FLASH PHOTOLYTIC PRODUCTION OF THE FCO RADICAL IN THE GAS PHASE

D. K. W. WANG and W. E. JONES

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia (Canada)

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SUMMARY

The FCO radical has been produced by flash photolysis of a mixture of N_2F_4, CO and N_2. The absorption spectrum of FCO exists for approximately 50 μsec after the photolysis flash. The spectrum has an extensive series of bands between 2200 and 3400 Å. The principal progression appears to have a spacing of approximately 650 cm^{-1}. A possible reaction mechanism for the production of FCO is proposed.

INTRODUCTION

A spectrum attributed to the FCO radical has been obtained by Milligan *et al.*[1] in CO and Ar matrices at 4, 14 and 20 K. They obtained both infra-red and ultra-violet spectra from various photolytic sources of F atoms and/or FCO. The infra-red identification of FCO was confirmed by isotopic studies. Their ultra-violet absorption studies showed an extensive series of bands between 2200 and 3400 Å. The most prominent progression involved bands spaced at intervals of approximately 650 cm^{-1}.

This paper describes the production of the FCO radical in the gas phase. The FCO radical is observed by its ultra-violet absorption spectrum following the isothermal flash photolysis of a mixture of N_2F_4 and CO.

EXPERIMENTAL

The flash photolysis apparatus was of conventional design. The flash and reaction tubes were prepared from 50 cm lengths of 10 mm i.d. Suprasil tubing. The main flash dissipated an energy of 800 J (33 μF, 7000 V). The absorption continuum was provided by a Lyman capillary flash lamp fired by a 2 μF capacitor charged to 8000 V.

The spectrum of FCO was observed following the flash photolysis of mixtures consisting of 4 torr N_2F_4 (Air Products and Chemicals), 20 torr CO (Matheson of Canada Ltd.), and a large excess of N_2 (Canadian Liquid Air Ltd.). The FCO spectrum was also observed when N_2 was replaced by Ar or He, but not when replaced by O_2.

A Hilger medium quartz spectrograph, Model E498, was used to record the spectra on Ilford HP3 plates. The band heads were measured on an Abbe comparator, using iron lines as reference.

RESULTS

The gas phase spectrum of FCO appears immediately after the photolysis flash and exists for approximately 50 μsec. An example of the spectra obtained at various delay times is shown in Fig. 1. Figure 2 shows an enlargement of the FCO
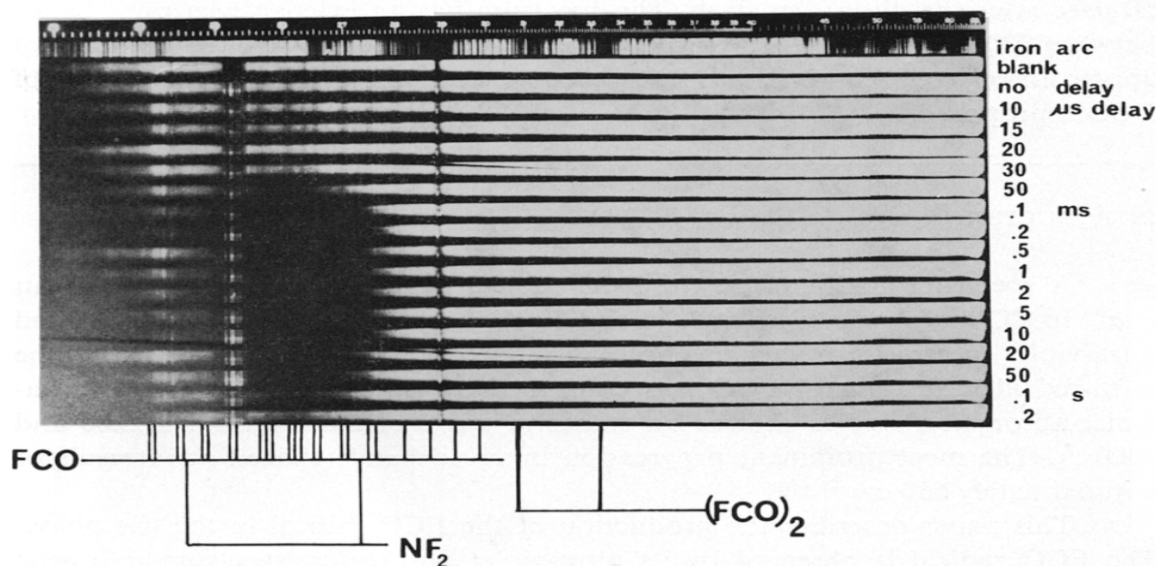

