 3400–3670 Å group, as shown in figure 1a consists of eight bands which show degradation towards longer wavelengths; the band at 3667·01 Å shows sharp heads while the bands at 3530·18 and 3528·00 Å show heads which are slightly diffuse and the band at 3400·38 Å is still more diffuse. The 3080–3400 Å group, shown in figure 1b consists of 33 bands. The strong bands at 3333·60, 3287·25 and 3184·80 Å show five or six heads characteristic of the *K*-structure of an asymmetric top molecule. The coarse structure (*K*-structure) and the fine structure (*J*-structure) of these bands show red-degradation.

4. Analysis and discussion

4.1 *The* 3400–3670 Å *system*

The intense band on the long wavelength side of the group, *i.e.* the band at 3667·01 Å represents the origin band (O–O band) of this system. The frequency separations of all

Table 1. Band head data and assignments for the 3400–3670 Å system.

λ_{air} (Å)	Intensity (visual estimate)	ν_{vac} (cm^{-1})	$\Delta\nu$ from (O–O) band (cm^{-1})	Assignment
3667·01	10	27262·4	0	(O–O)
3665·86	5	27271·0	8·6	
3664·64	1	27280·1	17·7	
3530·18	8	28319·1	1056·7	(O–O) + 1057
3529·31	3	28326·0	1063·6	
3528·00	5	28336·5	1074·1	(O–O) + 1074
3526·73	1	28346·8	1084·4	
3400·38	3	29400·0	2137·6	(O–O) + 1057 + 1074

Table 2. Band head data and assignments for the 3080–3400 Å system.

λ_{air} (Å)	Intensity (visual estimate)	ν_{vac} (cm^{-1})	$\Delta\nu$ from (O–O) band (cm^{-1})	Assignment
3395·64	5	29441·1	547·9	
3393·85	1	29456·6	532·4	
3391·80	1	29474·4	514·6	
3390·95	5	29481·8	507·2	(O–O) – 507
3361·73	1	29738·1	250·9	
3349·49	3	29846·7	142·3	
3347·58	2	29863·7	125.3	
3342·09	7	29912·8	76·2	
3338·34	10	29946·4	42·6	
3334·34	9	29982·3	6.7	
3333·60	7	29989·0	0	(O–O)
3300·46	1	30290·1	301·1	
3299·05	1	30303·1	314·1	
3297·71	2	30315·3	326·3	
3296·36	2	30327·8	338·8	
3293·81	1	30351·3	362·3	
3292·40	4	30364·2	375·2	
3290·27	4	30383·9	394·9	
3289·55	3	30390·5	401·5	
3288·44	9	30400·8	411·8	
3287·25	7	30411·8	422·8	(O–O) + 423
3241·03	9	30845·5	856·5	
3236·20	1	30891·5	902·5	
3234·09	1	30911·7	922·7	
3231·22	2	30939·1	950·1	
3229·24	7	30958·2	969·2	(O–O) + 969
3195·68	3	31283·2	1294·2	
3190·54	1	31333·6	1344·6	
3189·58	5	31343·0	1354·0	
3186·06	8	31377·7	1388·7	
3184·80	5	31390·1	1401·1	(O–O) + 423 + 969
3088·78	1	32365·9	2376·9	
3088·14	1	32372·5	2383·5	(O–O) + 423 + 2 × 969

the other bands from the O–O band are shown in table 1. These frequency separations can be represented in terms of two prominent vibrational frequencies in the excited state, *viz* 1057 and 1074 cm^{-1}. The O–O band is accompanied on the shorter wavelength side by three closely-spaced components with separations of 8·6 and 9·1 cm^{-1}. The relative intensities of these components suggest that they could be ascribed to the sequence structure (*i.e.* 1-1, 2-2) involving a vibrational mode of low magnitude in the lower and excited electronic states. The O–O band shows a simple rotational structure with a single head which is characteristic of a transition which involves a linear conformation of the molecule in atleast one of the combining states

