ANALES ASOC. QUÍM. ARGENTINA, 59, 193-204 (1971)

THE PRODUCTION OF CARBON DIOXIDE FROM CARBON MONOXIDE AND OXYGEN SENSITIZED BY PHOTOLYSIS OF BIS(PERFLUOROMETHYL)PEROXIDE

BY M. A. BLESA AND P. J. AYMONINO

Cátedra de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata.

To Professor H. J. Schumacher on the occasion of his 65th birthday

RESUMEN

Se describe el estudio cinético de la reacción en cadena que tiene lugar cuando se fotoliza peróxido de bis(perfluorometilo) en presencia de mezclas de monóxido de carbono y oxígeno. La reacción conduce a la formación cuantitativa de dióxido de carbono.

SUMMARY

When bis(perfluoromethyl)peroxide is photolyzed in the presence of mixtures of carbon monoxide and oxygen a chain reaction takes place leading quantitatively to carbon dioxide. A kinetic study of this reaction is reported.

INTRODUCTION

Oxygen is a well known efficient scavenger of free radicals in gas-phase reactions. In the case of perfluorinated organic systems peroxidic substances are often found as the main reaction products when oxygen is present. In fact, oxygen is known to react rapidly with perfluoromethyl [1-3] and fluoroformyl [4] radicals.

Whilst in the case of alkyl, alkoxyl and acyl radicals the peroxidic compounds are often unstable, peroxidated derivatives of perfluorinated compounds have shown a remarkable stability (see, for example, Ref. [5]).

When either fluoroxiperfluoromethane, CF_3OF, or bis(perfluoromethyl) peroxide (BPFMP), CF_3OOCF_3, are photolyzed in the presence of carbon monoxide, the perfluoromethoxicarbonyl radical, $CF_3\dot{O}CO$, is the only initial product of the original perfluoromethoxyl radicals, $CF_3O\cdot$ [6, 7].

* Results reported in this paper have been included in a communication presented at the 13th Argentine Chemical Meeting held in San Luis, November 1970.

As reported previously [6, 8], addition of oxygen quenches the subsequent reactions of the perfluoromethoxicarbonyl radicals but, perhaps surprisingly, only trace amounts of peroxidic substances are originated.

In this paper we report a more thorough study of the reaction taking place when BPFMP is photolyzed in the presence of carbon monoxide and oxygen.

EXPERIMENTAL

BPFMP was prepared according to the method of Porter and Cady [9], by passing a stream of carbon monoxide and fluorine (diluted with nitrogen) over perfluorinated silver-plated copper wire.

Carbon monoxide was prepared as usual from sulfuric and formic acids, and purified by passage through a cold trap ($-76°$) and through two towers filled with KOH and P_2O_5 sublimed over Pyrex wool respectively.

Oxygen was generated electrolytically from a 40 % KOH solution on a nickel anode; traces of hydrogen were burnt in a furnace filled with copper oxide, and the residual oxygen was dried by passage through a series of traps containing concentrated H_2SO_4, KOH pellets and P_2O_5.

Carbon dioxide was obtained from commercial dry-ice by repeated sublimation *in vacuo*.

The reactions were performed in a conventional cylindrical photochemical reactor made from quartz and provided with flat optical windows. This vessel was attached to a quartz spiral manometer (according to Bodenstein) and fitted to a standard vacuum line through a quartz-Pyrex tapered joint. Monel needle valves and glass stopcocks lubricated with Halocarbon grease were used in the vacuum manifold.

The radiation source was a high pressure mercury lamp (Osram HBO 500); the beam of light, after being adequately collimated with quartz optics, impinged unfiltered on the frontal window of the reactor. On account of the fact that BPFMP begins to absorb at ca. 300 nm, no attempt was made to monochromatize the radiation in order to assure a conveniently high rate of reaction, making use of the whole group of lines of wavelength up to 300 nm [10].

This work was initiated with an old UV-lamp but when about two-thirds of the experiments were completed it was necessary to replace the lamp; with the new one, reaction rates increased about 80 %.

The reactor was thermostatized by circulating water from a Lauda Ultrathermostat.

The reaction products were identified and their concentrations estimated by IR spectroscopy, as performed in a Perkin Elmer 221 spectrophotometer with the NaCl prism-grating interchange.

