

QUANTUM YIELD AND TOTAL PRESSURE EFFECT IN PERFLUOROGLUTARIC ANHYDRIDE PHOTOLYSIS IN THE GAS PHASE[†]

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Summary

The quantum yield of the photolysis of perfluoroglutaric anhydride (PFGA) in the gas phase ($\phi_{CO} = 0.34 \pm 0.07$) was determined in runs using light of wavelength 254 nm. This value is intermediate between the quantum yields of open-chain perfluorinated anhydrides and of strained cyclic perfluorinated anhydrides. The PFGA quantum yield is independent of time and total pressure.

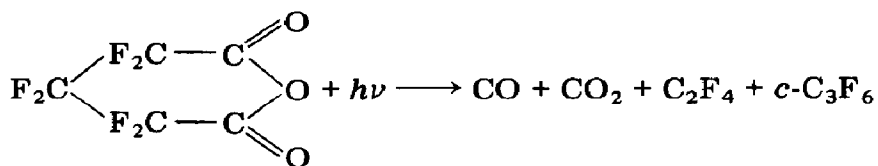
The photolysis of PFGA vapour produces CO, CO₂, C₂F₄ and *c*-C₃F₆. The ratio [C₂F₄]/[*c*-C₃F₆] is significantly dependent on the total pressure as shown by runs with the addition of inert gases such as helium, argon, oxygen, nitrogen, CCl₂F₂ and C₂Cl₃F₃. Each of these gases produces a specific effect as can be seen from their collisional deactivation coefficients.

1. Introduction

It is known that in the gas phase the quantum yields in open-chain perfluorinated anhydrides are between 0.23 and 0.29 and show no pressure dependence [1 - 3], whereas in perfluorosuccinic anhydride (PFSA) they vary from 0.50 for lower pressures to almost unity for higher pressures [4, 5]. Since the latter contains a strained ring, we thought it would be of interest to study a non-strained cyclic compound such as perfluoroglutaric anhydride (PFGA) as the above discrepancy has already been explained in structural terms. We have reported a quantum yield of about 0.33 in a preliminary study of the vapour photolysis of PFGA [6]. We now present additional evidence that confirms this result.

[†]Taken from a Ph.D. Thesis by Gerardo A. Argüello, Universidad Nacional de Córdoba, 1983.

The decomposition of PFGA occurs through the overall reaction



In this early study [6] we found that the $[\text{C}_2\text{F}_4]/[c\text{-C}_3\text{F}_6]$ ratio depends on the total pressure. This suggests the presence of an excited species which could yield either product via the different paths in the reaction mechanism. We now show the results obtained by adding inert gases such as helium, argon, nitrogen, oxygen, CCl_2F_2 and $\text{C}_2\text{Cl}_3\text{F}_3$ to the system. Although oxygen cannot generally be described as an "inert" gas in a system where free radicals may be present, it is inert in this particular case. A mechanism is proposed to explain our results.

2. Experimental details

Commercially available samples of PFGA (Florochem) and perfluoroacetic anhydride (PFAA) (P.C.R.) were purified by trap-to-trap distillation. C_2F_4 was prepared by pyrolyzing Teflon. $c\text{-C}_3\text{F}_6$ was obtained by chromatographic separation of the other reaction products from the vapour photolysis of PFGA [7]. Helium (Air products), nitrogen (La Oxigena) and argon (La Oxigena) were bubbled through pyrogallol and sulphuric acid and were passed through traps at -160°C . Oxygen (La Oxigena) was bubbled through sulphuric acid; CO_2 (Pezza), CCl_2F_2 (Dupont) and $\text{C}_2\text{Cl}_3\text{F}_3$ (P.C.R.) from cylinders were purified by distillation with the middle sections being retained. No impurities were detected by IR spectroscopy or gas chromatography.

2.1. Apparatus and procedure

The apparatus and procedure were essentially the same as those previously described in ref. 6. Briefly, the experiments were performed in a conventional vacuum line. The reaction vessel consisted of a quartz cylinder 10 cm long and 5 cm in diameter with a rear glass window sealed by halo-carbon wax; the pressure was read using an MKS Baratron manometer.

