395. *The Origins of the Fluorescences obtained from Formic Acid and Methylene Iodide.*

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Comparison of the emissions from $H{\cdot}CO_2H$, $D{\cdot}CO_2H$, $D{\cdot}CO_2D$, $H{\cdot}CO_2Me$, and $H{\cdot}CO_2Et$ indicates that the emitter is $H{\cdot}CO_2$. Photo-dissociation of methylene iodide by radiation in the Schuman region is shown to yield as an immediate product an excited I_2 molecule, whose excitation energy is radiated as a fluorescence; there was no evidence of any emission from the CH_2 radical, which was presumably produced simultaneously.

ONE of the difficulties encountered in previous work with the Allen hydrogen arc (*J. Opt. Soc. Amer.*, 1941, **31**, 268) was the short life of the filament, which seldom exceeded 50 hours and was often as short as 5 hours. At the commencement of the work now described we became aware of a report [Wyckoff, M.I.T. Quart. Progr. Reports (Electronics), July 1949, p. 80], in which it was pointed out that the filament should be turned through 90° from the position shown in Allen's diagram. This small change increased the life to several hundred hours with an arc current of 10—14 amps. The dimensions of the constriction, through which the discharge passes, were also modified as recommended in the same report. The increased current now possible, and the new constriction, increased the fluorescent intensity at least three-fold, as estimated from the exposures required to obtain the 3064-Å band of OH from water vapour.

It was also desirable to be able to detect the occurrence of ultra-violet emission by a process less tedious than photography. This was particularly important with the f 1·8 spectrograph used, since at any one setting a range of only about 7000 cm.$^{-1}$ could be focused on the photographic plate. A 27 M3 photo-multiplier, whose output was further amplified, had sufficient sensitivity to enable any reasonably extensive fluorescence, which could be photographed in not more than 6 hours, to be detected and its approximate spectral range determined.

The re-investigation of the formic acid emission immediately followed the use of alkyl nitrites and nitrates, substances which do not fog the window. It was then found that fogging of the window, which had previously defeated all attempts to obtain photographs of the emission of methyl formate, did not interfere. (What may have been a similar effect of oxides of nitrogen was observed about 20 years ago. An attempt was then made to remove a deposit of sulphur produced by the photolysis of carbonyl sulphide in the presence of oxygen by treatment with nitrogen dioxide, first photochemically and secondly by heat. During the heating, the sulphur distilled on to the cooler parts. After a few repetitions of this treatment deposition of sulphur, which had previously completely obscured the window in a few minutes, gave no further trouble.)

Formic Acid.—Replacement of the ionisable hydrogen atom in formic acid by deuterium evoked no detectable change in the spectrum excited by a high-frequency discharge, but replacement of both hydrogen atoms by deuterium produced noticeable shifts towards the violet of bands in the region of 4000 Å (Plate 1). The emitter must therefore contain the hydrogen atom directly linked to carbon, and the origin of the system probably lies towards or beyond the short wave-length end of the emission.

The fluorescences obtained from methyl and ethyl formates are compared with that given by formic acid in Plate 2. Apart from a general broadening of the ester bands, so that close bands, which are distinctly separated with the acid, become largely merged with the esters, the general correspondence is so close that there can be little doubt that the same molecule is responsible for all three spectra. The emitter must, therefore, be some fragment common to formic acid and its esters. Radicals consistent with this requirement and the influence of deuterium substitution in the acid are $H{\cdot}CO$ and $H{\cdot}CO_2$. The spectrum is quite distinct from the ethylene flame bands, which supposedly arise from $H{\cdot}CO$. The difference of *ca.* 1130 cm.$^{-1}$, which appears prominently in this fluorescence, is improbable for the ground state of CHO, which would be the only likely lower state if $H{\cdot}CO$ were the emitter.

$H{\cdot}CO_2$ is accordingly favoured as the molecule responsible for this fluorescence, 1130 cm.$^{-1}$ being perhaps the symmetrical CO valency vibration. The greater width of the bands when excited from the esters is explicable as due to the greater angular momentum imparted to the $H{\cdot}CO_2$ radical by the expulsion of an alkyl radical than of the hydrogen atom (cf. the differing rotational energy distribution of OH excited from water and hydrogen peroxide, Dyne and Style, *Nature*, 1951, **167**, 899).

Methylene Iodide.—If the iodine fluorescence obtained from methylene iodide was excited by secondary processes such as (2) or (3) of the previous paper (Dyne and Style, *J.*, 1952, 2122), its intensity would only in exceptional circumstances be proportional to both the intensity of the exciting light and the concentration of methylene iodide vapour, whereas, if an excited I_2 molecule is an immediate product of the photodissociation and emits, the fluorescent intensity should always be directly proportional to the exciting intensity and the pressure of methylene iodide. The determination of the relation between the fluorescent intensity and these variables was complicated by the rather rapid decrease in the intensity of fluorescence with time, caused by the fogging of the fluorite window, the extent of which had to be repeatedly measured by determining the intensity of the fluorescence under a standardised set of conditions. Determination of the dependence on methylene iodide was further complicated by the experimental necessity of using the fluorescence emitted from a point about 3 mm. from the fluorite window, in order that light from the exciting source scattered by the window or deposits on it should not enter the spectrograph. Even with low pressures of methylene iodide a considerable fraction of the exciting radiation is absorbed in 3 mm. The curvature of the plot shown in Fig. 1 is mainly, if not entirely, produced by this absorption rather than by quenching.