Carbon dioxide was practically the only reaction product, its yield being ca. 100 %, as referred to CO and O_2 consumed. Only traces of other substances could be detected by collecting the product of several experiments and distilling off volatiles at $-120°$. The residue was of carbonylic nature and its yield relative to carbon dioxide was less than 1×10^{-3}. The very small quantities of residue obtained precluded any further investigation concerning its identity (see, however, Ref. 8). BPFMP was not consumed to any detectable extent.

It is notheworthy that carbonyl fluoride was not found at all.

Accordingly, the pressure decrease was taken as a safe measure of the rate of the reaction:

$$CO + 1/2\ O_2 \rightarrow CO_2$$

RESULTS

The reaction was found to exhibit a long induction period, after which a constant rate was achieved and maintained until less than 5 mm Hg of carbon dioxide or oxygen were left (according which reactant was in defect). Fig. 1 shows the plot of the rate (v), measured by the pressure decrease in mm Hg/min., a a function of the total pressure in mm Hg for two typical experiments. We have supposed that the following relationships are valid:

$$v = -\frac{\Delta p}{\Delta t} = \frac{1}{2}\frac{dp_{CO_2}}{dt}$$

$$p^0_{total} - p_{total} = 1/2\, p_{CO_2}$$

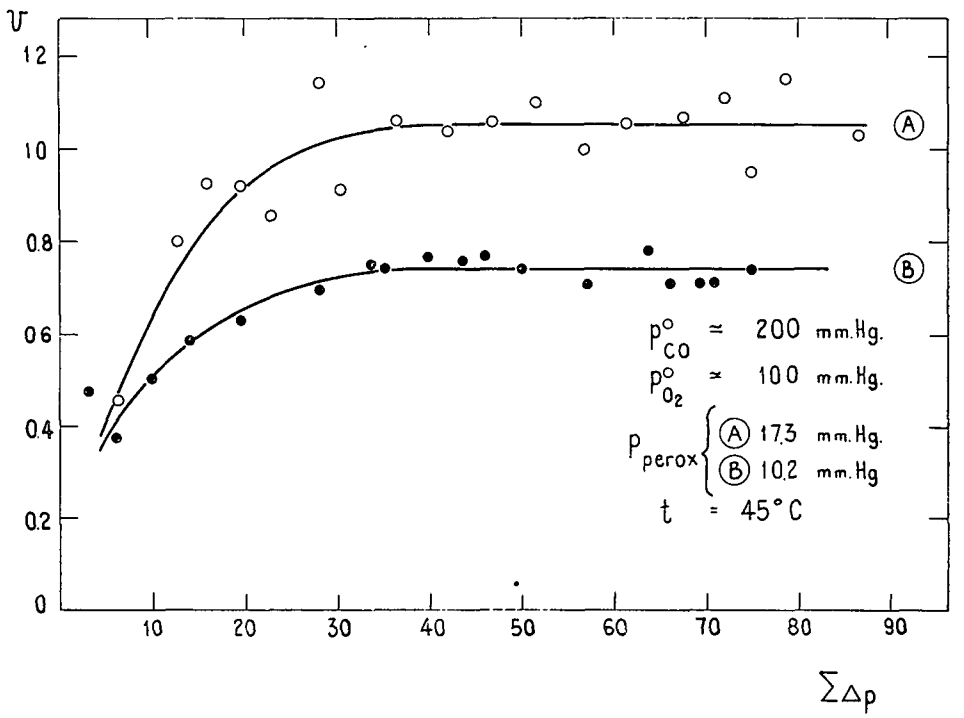

Fig. 1. — Results of two typical experiments

Fig. 1 shows that v is independent on the concentration (pressure) of either carbon monoxide or oxygen, and this fact was further confirmed by changing the initial pressure of each reactant. The results are shown in Figs. 2 and 3.

In Fig. 4 we have combined the results of experiments performed at different pressures of peroxide and with a wire grating of 35 % transmittance

interposed in the light beam (X = 35; otherwise X = 100). Data agree with the following relations:

$$v = -\frac{\Delta p}{\Delta t} = k \cdot I_{abs}^{0.60} = k' \cdot p_{perox}^{0.60}$$