Runs for quantum yield determination were carried out using monochromatic light of wavelength 254 nm from a 200 HBO Osram high pressure mercury lamp fitted in a Bausch and Lomb monochromator; those for determining the total pressure effect were carried out using a full arc mercury lamp. PFGA was carefully degassed several times before introducing it into the vessel; after illumination the reactant and the products were condensed in a liquid air cold trap and the non-condensed product was measured using a Toepler pump-gas burette. The trap was then warmed to -90°C and the non-condensed gases were collected and transferred to a Varian 3700 or 1420 chromatograph for quantification using Porapak Q attached to a silica

gel column. Chromatographic runs of standard samples were used for testing retention times and for obtaining calibration curves.

The light intensity was measured by photolysis using PFAA as the actinometer [1].

3. Results

3.1. Quantum yield

We have previously reported an approximate value for the quantum yield in the PFGA photolysis obtained from preliminary experiments. In this paper we present a more accurate value taken from experiments which were carried out as before at room temperature using light of wavelength 254 nm and illumination times between 32 and 480 min.

Two series of runs were performed. In the first the PFGA vapour pressure was varied over the 0.95 - 38.7 Torr range. The quantum yield was obtained by measuring the CO formation and was found to have an average value of 0.34 ± 0.07 (Table 1). As can be seen it is independent of pressure and illumination time. In some runs CO_2 was added as the inert gas. In the

TABLE 1

Quantum yield of perfluoroglutaric anhydride at 254 nm

<i>Time</i> (s)	<i>PFGA pressure</i> (Torr)	<i>Added CO₂ pressure</i> (Torr)	ϕ_{CO}
480	0.95	—	0.40
300	2.0	—	0.43
360	5.7	—	0.35
360	5.8	94.1	0.38
360	5.8	304.6	0.26
360	5.9	—	0.27
360	5.9	52.4	0.43
360	5.9	144.3	0.40
360	5.9	—	0.26
360	6.0	—	0.34
360	6.0	—	0.38
360	6.1	—	0.28
180	7.0	—	0.38
180	10.2	—	0.41
120	12.3	—	0.26
180	13.4	—	0.36
360	14.9	—	0.33
150	16.7	—	0.31
120	20.5	—	0.35
120	20.9	25.6	0.31
360	22.5	—	0.30
120	25.7	—	0.31
60	32.4	—	0.37
32	38.7	—	0.33

second series of runs the PFGA pressure was constant at 2 or 5 Torr and various pressures of inert gases such as nitrogen or oxygen were added. Non-monochromatic light was used. The $\phi_{(C_3+2/3C_2)}$ value was obtained by gas chromatography quantification of the products C_2F_4 and $c-C_3F_6$. The results show no variation in the quantum yield value (Table 2).

TABLE 2

Effect of adding oxygen and nitrogen on ϕ_{CO} in the photolysis of perfluoroglutaric anhydride

$P_{PFGA} = 2 \text{ Torr}$		$P_{PFGA} = 5 \text{ Torr}$		$P_{PFGA} = 2 \text{ Torr}$	
P_{O_2}	ϕ_{CO}	P_{O_2}	ϕ_{CO}	P_{N_2}	ϕ_{CO}
10.0	0.54	50.1	0.26	9.9	0.24
10.0	0.20	50.0	0.41	10.1	0.34
23.1	0.22	99.9	0.32	55.1	0.26
50.0	0.42	150.5	0.37	150.5	0.37
99.0	0.32	151.1	0.41	150.6	0.35
100.0	0.40	207.5	0.30	450.1	0.51
209.5	0.34	207.7	0.33	451.7	0.45
207.5	0.36	346.4	0.34	599.7	0.40
208.4	0.54	350.1	0.34	600.0	0.30
348.5	0.16	500.1	0.39	—	—
350.2	0.28	500.7	0.28	—	—
353.2	0.33	600.2	0.31	—	—
511.0	0.31	601.5	0.34	—	—
512.3	0.24	—	—	—	—
648.3	0.31	—	—	—	—
650.1	0.35	—	—	—	—