FIG. 1.

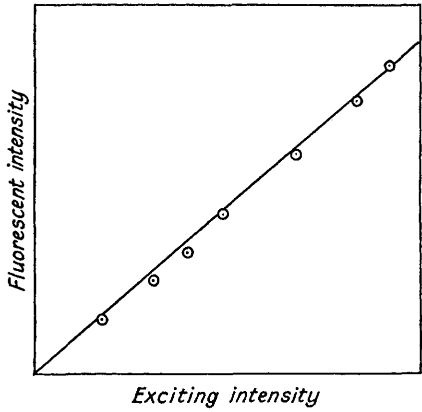
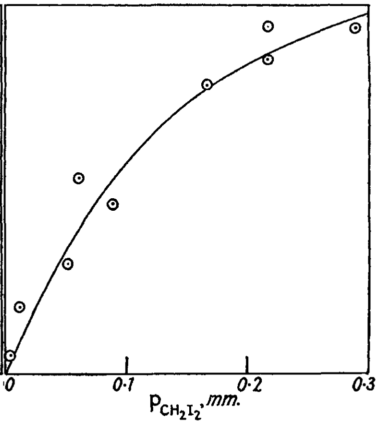


FIG. 2.



The dependence on the exciting intensity is strictly linear (Fig. 1), and at low methylene iodide pressures the dependence on $p_{CH_2I_2}$ is very probably linear (Fig. 2). Similar curves were obtained for the visible emission. This evidence favours immediate photo-dissociation of methylene iodide into methylene and excited iodine. More conclusive evidence that this is so was obtained by placing a fine wire in the exciting beam and observing visually with a lens its "shadow" in the fluorescence. Even with methylene iodide pressures of only a few hundredths of a millimetre, when the mean free path was probably as great as the diameter of the wire, no blurring of the shadow was observed.

The last observation excludes all mechanisms for the generation of the fluorescence except :

$$CH_2I_2 + h\nu_1 \longrightarrow CH_2 + I_2^*$$
$$I_2^* \longrightarrow I_2 + h\nu_2$$

The shadow experiment was confined to the visible emissions but, in view of the very similar behaviour of the visible and ultra-violet emissions in other respects, it is believed that the same mechanism may be safely assumed to apply to the ultra-violet bands also.

Methylene iodide thus falls into line with certain other iodides (stannic and bismuth iodide) which according to Terenin and Tschubarov (*Acta Physiochim., U.R.S.S.*, 1937, **7**, 1) dissociate directly into a radical and an excited I_2 molecule.

The failure to detect any emission from CH_2 does not necessarily imply that this radical possesses no observable transition in the range 5000—2400 Å covered by this investigation. Dissociation of methylene iodide to give excited methylene may not occur at wave-lengths where the source is sufficiently intense.

EXPERIMENTAL

Preparation of $H{\cdot}CO_2D$.—Commercial 98% formic acid was dissolved in excess of 99% deuterium oxide and distilled off from boric oxide under reduced pressure at room temperature. The product was again treated in the same way, to yield an acid which, judging from the OH band, was essentially $H{\cdot}CO_2D$.

Preparation of $D{\cdot}CO_2D$.—Anhydrous oxalic acid was converted into $(CO_2D)_2$ by twice recrystallising it from 99% deuterium oxide. The deuterium oxide of crystallisation was removed by heating the acid *in vacuo* and $(CO_2D)_2$ was then pyrolysed to $D{\cdot}CO_2D$, which was dried with boric acid before use. This follows the procedure of Herman and Williams (*J. Chem. Phys.*, 1 940, **8**, 447).

The Manometer.—This consisted of a Pyrex spiral whose movement was amplified by a bifilar suspension and optical lever, to give a sensitivity of 120 mm. scale for 1 mm. Hg.

Intensity Measurement.—The photo-multiplier was located behind a slit, which replaced the camera when the photo-cell was in use. In order to amplify the photo-current from the cell without interference from the dark current, the light entering the spectrograph was chopped. The three-stage resistance-capacity coupled amplifier was coupled to the photo-cell through either a 1 MΩ or a 10 MΩ resistance and to the mechanical rectifier through a step-down centre-tapped transformer. The rectifier consisted of a high-speed relay operated by a commutator on the same shaft as the chopping disc. The rectified current was measued by a microammeter giving a full-scale deflection with 25 μamp. The selectivity of the system could be increased by overdamping the microammeter. The amplification available exceeded that which could be usefully employed without cooling of the photo-cell.

Variation of the exciting intensity was produced by changing the current carried by the hydrogen arc. The intensity of the visible emission of the arc was measured with a selenium barrier-layer photo-cell, and the intensity of the H_2 bands in the region of 1300 Å by the photo-multiplier current produced by the OH band emission from water vapour. Both the visible and the ultra-violet emission of the arc showed the same, not quite linear, dependence on the arc current. In determination of the relation between the exciting intensity and the fluorescent intensity of methylene iodide the loss of transparency of the window had to be allowed for. The correction was applied under the assumption, justified by the curve of Fig. 1, that the intensity of the fluorescence was proportional to that of the exciting light.

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