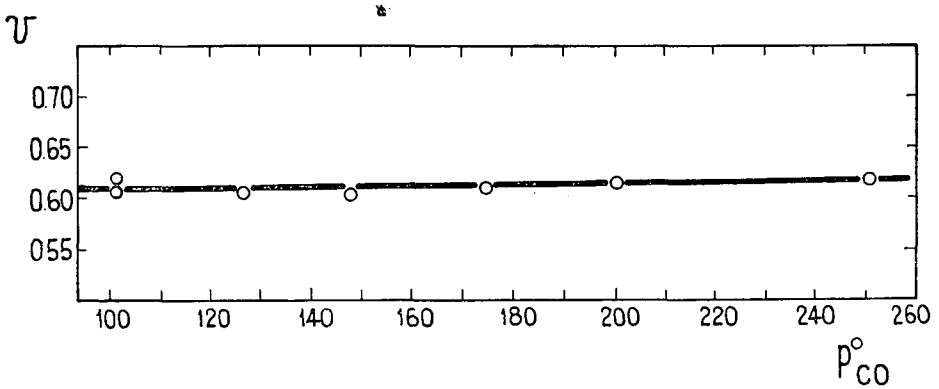

Fig. 2. — Constancy of rate with initial pressure of oxygen

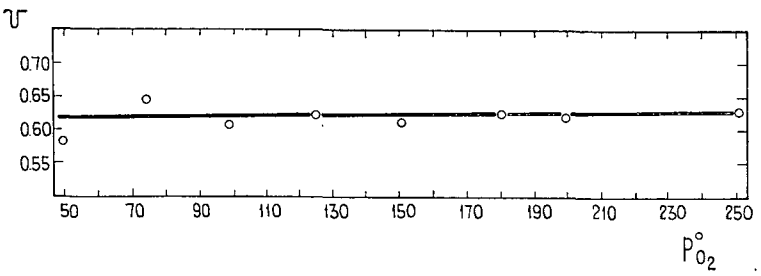

Fig. 3. — Constancy of rate with initial pressure of carbon monoxide

A very interesting feature is that, although no reaction took place in the dark when the reactants were mixed, there was a fast thermal reaction following the photochemical process when the light was cut off. In fact, after cutting off the illumination the reaction proceeded with an initial rate equal to the (previous) photochemical rate. Fig. 5 shows the results of an experiment performed with intermitent light at 35°, with 36.1 mm Hg of BPFMP, 200.3 mm Hg CO and 102.2 mm Hg O_2.

The dark reaction was attributed to some unstable intermediate which could maintain the reaction chain. Efforts directed to the isolation, or at least to detect this intermediate were unsuccessful. Thus, a mixture of reactants was irradiated in an infrared cell through one of the NaCl windows and the spectrum scanned immediately after different irradiation periods, looking