3.2. Effect of inert gases on reaction products

The photolysis of PFGA at 254 nm [6] showed that $\phi_{CO} = \phi_{CO_2}$ was independent of the total pressure whereas the $[C_2F_4]/[c-C_3F_6]$ ratio showed a marked pressure dependence. To examine this in more detail a series of runs was performed by adding inert gases at a constant pressure of 2 Torr of PFGA. The full arc of the lamp was used to obtain larger amounts of products in less time. The added gases were helium, argon, neon, oxygen, CCl_2F_2 and $C_2Cl_3F_3$. Plots of $[c-C_3F_6]/[C_2F_4]$ ($[S]/[D]$) against the total pressure of the system are shown in Figs. 1 and 2.

4. Discussion

4.1. Quantum yield

The data presented here show that the quantum yield $\phi_{CO} = \phi_{CO_2} = \phi_{(C_3+2/3C_2)}$ has a value of 0.34 ± 0.07 independent of pressure and photolysis time which confirms our previous results.

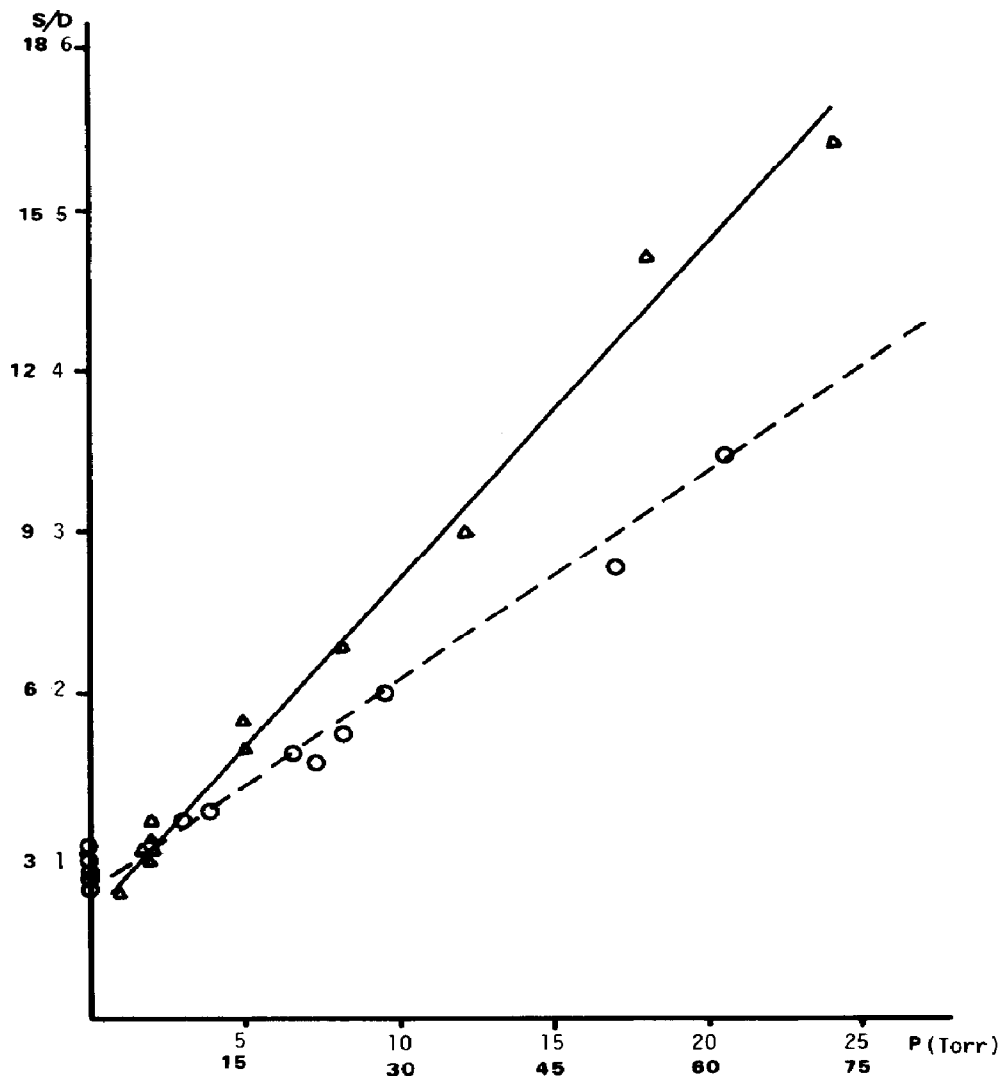


Fig. 1. Pressure dependence of the $[S]/[D]$ ratio for added inert gases in the photolysis of PFGA: Δ —, the pressure of PFGA is varied (inner S/D scale (light face numbers)); \circ — —, CCl_2F_2 (outer S/D scale (bold numbers)).

