Biological Station, Port Erin. To all of them our thanks are due.

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PRODUCTION AND PROPERTIES OF DI-FLUOROCARBENE

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THE di-fluorocarbene molecule, CF_2, was first detected spectroscopically in 1950, when its emission[1] and absorption[2] spectra in the ultra-violet region were photographed following the decomposition of fluorocarbon vapours in an electrical discharge. The observation that, provided the containing vessel were large enough, the absorption spectrum could still be detected seconds after the discharge was discontinued[2] was striking; it was inferred that CF_2 was a remarkably stable species, and that it disappeared after diffusion to the wall of the vessel.

Since 1950, CF_2 has been produced (and detected spectroscopically) by such a variety of methods that it is now apparent that its formation must be a favoured process. Table 1 lists some parent molecules which have been used and the methods of decomposition adopted. A zero order for the rate of disappearance of CF_2 produced in flash photolysis has been reported, and its long life-time confirmed[3].

Table 1

Parent molecule	Method	Reference
Fluoro-carbons	Elec. discharge	1, 2
CF_4	Furnace	4
CF_3COCF_3	Flash photolysis	5
CF_2Br_2	,, ,,	6
CF_2HBr	,, ,,	7
$CF_2ClCOCF_2Cl$	,, ,,	3
$CF_2:CF_2$	,, ,,	8
CF_3COOH	,, ,,	8

It has been suggested[9] that the production of CF_2 in the flash photolysis of hexa-fluoroacetone might follow the disproportionation:

$$2CF_3 \rightarrow CF_4 + CF_2$$

However, when the photolysis of CF_3I is used as a source of CF_3 radicals, no CF_4 can be detected among the volatile reaction products although there is an abundance of C_2F_6 (ref. 10). Further, although flash photolysis of CF_2Br_2 and CF_2HBr in the quartz ultra-violet region produces a high yield of CF_2, no CF_2 absorption could be detected following the flash photolysis of CF_3I (ref. 11) and CF_3Br (ref. 8) under the same conditions. Indeed, only when the latter molecules were photolysed in a specially constructed flash discharge cell which was transparent to wavelengths well below 2000 Å. (see Fig. 1) was it possible to observe a faint absorption spectrum of CF_2. It follows that a far greater energy input is required to obtain CF_2 from CF_3Br than from CF_2Br_2 or CF_2HBr, although the C—Br bond dissociation energies in the molecules would not differ very greatly. If the CF_2 production occurs through the disproportionation of substituted methyl radicals, then it is hard to understand why the disproportionation of CF_2Br and CF_2H should be so favoured as compared with CF_3.

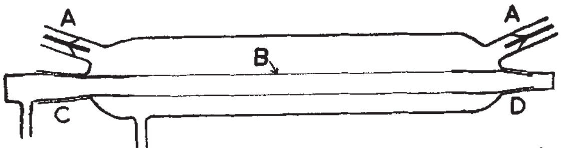

Fig. 1. Silica cell for flash photolysis at wave-lengths < 2000 Å. (Drawing not to scale.) *A*, Electrodes; *B*, thin silica (thickness 0·5 mm.); *C*, socket and cone, *B*.19; *D*, socket and cone, *B*.14

Finally, we have found that if CF_2Br_2 is flashed (under conventional conditions) in the gas phase in the presence of a large excess of oxygen, very few bromine atoms are produced, since the expected absorption spectrum of the BrO radical is barely detectable. (Flash photolysis of CCl_2Br_2 under the same conditions resulted in a very intense transient spectrum of BrO.) In particular, the yield of CF_2 is virtually independent of the oxygen pressure, which must exclude CF_2Br radicals as the precursors to CF_2 formation.

The data presented are all consistent with the primary production of CF_2 in a molecular split, as:

$$CF_2Br_2 + h\nu \rightarrow CF_2 + Br_2$$
$$CF_2HBr + h\nu \rightarrow CF_2 + HBr$$
$$CF_3COCF_3 + h\nu \rightarrow CF_2 + CF_3COF$$

and so on. A similar primary decomposition has been proposed in the xenon photosensitized decomposition of CF_4 (ref. 12). Such modes of decomposition are not in conflict with the suggestion that CF_2 is a relatively stable species having the properties of a two-electron deficient molecule rather than a di-radical. This hypothesis is favoured by: (1) the observation of an intense absorption spectrum of CF_2 following flash photolysis of tetra-fluoroethylene in the gas phase[8], which demonstrates the relative weakness of the carbon–carbon bonding in the olefine; (2) the lack of reactivity of CF_2 towards molecular oxygen, and (3) its zero-order rate of decay, demonstrating its lack of reactivity to other molecules of the same kind.