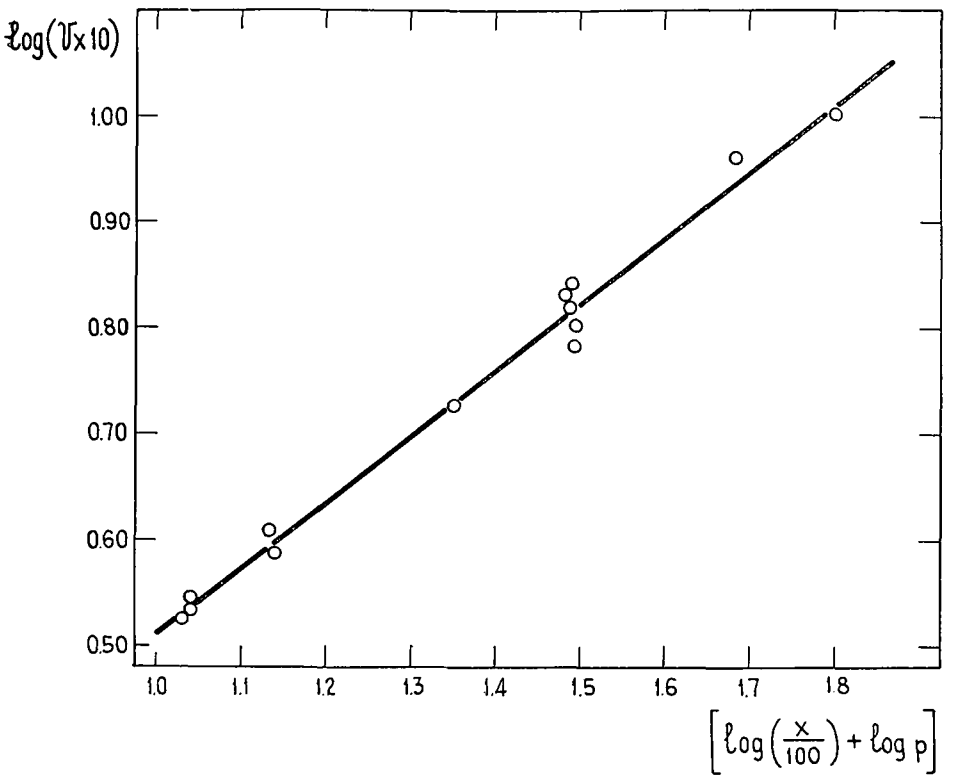

Fig. 4. — Determination of the exponent on I_{abs} and p_{perox}

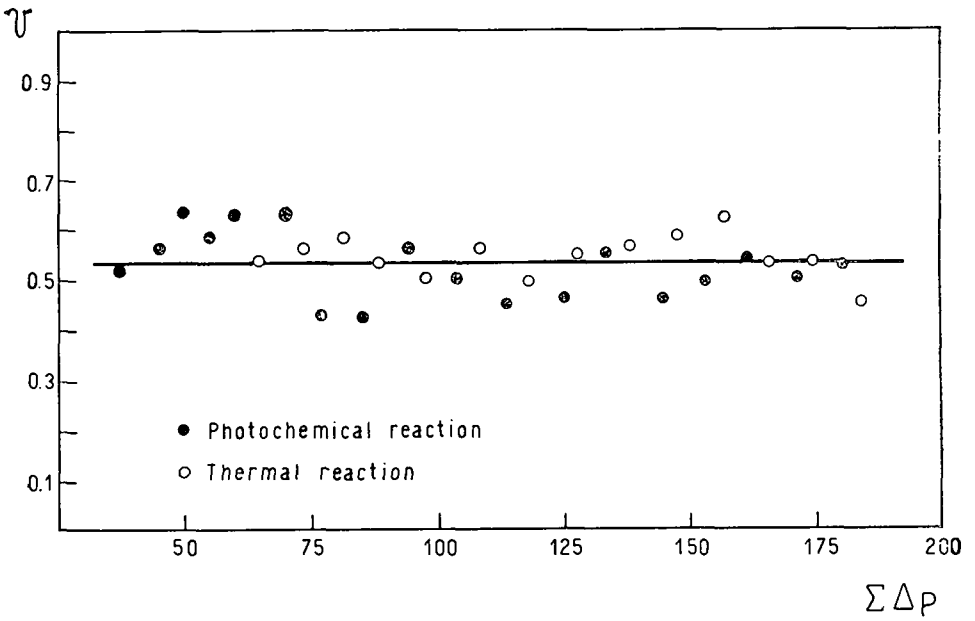

Fig. 5. — Experiment with intermitent light

for some carbonylic substance. No band was found in the C = O stretching region, indicating that the concentration of the intermediate, if any at all, was not high enough to be detected by IR spectroscopy.

In another experiment, 150 mm Hg of carbon monoxide, 150 mm Hg of oxygen, and BPFMP at is vapour pressure were photolyzed in a 700 ml reactor provided with an immersion mercury resonance lamp (PL 313 from Quarzlampengesellschaft, Hanau, Germany). The reactor was immersed in a Dewar flask containing dry ice-ethanol. After illuminating for 50 h the product was fractionated by low temperature distillations, but it was again impossible to detect by IR spectroscopy any intermediate.

DISCUSSION

There are not very many plausible schemes which can fit the kinetic law found, and at the same time allow for the thermal reaction. First of all, it should be noted that the direct photochemical reaction between oxygen and carbon monoxide under 2537 Å-radiation can be safely discarded as an important process. The available data [11] show that in liquid carbon monoxide this direct reaction has a quantum yield smaller than 1. Ozone could not be either the intermediate, as it would not react in the dark with carbon monoxide [12]. In any case, a mixture of carbon monoxide and oxygen irradiated in the same experimental conditions showed no pressure drop when the peroxide was absent.

Indeed, the initiation step cannot be other than:

$$(CF_3O)_2 + h\nu \rightarrow 2\,CF_3O\cdot \qquad (1)$$

(previous photochemical studies on this substance support this reaction [7]).

The following step has also been elucidated in previous works [6, 7]:

$$CF_3O\cdot + CO \rightarrow CF_3OCO \qquad (2)$$

and it must be followed by:

$$CF_3OCO + O_2 \rightarrow CF_3OC(O)O\cdot_2 \qquad (3)$$

The reaction $CF_3O\cdot + O_2$ is not included in view of the high scavenging ability of carbon monoxide for $CF_3O\cdot$ [6]. Even if such a reaction took place to a certain extent, the products would surely decompose under irradiation, and would not affect the kinetic scheme.