In Table 2 we can see that neither oxygen nor nitrogen have any effect on the quantum yield. It is well known that oxygen is a good deactivant of electronically excited molecules in singlet as well as triplet states, whereas nitrogen is not as effective for the triplet state. The rate of deactivation of these states by oxygen is of the order of the frequency of collisions. Nevertheless, the half-life of the singlet states is shorter than that of the triplet states. Consequently the interaction of singlet states with oxygen is of little importance at the pressures under investigation. From Table 2 we see that neither oxygen nor nitrogen produces any effect on ϕ_{CO} which makes it reasonable to assume that the primary process of photochemical decomposition of PFGA involves an excited singlet state rather than a triplet state, or

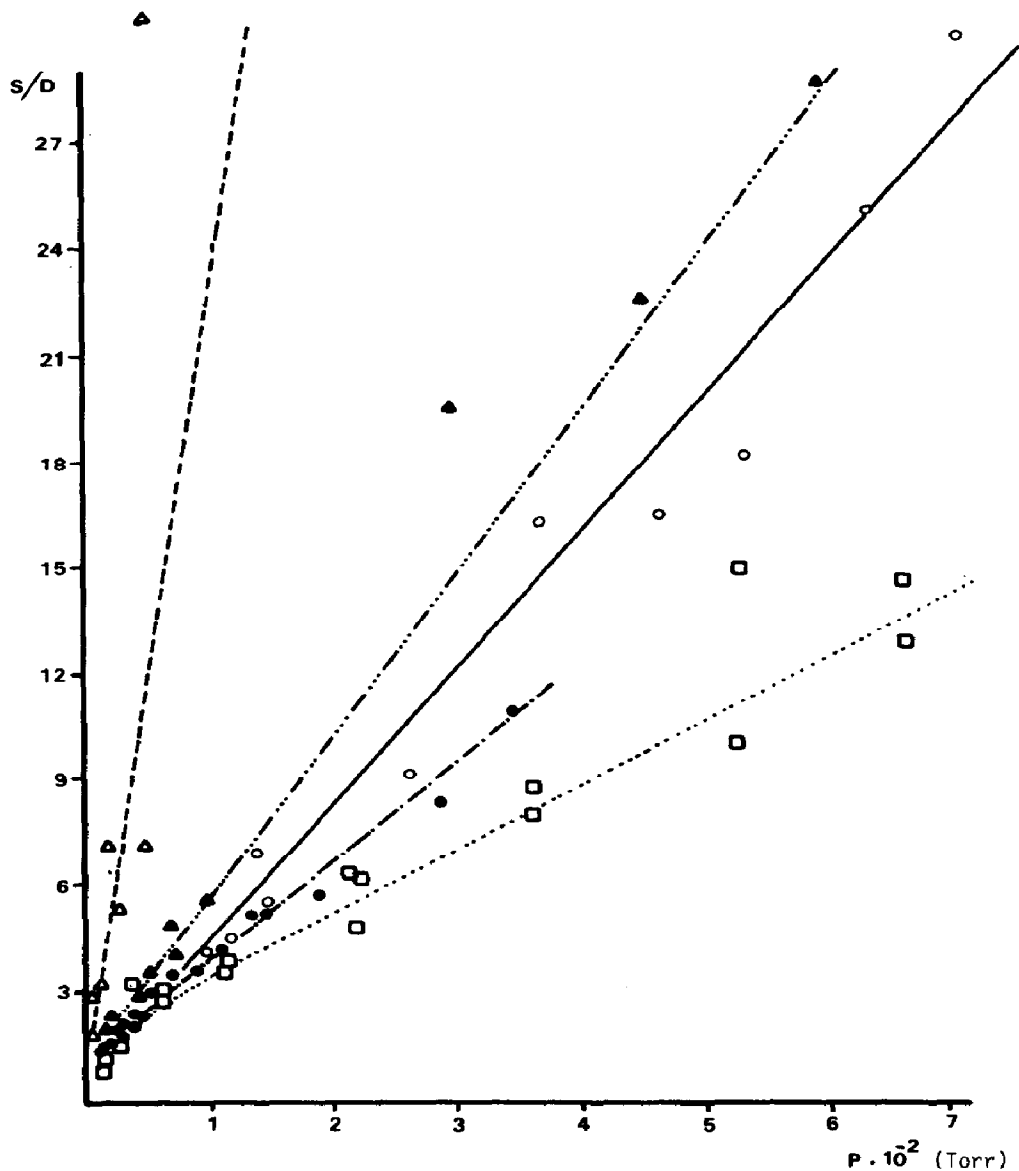


Fig. 2. Pressure dependence of the $[S]/[D]$ ratio for added inert gases in the photolysis of PFGA: \circ —, helium; \bullet - · - ·, argon; \blacktriangle - - - -, nitrogen; \square ·····, oxygen; \triangle - - - -, $C_2Cl_3F_3$.

else that the latter has a half-life which is much shorter than the collision frequency. The lack of evidence for the participation of the triplet states is in agreement with the photochemistry of perfluoroanhydrides [5].

Then the primary process can be explained in terms of the following mechanism:



where $A(\text{SO})$ is a thermal molecule in its ground state, $A^n(\text{SI})$ is a molecule in its lowest singlet excited state with vibrational energy n and $A^{n'}(\text{SO})$ is a vibrationally excited PFGA molecule in its electronic ground state (n denotes the various vibrational states). This leads us to

$$\phi_{\text{CO}} = \frac{k_2}{k_2 + k_3}$$

$\phi_{\text{CO}} = 0.34$ and therefore

$$k_3/k_2 = 2.0$$

which implies that the internal conversion is twice as fast as the decomposition.