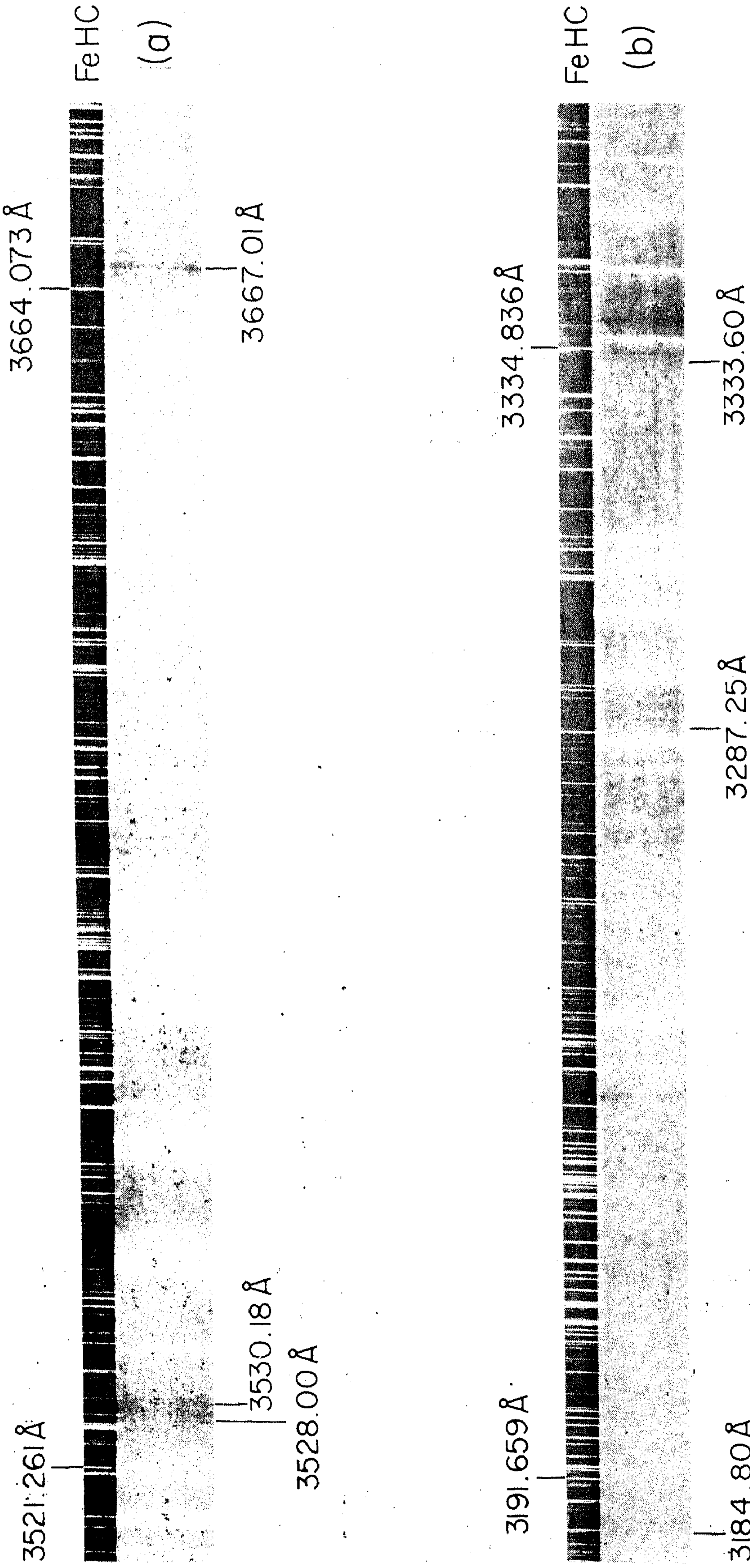

Figure 1. Absorption bands of HCCO radical obtained in the flash photolysis of isoxazole-argon mixture. **a.** 3400–3670 Å system. **b.** 3080–3400 Å system.

(Herzberg 1966). The structure of this band is similar to that of the O–O band of the HCCS radical at 4113·73 Å which corresponds to a linear-linear or linear-bent transition (Krishnamachari and Ramsay 1981). The excited state fundamental frequencies of 1057 and 1074 cm^{-1} represent the CO stretching and CH bending modes. Thus the 3400–3670 Å system would represent a transition of HCCO analogous to the 4114 Å system of HCCS. The occurrence of HCN as an end product (detected by its IR spectrum) shows that the photodissociation of the parent compound results in ring scission forming an excited HCN and HCCO.

4.2 *The* 3080–3400 Å *system*

This system, compared to the earlier one, is more extended indicating a large change in the geometry of the molecule between the lower and excited electronic states. The intense band on the longer wavelength end *i.e.* the band at 3333·60 Å represents the O–O band of this system. The main progression forming frequency is the 969 cm^{-1} one. Another prominent frequency interval is the one with the 423 cm^{-1} separation; most of the observed frequency separations could be interpreted in terms of the 969 and 423 cm^{-1} intervals. These intervals thus represent the excited state fundamental frequencies; the 969 cm^{-1} frequency represents the CH bending mode while the 423 cm^{-1} represents a bending mode involving relatively heavier atoms and this could be correlated with the CCO bending mode. As mentioned earlier the strong bands at 3333·60, 3287·25 and 3184·80 Å show a rather complex rotational structure consisting of a large number of heads characteristic of a transition of an asymmetric top molecule. This implies that the molecule should be nonlinear in both the electronic states involved in the transition. The structure of these bands is similar to those observed for the bands in the region 3400–3640 Å of the HCCS radical. Thus the 3080–3400 Å system represents the transition of HCCO analogous to the 3640 Å system of HCCS.

5. Conclusions

The transient absorption bands occurring in the regions 3400–3670 Å and 3080–3400 Å in the flash-photolysis of oxazole and isoxazole could be assigned to the HCCO free radical on the basis of their method of production, vibrational and gross-rotational structures. These two systems are analogous to the 4114 Å and 3640 Å systems of HCCS.

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