Up to this point the sequence is straightforward, but from now on the proposed steps must be considered as speculative.

Previous data on polyoxigenated perfluorinated radicals point out to the possibility of steps such as:

$$2\ CF_3OC(O)O\cdot_2 \rightarrow CF_3OC(O)O_2C(O)OCF_3 + O_2 \qquad (4)$$

or even:

$$2\ CF_3OC(O)O\cdot_2 \rightarrow CF_3OC(O)O_xC(O)OCF_3 + (4-x)\ O \qquad (5')$$

where x = 3 or 4.

These reactions would be analogous to reactions giving rise to polyoxides such as $FC(O)O_2C(O)F$ [4], $CF_3O_2CF_3$ and $CF_3O_3CF_3$ [1-3] or $FC(O)O_2CF_3$ [3], but they cannot be the main reaction pathway in our system.

The results obtained on alkyl-, alkoxyl- and acyl-radicals oxidation [13] suggest that other conceivable pathway in addition to those previously considered is:

$$2\ CF_3OC(O)O\cdot_2 \rightarrow 2\ CF_3OC(O)O\cdot + O_2 \qquad (6)$$

which could be followed by:

$$CF_3OC(O)O\cdot \rightarrow CF_3O\cdot + CO_2 \qquad (7)$$

The kinetic evidence is nevertheless conflicting with steps 6 and 7 being the main path to carbon dioxide; if this were the case, a first power dependance on light intensity should be expected. The only way to explain the fractional (nearly 0.5) value found for the exponent on I_{abs} is to postulate a key step involving a first order decomposition of $CF_3OC(O)O\cdot_2$ such as:

$$CF_3OC(O)O\cdot_2 \rightarrow CF_3O\cdot + CO_3 \qquad (8)$$

which could be followed by reaction (9) (cf. Ref. [14 a-d]):

$$CO_3 + CO \rightarrow 2\ CO_2 \qquad (9)$$

In fact, any type of unimolecular decomposition of $CF_3OC(O)O\cdot_2$ leading to $CF_3O\cdot$ and CO_2 will fit the kinetic scheme.

Process(es) 4 and/or 5 could then be the chain terminating step(s).

Nevertheless, an explanation for the long induction period and the dark reaction needs to postulate the establishment of an equilibrium, and a reasonable mechanism which could explain both the dependence on light intensity and the thermal reaction would be to consider (4) as the chain-terminanting step and to replace (5') by an equilibrium:

$$2\ CF_3OC(O)O\cdot_2 \rightleftarrows \textit{Intermediate} \qquad (5, -5)$$

wich is far removed to the left. It is not unreasonable to think that the intermediate could be $CF_3OC(O)O_4C(O)OCF_3$. Analogous equilibria have been postulated for RO_4R, where R = t-butyl radical [16]. It should be emphasized that the concentration of this intermediate should be very low, as there is no reason to prefer reaction 5 to reaction 4. This low concentration is not in

disagreement with the high yield of the thermal reaction, because the chain involved must be very long. Thus, in a typical experiment, the dark reaction amounted to 30 mm Hg of pressure drop at 35° (60 mm Hg of CO_2 produced). The yield in chain ending product(s) seems to put 10^3 as a lower limit to the quantum yield for CO_2 production, and this in turn would indicate an equilibrium pressure not higher than 0.1 mm Hg for the intermediate in the experiment just mentioned. The estimation of the CO_2 quantum yield has been confirmed by results obtained in a study of the reaction between carbon monoxide and oxygen sensitized by photolysis of fluoroxiperfluoromethane [15].

Reactions 6 and 7 may take place to a certain extent and be responsible for the deviation from the value of 0.50 in the power of the intensity of light. Nevertheless, this fact can also be explained on the basis of a unimolecular termination step taking place alongside with 4; this reaction could occur either homogeneously or on the surface of the reactor:

$$CF_3OC(O)O\cdot_2 \xrightarrow{\text{wall}} products \qquad (10)$$

In some experiments, carbon dioxide was added to determine the influence of total pressure. The effect of adding carbon dioxide, if any, was to increase slightly the rate of reaction. The same conclusions can be applied to the reactions performed by adding fresh reactants (carbon monoxide and oxygen) to the reaction mixture of a previous run. This slight increase of the rate with total pressure is shown in Table 1 and this result would indicate that the termination step competing with process 8 is reaction 10 rather than 6 and 7.

