394. *Fluorescence obtained from Formic Acid, Carbonyl Chloride, and Methylene Iodide.*

By P. J. Dyne and D. W. G. Style.

A fluorescence emitted by formic acid is described. The emission of part of the McClennen system of iodine from illuminated methylene iodide and of the analogous system of chlorine from illuminated carbonyl chloride is described and the origin of the excited halogen molecule discussed.

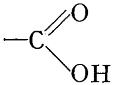
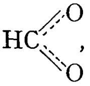
This paper describes further work on the excitation of fluorescence from simple molecules by light of wave-length 1250—2000 Å. The apparatus was essentially that already described (Dyne and Style, *Discuss. Faraday Soc.*, 1947, **2**, 1591), apart from minor changes introduced to facilitate the dismantling of the hydrogen lamp from the fluorescence chamber and the frequent cleaning of the fluorite window, which was necessary with some of the substances investigated.

Formic Acid.—Terenin and Neujmin (*Acta Physicochim., U.R.S.S.*, 1935, **5**, 465) reported a blue fluorescence to be emitted by flowing formic acid vapour when irradiated with light from a hydrogen discharge through a fluorite window. The active wave-length was shown to lie below 1600 Å by the absence of fluorescence when a thin silica window was inserted in the exciting beam. They apparently experienced great difficulty in obtaining adequate exposures owing to the formation of an opaque deposit on the window (probably of paraformaldehyde), since they give no reproduction, wave-lengths, or adequate description of the emission. Their suggestion that the emitter of the band system is CHO is scarcely justified by their evidence. They observed that the same system was emitted from formic acid in a high-frequency discharge.

In the present work it was found that the intensity of the fluorescence fell off rapidly with time, but that by cleaning the window at half-hourly intervals with a cotton-wool pad, moistened first with acetone and then with alcohol, well-exposed plates could be obtained. Occasionally the occlusion of the window was delayed for several hours. The effectiveness of this cleansing procedure gradually diminished. Removal of the window and prolonged treatment with refluxing absolute alcohol at first restored the transparency, but this procedure also became progressively less effective. The loss in transparency by fluorite has been observed previously, notably by Platt and Klevens (*Rev. Mod. Physics*, 1944, **16**, 182), who found that neither cleaning nor regrinding and polishing would restore it. They ascribe the loss of transparency to the formation of a surface film, but it seems more likely that changes in the body of the fluorite are responsible. The prolonged, and, on heating, quite intense phosphorescence, which may be observed with fluorite after exposure to the hydrogen arc, demonstrates the existence of defect or impurity levels in fluorite.

The formic acid bands excited by a high-frequency discharge through the flowing vapour were also investigated. An oscillator of the type described by Fairbrother and Tuck (*Trans. Faraday Soc.*, 1935, **31**, 520) was used. The leads from the secondary of the high-frequency transformer were twisted round the outside of a constriction of 4 mm. internal diameter in a short length of wider bore Pyrex tube at a separation of 3—4 cm. A rapid stream of vapour was distilled through the tube and the emission observed, end on, through a quartz window. At low pressures the spectrum was complex, bands of OH, CH, and CO being prominent, but at the highest pressure at which the discharge could be maintained (*ca.* 0·5 mm.), and with high rates of flow, the formic acid system was emitted with only slight interference from other spectra.

The fluorescence and high-frequency band systems are clearly identical (see Plate). The bands have no structure resolvable by a 10-cm. base glass prism. Some thirty bands can be distinguished. A satisfactory analysis has not been made, but there appears to be present a repeating pattern of four bands, which is most obvious at the short wave-length end of the system. The centres of these patterns are separated by *ca.* 1130 cm.$^{-1}$, and the internal intervals in the direction of increasing wave-length are 130, 460, and 180 cm.$^{-1}$. Methyl formate gave a fluorescence of similar colour to that of formic acid. The window was, however, completely fogged in 2—3 minutes and it was impossible to photograph the spectrum.

For the emitter of the system there would seem to be four possibilities; H·CO$_2$H, , , or H·CO. The above evidence is inadequate to permit of any closer identification.

Carbonyl Chloride.—It was hoped, by analogy with formaldehyde, that carbonyl chloride would give rise to a spectrum of COCl. Indeed, a single diffuse emission at *ca.* 2500 Å was found, but in its position, its appearance, and the shape of its photometer trace it corresponded so closely with the group of bands previously obtained by Elliott and Cameron (*Proc. Roy. Soc.*, 1949, *A*, **169**, 463) from chlorine excited by active nitrogen, that there was no doubt that the emitter of the fluorescence was the chlorine molecule.