Fig. 1. Flash photolysis of a mixture of N_2F_4 (5 torr), CO (10 torr) and N_2 (400 torr) showing various delay times after main flash.
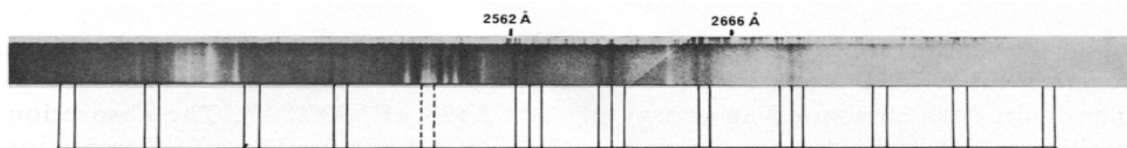

Fig. 2. Enlarged reproduction of the FCO spectrum in the region 2400–2750 Å.

spectrum. Twenty-four bands between 2200 and 3400 Å are attributed to FCO. At delay times of 100 μsec or longer a very broad absorption appears in the region 2500–2700 Å and is attributed to NF_2[2]. Although not shown in Fig. 1, two very weak bands are observed at 3080 Å and 3300 Å for delay times greater than 50 μsec. These bands are believed to be due to the oxalyl fluoride, $(FCO)_2$, molecule[3].

The measurements of the band heads of the FCO spectrum are given in Table 1. Under our resolution the bands appear diffuse and since no rotational structure is observed, the precision of locating the band heads is poor. The spectrum consists of two fairly regularly spaced series, indicated as A and B, each having a spacing of approximately 650 cm^{-1}.

Milligan et al.[1] found in their matrix studies a fairly intense progression with a spacing of about 650 cm^{-1}. They also found that most of the peaks of the more intense series had a less intense secondary peak about 240 cm^{-1} to the short wavelength side of the main peak. In the present work the two series appear with about the same intensity and it is therefore impossible to state definitely which corresponds to the more intense progression found by Milligan et al. If series A corresponds to the more intense peaks, the bands in the gas phase appear to be displaced by about 100 cm^{-1} to longer wavelengths. In addition, the spacing between the main band and its accompanying band is reduced to about 80 cm^{-1}. These differences are not unusual, however, since matrix shifts of the order of 200–300 cm^{-1} are common in ultra-violet spectra. The positions of our series A and the more intense series found by Milligan et al.[1] are compared in Table 1. This Table also presents the spacing between our series A and B and the spacing Δv_A and Δv_B within each series.

TABLE 1

WAVE NUMBERS OF THE BAND HEADS OF THE ULTRAVIOLET ABSORPTION SPECTRUM OF FORMYL FLUORIDE (cm^{-1})

A	Milligan et al.	Matrix shift.Δ	B	A–B	Δv_A	Δv_B
42936	43042	106	42887	49	596	609
42340	42437	97	42278	62	655	678
41685	41793	108	41600	85	641	628
41044	41153	109	40972	72	634	661
40410	40503	93	40311	99	650	618
39760	39858	98	39693	67	684	712
39076	39216	140	38981	95	617	615
38459	38559	100	38366	93	667	660
37792	37902	110	37706	86	657	658
37135	37245	110	37048	87	674	667
36461	36577	116	36381	80	610	640
35851	35924	73	35741	110		

DISCUSSION

It is difficult with the present information to positively identify the species responsible for the bands listed in Table 1. The similarity between the matrix spectra reported by Milligan *et al.*[1] and the present spectra suggests very strongly that the precursor of the bands is FCO. Furthermore, since the spectrum does not occur when N_2F_4 or CO are flashed separately, the species responsible must be a result of reaction between dissociation products of the gaseous mixture.