TABLE 1

Influence of added CO_2

$t = 35°$

Exp. N°	$p°CO$	$p°O_2$	p_{perox}	$p°CO_2$	r	$k' \times 10$
31	148.0	84.1	31.6	—	0.760	0.96
32	147.4	83.7	31.6	ca. 148	0.854	1.08 *
33	147.0	83.8	32.0	—	0.810	1.01
34	145.8	84.9	32.0	ca. 147	0.854	1.07 *
35	144.7	86.7	32.9	199.8	0.814	1.00
36	145.8	86.7	33.0	199.3	0.829	1.02
37	148.2	83.2	32.5	361.1	0.815	1.01

* Performed on the preceding mixture.

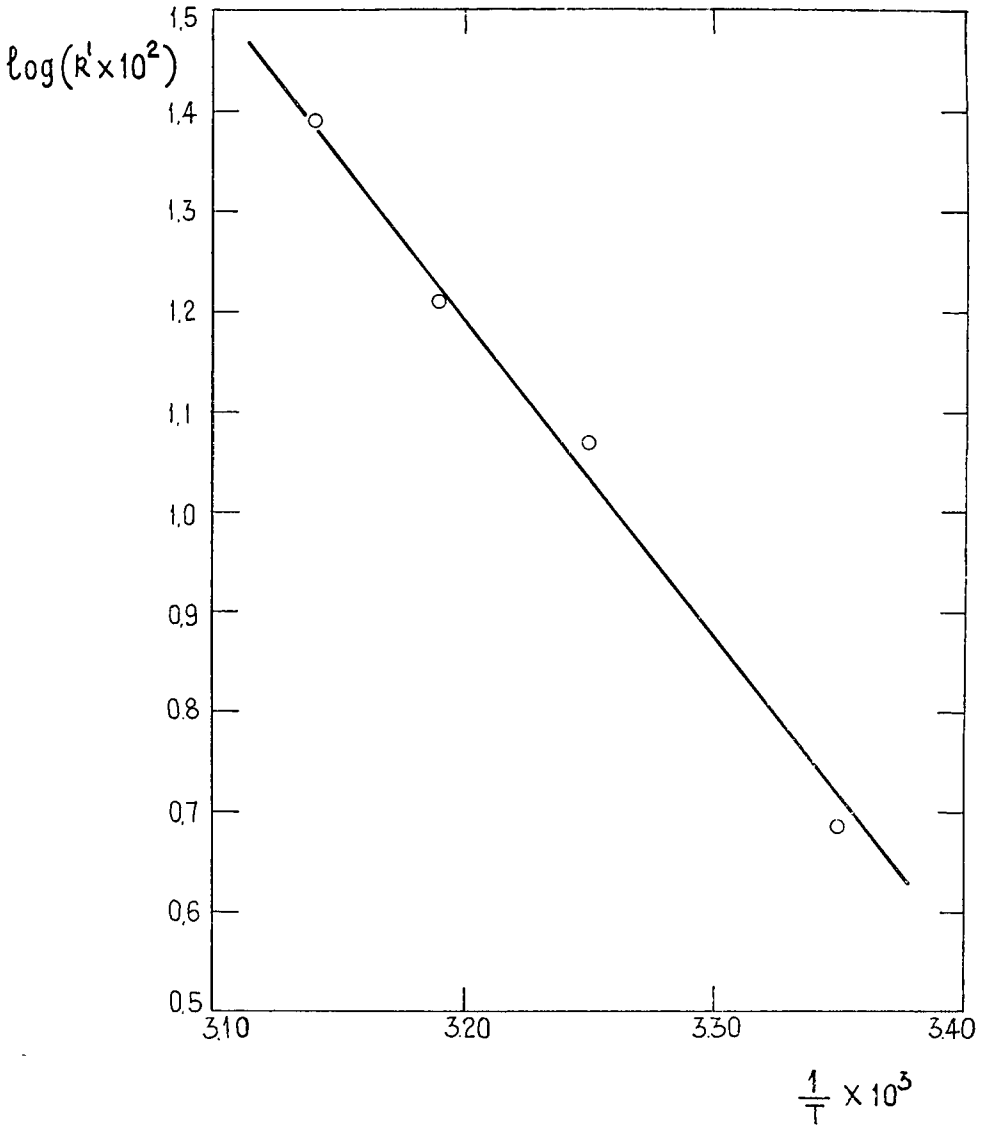

Fig. 6. — Arrhenius' plot

The simple scheme predicting the one-half power on light intensity for the formation of carbon dioxide can be accounted by the following rate expression:

$$+\frac{dp_{CO_2}}{dt} = \frac{2\,k_8}{k_4^{1/2}} \cdot I_{abs}^{1/2}$$

Accordingly:

$$k'_{(teor.)} = \frac{2\,k_8}{k_4^{1/2}} (\bar{\alpha} \,.\, l \,.\, I_0)^{1/2}$$