The difficulty in forming CF_2 following photolysis of CF_3Br is understandable in view of the energetics of the decomposition:

$$CF_3Br \rightarrow CF_2 + BrF$$

Such difficulty would not be anticipated in the cases of CF_2Br_2 and CF_2HBr, since in the first case both the bonds broken are weak, and in the second there is a considerable energy 'rebate' in the formation of the HBr molecule.

The ready decomposition of tetra-fluoroethylene into two CF_2 molecules, taken together with the other experimental results presented, suggests that in the fluorocarbon series it is not unreasonable to regard di-fluorocarbene as the simplest of the olefines. The splitting out of CF_2 from the substituted methanes and ketones listed is then analogous to the production of ethylene from ethyl iodide[13], and the Norrish Type II split in ketones containing hydrogen. Indeed, it has been proposed very recently[14] that the primary steps in the pyrolysis of hexa-fluoroacetone include the molecular decomposition:

$$CF_3COCF_3 \rightarrow CF_2 + CF_3COF$$

as well as the radical decomposition:

$$CF_3COCF_3 \rightarrow 2CF_3 + CO$$

The striking stability and the lack of chemical reactivity in di-fluorocarbene may be attributed, no doubt, to the influence of the strongly electronegative fluorine atoms. These would tend to attract the two electrons residing in the most weakly bound of the molecular orbitals, away from the neighbourhood of the carbon atom, on which they would otherwise be localized. As a result, the possibility of electron exchange interaction with other species would be much reduced, since there would be less possibility of electron overlap. This effect would not be anticipated in other di-halogenocarbenes, such as CCl_2 and CBr_2, since the electronegativities of Cl and Br atoms are not so very different from that of carbon. On Pauling's electronegativity scale, F = 4·0, Cl = 3·0, Br = 2·8 and C = 2·5. Indeed, attempts to prepare CCl_2 and CBr_2 photochemically from parent molecules analogous with those used for CF_2 production have so far proved unsuccessful[7].

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ACTION OF RADIATION ON SYNTHESIS OF DEOXYRIBONUCLEIC ACID IN NORMAL AND TUMOUR STRAIN CELLS

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HOWARD and Pelc[1,2] first showed that relatively small doses of radiation (50–200 r.) given during the deoxyribonucleic acid (DNA) pre-synthetic period, delayed the entry of cells into DNA synthesis, whereas cells already in DNA synthesis at the time of irradiation were unaffected by the doses given. These authors used phosphorus-32 uptake into DNA of bean root cells, and examined by autoradiography the number of cells synthesizing DNA over short periods up to 24 hr. during the interphase following irradiation. Holmes and Mee[3] and Kelly *et al.*[4], using regenerating liver and uptake of phosphorus-32 into DNA, again found that radiation doses of about 300 r. given during the pre-synthetic period delayed the onset of DNA synthesis : much larger doses (~2,000 r.) were required to depress DNA synthesis once it had commenced.

Lajtha *et al.*[5] found that doses of ~ 200 r. given to human bone marrow cells in culture during the pre-synthetic period delayed the entry of cells into DNA synthesis: the incorporation of ^{14}C-formate into DNA was observed by autoradiographic methods after various fractions of the interphase period following irradiation. On the other hand, it was found that a dose of 2,000–5,000 r. was required to reduce the rate of DNA synthesis to half, in cells which were already in synthesis.

In considering the effects of radiation on solid tumours *in vivo*, it is difficult to dissociate direct effects on the tumour from indirect effects acting through the surrounding host tissues[6]. In addition one such tumour usually represents a great variety of cell types ; one way out of this difficulty is to use a tumour strain growing *in vitro*, and another possibility is to use an ascites tumour.

Painter and Robertson[7] used HeLa carcinoma strain cells in culture in conjunction with thymidine uptake and autoradiography, and found an increase in the number of cells in DNA synthesis at times up to 8 hr. after 500 r. of X-irradiation, and a decrease in the number of synthesizing cells after 17 hr. These results could partly be explained by inhibition of mitosis; first, an increase by retention in synthesis of cells which would normally have divided and, later, a decrease from the consequent depletion of mitosis; first, an increase by retention in synthesis Robertson pointed out, the results are certainly inconsistent with a delay in onset of DNA synthesis induced by radiation in the pre-synthetic period[7]. Again, using HeLa cells with thymidine and autoradiography, Yamada and Puck[8] found that radiation doses of 34–135 rads produced mitotic inhibition, but not a delay in the onset of DNA synthesis in these cells ; this was in contrast with their findings with normal human cells in culture which showed a pre-synthetic delay in addition to inhibition of mitosis.

Dickson, Paul and Davidson[9] used *L* mouse strain cells in culture in conjunction with incorporation of ^{14}C-formate into DNA. These authors concluded that the effect of X-irradiation (800 r.) was to inhibit