It is interesting to consider the reactions which might lead to the formation of FCO. It is probable that FCO arises from the reaction of F atoms and CO as:

$$F + CO + M \rightarrow FCO + M \tag{1}$$

This reaction has been proposed by Heras *et al.*[4] as a possible reaction in their study of the reaction of $F_2 + CO$. They state that reaction (1) is very fast. In their system where oxygen was also present they also observed the fast reaction:

$$FCO + O_2 \rightarrow FCO \cdot O_2 \tag{2}$$

This might explain why no FCO was found when O_2 was used in place of N_2 in the present study.

There are two possible sources for F atoms in the photolysis of N_2F_4. Johnson and Colburn[5] have found that at room temperature and a few torr, approximately 2% of the N_2F_4 is in the form of the free radical NF_2. The dissociation of the NF_2 radical by reactions (3a) and (3b) is probably the most important source of F atoms.

$$NF_2(^2B_1) \rightarrow F(^2P) + NF(^1\Delta) \tag{3a}$$
$$NF_2(^2B_1) \rightarrow F(^2P) + NF(^3\Sigma) \tag{3b}$$

It has also been reported that F atoms can be produced[6] by a weak absorption of N_2F_4 below 2100 Å. Since, in the present work, Suprasil tubing was used for both flash and reaction tubes, it is possible that F atoms produced by this direct dissociation played a significant role.

Brus and Lin[7] studied the photodecomposition of N_2F_4 and from the presence of N_2, F_2, N_2F_2 and NF_3 detected by mass spectroscopy, they proposed the mechanism:

$$N_2F_4 \rightleftharpoons 2NF_2 \tag{K_{eq}}$$
$$NF_2 + h\nu \rightarrow NF + F \tag{3}$$
$$N_2F_4 + h\nu \rightarrow N_2F_3 + F \tag{4}$$
$$2NF \rightarrow N_2 + 2F \tag{5}$$
$$NF + N_2F_4 \rightarrow NF_2 + N_2F_2 + F \tag{6}$$

Reaction (5) is very fast ($k = 2.5 \times 10^{13}$ cm^3/mol sec)[8] and is a source of F atoms. It is suggested that reaction (6) is a bimolecular displacement reaction and also results in F atoms.

The F atoms formed above may undergo a number of reactions. However the reactions of interest here are:

$$F + CO \rightarrow FCO \tag{1}$$
$$F + FCO \rightarrow F_2CO \tag{7}$$

Reaction (1) explains the formation of FCO. Reaction (7) would be expected to occur but absorption by F_2CO occurs below 2000 Å and can not be detected in the present work. Reaction (7) along with reaction (8):

$$2FCO + M \rightarrow (FCO)_2 + M \tag{8}$$
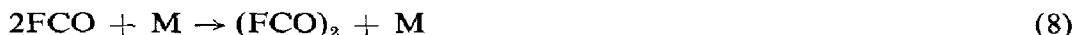
would explain the decrease in concentration of FCO which appears to begin at approximately 50 μsec. Reaction (8) also explains the presence of $(FCO)_2$ which appears for delay times greater than 50 μsec.

The increased concentration of NF_2 from 100 μsec to 100 msec is probably due to a delayed heating effect resulting in a shift in the equilibrium (K_{eq}).

An unsuccessful attempt was made to obtain high resolution plates of the FCO spectrum. The difficulty in obtaining the spectra at high resolution may be the result of either too low a concentration and diffuseness of the spectra or to difficulties in the flash apparatus, *i.e.* the photolysis lamps had a much longer flash duration than that of the apparatus used in the present work.

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