TABLE 2

Rate constants

t (°)	25.0	35.0	40.0	45.0
$k' \times 10$	0.486	1.14	1.62	2.46

It can be seen that the overall rate constant k' has no direct kinetic meaning, as it includes two unknowns, $\bar{\alpha}$ (average extinction coefficient) and I_0 (which should also be weighted according to the energy distribution of the lamp). The actual numbers found in this work for the overall rate constant k' have therefore little relevance. Nevertheless, results of a series of experiments performed with the UV lamp are given in Table 2. k' is dimensioned in mm-Hg and minutes.

The reaction was studied in the range 25-45°, and the Arrhenius' plot is given in Fig. 6, from which an apparent activation energy of 14.5 ± 1.2 kcal/mole can be inferred. Considering zero the activation energy of reaction (4), this value would correspond to the unimolecular process (8).

This apparent activation energy is in good agreement with the 12.4 ± 1.2 kcal/mole value found for the reaction sensitized by fluoroxiperfluoromethane, for which a similar mechanism is proposed [15].

The thermal reaction should provide a check to our discussion. According to our scheme, and once the light has been interrupted, the rate should fall according to the expression:

$$v = k_8 \left(\frac{k_{-5}}{k_{+5} + k_4} \right)^{1/2} \cdot [Intermediate]^{1/2}$$

As it stands, this expression is not useful because the concentration of the intermediate is unknown.

An integrated expression may be useful in its place, yielding the following relationship:

$$v = k_8 \left(\frac{k_{-5}}{k_5 + k_4} \right)^{1/2} \cdot [Intermediate]_0^{1/2} - \\ - \frac{1}{\lambda} k_8^2 \left(\frac{k_{-5}}{k_5 + k_4} \right) t$$

where λ is the chain length for carbon dioxide production, i.e., the rate decay should be lineal in time. In Fig. 7 results from experiments performed with the lamp at 35°, with ca. 35 mm Hg BPFMP, are plotted. In each case light was interrupted after reaching the constant rate and the dark reaction was

measured thereafter. Points fit fairly well a straight line of slope equal to 1.4×10^{-2} mm Hg. min^{-2}.

Finally, it is interesting to point out the different behaviour of the radicals $RC(O)O\cdot_2$ (R = F, CF_3O). Whilst $FC(O)O\cdot_2$ mainly recombines to yield $FC(O)O_2C(O)F$ [4], the supposed $CF_3OC(O)O\cdot_2$ seems to yield only carbon dioxide. This should be ascribed to a difference in the R-C bond-strenghts and perhaps to the stability of the $CF_3O\cdot$ radical.