Methylene Iodide.—Possible sources of the methylene radical are diazomethane, keten, and methylene halides. The first has not yet been investigated, and keten yields no emission detectable with the apparatus available, but methylene iodide emits a weak yellow-green fluorescence which fades very rapidly owing to the formation of a deposit on the window. Several plates of this emission were obtained, each with a total exposure of 5 hours or more, by interrupting the exposure at frequent intervals in order to clean the window with cotton-wool moistened with acetone. Visible and ultra-violet bands were present on the plates. All were rather weak, particularly those in the blue region, but were identifiable as parts of known iodine systems. The strongest part of the spectrum was the group of bands (which, except under high dispersion, appears to be a continuum) with a head at 3450 Å. These bands have been extensively studied by Elliott (*Proc. Roy. Soc.*, 1940, *A*, **174**, 273), Warren (*Phys. Review*, 1935, **47**, 1), and Venkatiswarlu (*ibid.*, 1951, **81**, 821). When obtained as a fluorescence from iodine vapour at a low pressure the 3450-Å group forms a weak part of an extensive band system, stretching to shorter wave-lengths. Elliott showed, however, that, in the presence of a considerable pressure of inert gas, the shorter wave-length part of the spectrum was repressed and the intensity of the 3450-Å group relatively increased so as to exceed that of the rest of the system. Our spectrograms closely resemble those obtained by Elliott in the presence of 10 and 76 cm. Hg of nitrogen, although the total pressure in our work was less than 0·5 mm.

Although iodine molecules will accumulate to some extent in the fluorescence chamber, the fluorescence observed with methylene iodide cannot be produced by their secondary excitation by absorption of light since, if this were so, the other bands at shorter wavelengths should also have been recorded. The same is probably true also for the chlorine emission from carbonyl chloride, although, in this case, the evidence is less complete. Two types of process remain, which could explain the appearance of the halogen fluorescence; dissociation of RX_2 into R and an excited halogen molecule (molecular mechanism) or dissociation into radicals, one of which is excited and, by subsequent reaction, produces an excited halogen molecule (radical mechanism).

$$\begin{array}{lll}
\quad(1) & \quad(2) & \quad(3) \\
RX_2 + h\nu = R + X_2^* & RX_2 + h\nu = RX + X^* & RX_2 + h\nu = RX^* + X \\
 & (a)\ X^* + RX_2 = RX + X_2^* & (a)\ RX^* + RX_2 = R + RX + X_2^* \\
 & (b)\ X^* + X_2 = X + X_2^* & (b)\ RX^* + X_2 = RX + X_2^*
\end{array}$$

With both carbonyl chloride and methylene iodide the molecular mechanism is favoured thermochemically and could occur with absorption of light of wave-length *ca.* 1750 Å or less. Of the radical mechanisms (2) may be certainly excluded for carbonyl chloride, since the lowest relevant excited level of Cl ($^4P_{5/2}$) is 71,954 cm.$^{-1}$ above the ground state (Evans, *Proc. Roy. Soc.*, 1931, *A*, **133**, 417), and (2) would consequently require a wave-length beyond the transmission limit of fluorite. The $^4P_{5/2}$ iodine level is 54,632 cm.$^{-1}$ above the ground state, so that with a reasonable value (*ca.* 50 kcal.) (Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **37**, 19) for $D(CH_2I{-}I)$ (2) would be possible with light transmitted by fluorite. Reactions (2*a*) and (2*b*) would both be strongly exothermic, and since the excited iodine molecule must, on account of the emission spectrum, possess little vibrational energy, the heat of the reaction would have to appear mainly as translational energy. (2*b*) is therefore considered improbable.

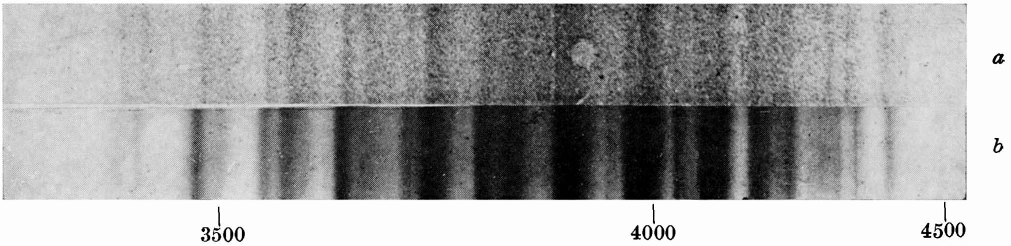
Nothing is known of the higher electronic levels of the radicals COCl and CH_2I, assumed in scheme (3). Further experiments, for which suitable apparatus was not available at the time this work was carried out, will be reported in a subsequent communication.