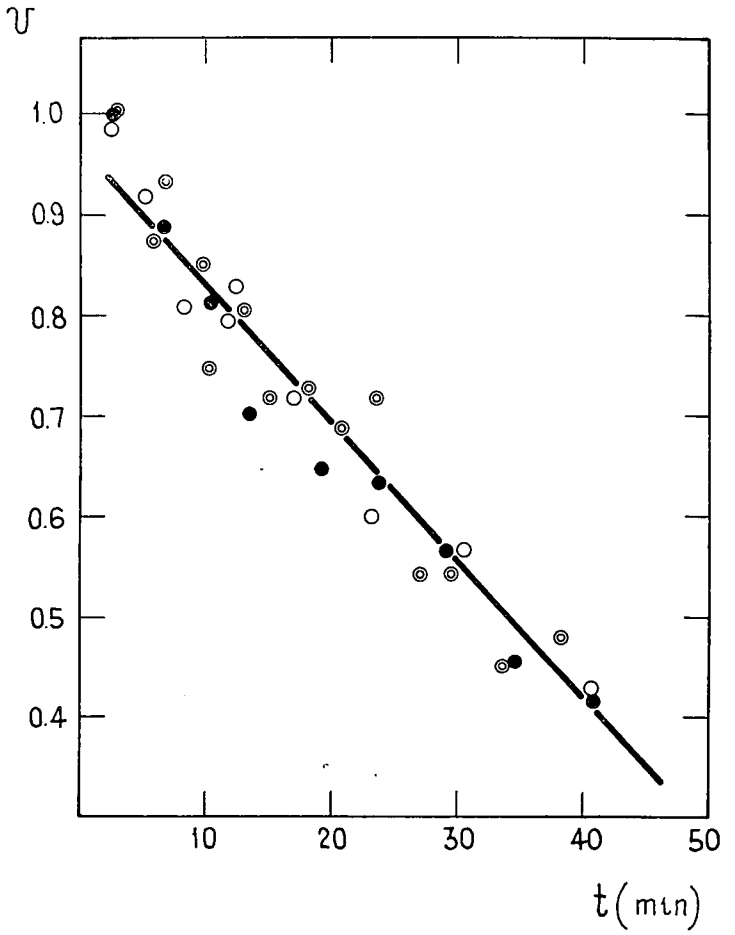

Fig. 7. — Dark reaction

ACKNOWLEDGMENTS

To Dr. L. R. Anderson and W. B. Fox (Allied Chemical Corp., U.S.A.) for a cylinder of fluorine. To Alexander von Humboldt Foundation, Germany, for a photochemical reactor. To Consejo Nacional de Investigaciones Científicas y Técnicas, for support. To Prof. H. J. Schumacher for facilities of ISI, FCE, UNLP. To Facultad de Ciencias Exactas, UNLP, for a special contract granted to M. A. B.

REFERENCES

1 V. A. Ginsburg, E. S. Vlasova, N. M. Vasil'eva, N. S. Mirzabekova, S. P. Makarov, A. I. Shchekotikhin and A. Ya. Yakubovich, *Dokl. Akad. Nauk. SSSR*, *149*, 97 (1963); *C. A.*, *59*, 5008 c (1963).

2 E. L. Varetti and P. J. Aymonino, *Anales Asoc. Quím. Arg.*, *58*, 23 (1970).

3 M. A. Blesa and P. J. Aymonino, *Anales Asoc. Quím. Arg.*, *58*, 27 (1970).

4a A. J. Arvía, P. J. Aymonino, C. H. Waldow and H. J. Schumacher, *Angew. Chem.*, *5*, 169 (1960).

4b J. M. Heras, A. J. Arvía, P. J. Aymonino and H. J. Schumacher, *Z. phys. Chem.*, *28*, 250 (1961); *Anales Asoc. Quím. Arg.*, *50*, 1 (1962).

5 R. L. Talbott, *J. Org. Chem.*, *33*, 2095 (1968).

6a P. J. Aymonino, *Chem. Comm.*, 241 (1965).

6b M. A. Blesa and P. J. Aymonino, *Anales Asoc. Quim. Arg.*, *56*, 101 (1968).

6c M. A. Blesa and P. J. Aymonino, *Anales Asoc. Quim. Arg.*, *56*, 113 (1968).

7a E. L. Varetti and P. J. Aymonino, *Chem. Comm.*, 680 (1967).

7b E. L. Varetti and P. J. Aymonino, *Anales Asoc. Quim. Arg.*, *55*, 153 (1967).

8 P. J. Aymonino, *Photochemistry and Photobiology*, *7*, 761 (1968).

9 R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, *79*, 5628 (1967).

10 J. G. Calvert and J. N. Pitts, "*Photochemistry*", John Wiley and Sons, New York, 1966.

11 O. F. Raper and W. B. DeMore, *J. Chem. Phys.*, *40*, 1047 (1964).

12 D. Garvin, *J. Am. Chem. Soc.*, *76*, 1523 (1954).

13 J. H. Raley, L. M. Porter, F. F. Rust and W. E. Waughan, *J. Am. Chem. Soc.*, *73*, 15 (1951).

14a R. A. Young and A. Y. M. Ung, *J. Chem. Phys.*, *44*, 3038 (1966).

14b T. G. Slanger, *J. Chem. Phys.*, *45*, 4127 (1966).

14c A. Y. M. Ung and H. I. Schiff, *Can. J. Chem.*, *44*, 1981 (1966).

14d M. Clerc and A. Reiffsteck, *J. Chem. Phys.*, *48*, 2799 (1968).

15 M. A. Blesa and P. J. Aymonino, 13th Argentine Chemical Meeting, San Luis, November 1970, to be published elsewhere.

16 J. E. Bennett, D. M. Brown and B. Mile, *Chem Comm.*, 504 (1969).

Received: November 1970.