Fluorescence of Molecular Nitrogen.—Jakovleva briefly reported (*Acta Physiochim., U.R.S.S.*, 1936, **9**, 547) the appearance of bands of the second positive system of nitrogen while investigating the fluorescence of cyanogen bromide and later (*Z. Physik, Sov. Union*, 1936, **9**, 547; *Bull. Acad. Sci., U.R.S.S.*, 1940, **4**, 59) of bands of nitrogen when nitrogen, air, cyanogen, and cyanogen bromide were illuminated with a hydrogen discharge through a fluorite window. The same phenomenon has been observed during attempts (which were unsuccessful) to excite a fluorescence in ethylene and glyoxal, when nitrogen entered the apparatus through a small leak. With flowing air or nitrogen at a pressure of about 0·5 mm. the intensity of the fluorescence was much greater and well-exposed plates were obtainable in an hour. The appearance of the 0–0 N_2^+ band was fickle but was, on occasion, as strong as the 0–0 band of the second positive system. The intensity of this emission faded with subsequent exposures and all efforts to resuscitate it failed. Indeed, numerous attempts, which have since been made by Mr. Ward, to excite this fluorescence, have all proved abortive.

The upper state of the N_2^+ band lies more than 151,000 cm.$^{-1}$ above the ground state of the nitrogen molecule (Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, D. Van Nostrand, 2nd Edn., 1950) and at least two quanta of any radiation to which fluorite is transparent would be required to supply this energy. One quantum would probably also be inadequate to excite the nitrogen molecule to the upper state of the second positive system. During the excitation of the fluorescence in air and nitrogen polymeric substances derived from glyoxal and ethylene were present in the fluorescence chamber. If this emission is genuine and not merely false light scattered from the exciting source, which on these occasions only, by coincidence contained nitrogen as an impurity, the presence of molecules other than nitrogen would seem to be necessary for its appearance.

KING'S COLLEGE, STRAND, LONDON, W.C.2.

[*Received, January* 21*st*, 1952.]

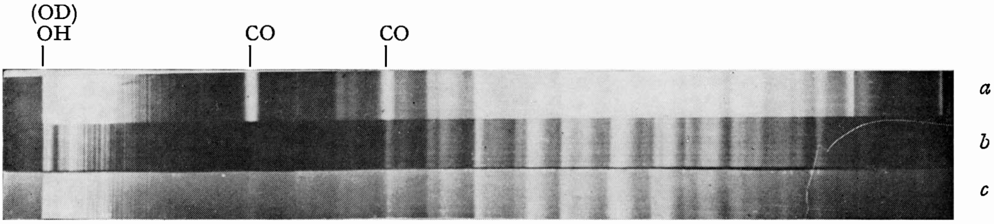


Emission from $H{\cdot}CO_2H$.

(*a*) *Fluorescence.* (*b*) *High-frequency discharge.*

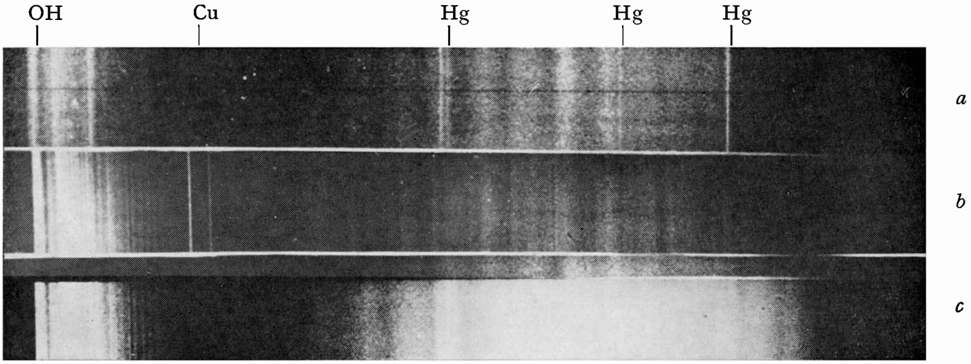
(Paper No. 394.)

PLATE 1.



High-frequency discharge in (*a*) $\mathrm{H{\cdot}CO_2H}$, (*b*) $\mathrm{H{\cdot}CO_2D}$, (*c*) $\mathrm{D{\cdot}CO_2D}$.

PLATE 2.



Fluorescence from (*a*) $\mathrm{H{\cdot}CO_2Et}$, (*b*) $\mathrm{H{\cdot}CO_2H}$, (*c*) $\mathrm{H{\cdot}CO_2Me}$.

(Paper No. 395.)