If the decomposition involved the breakage of a C—C or C—O bond, 83 - 86 kcal mol⁻¹ would be needed. We used light of wavelength 254 nm which is equivalent to 112 kcal mol⁻¹. In the above mechanism, the internal conversions $A^n(\text{SI}) \rightarrow A^{n'}(\text{SO})$ imply that the species $A^{n'}(\text{SO})$ has an energy 26 - 29 kcal mol⁻¹ above the threshold for decomposition according to $A^{n'}(\text{SO}) \rightarrow \text{CO etc.}$ We do not consider this last step because ϕ_{CO} showed no pressure dependence. The efficiency of the internal conversion (step (3)) for open-chain perfluoroanhydrides was interpreted in terms of the formation of cyclic intermediates [2]. The photochemical excited species undergoes valence isomerization forming the cyclic intermediate where the carbonylic and anhydride oxygen atoms interchange, returning to the electronic ground state with an excess of vibrational energy but without any possibility of decomposing.

The open-chain perfluoroanhydrides have ϕ_{CO} values between 0.23 and 0.29. The ϕ_{CO} of PFSA has a value of 0.50 at pressures above 30 Torr and approaches unity as P approaches zero. The rigid structure of the strained ring of PFSA has less probability of forming a similar intermediate; therefore if the internal conversion is less efficient, the half-life of the species $A^n(\text{SI})$ in PFSA will be longer, thus making decomposition easier and more sensitive to changes in pressure. The quantum yield found in this work has a value intermediate between those of open-chain perfluoroanhydrides and PFSA. This is correct in view of the fact that PFGA has a non-strained ring structure so that valence isomerization is more probable than in the case of PFSA.

4.2. Effect of pressure on the ratio $[c\text{-C}_3\text{F}_6]/[\text{C}_2\text{F}_4]$

Figures 1 and 2 show that the $[c\text{-C}_3\text{F}_6]/[\text{C}_2\text{F}_4]$ ratio is significantly influenced by the total pressure, with each added gas having a specific effect.

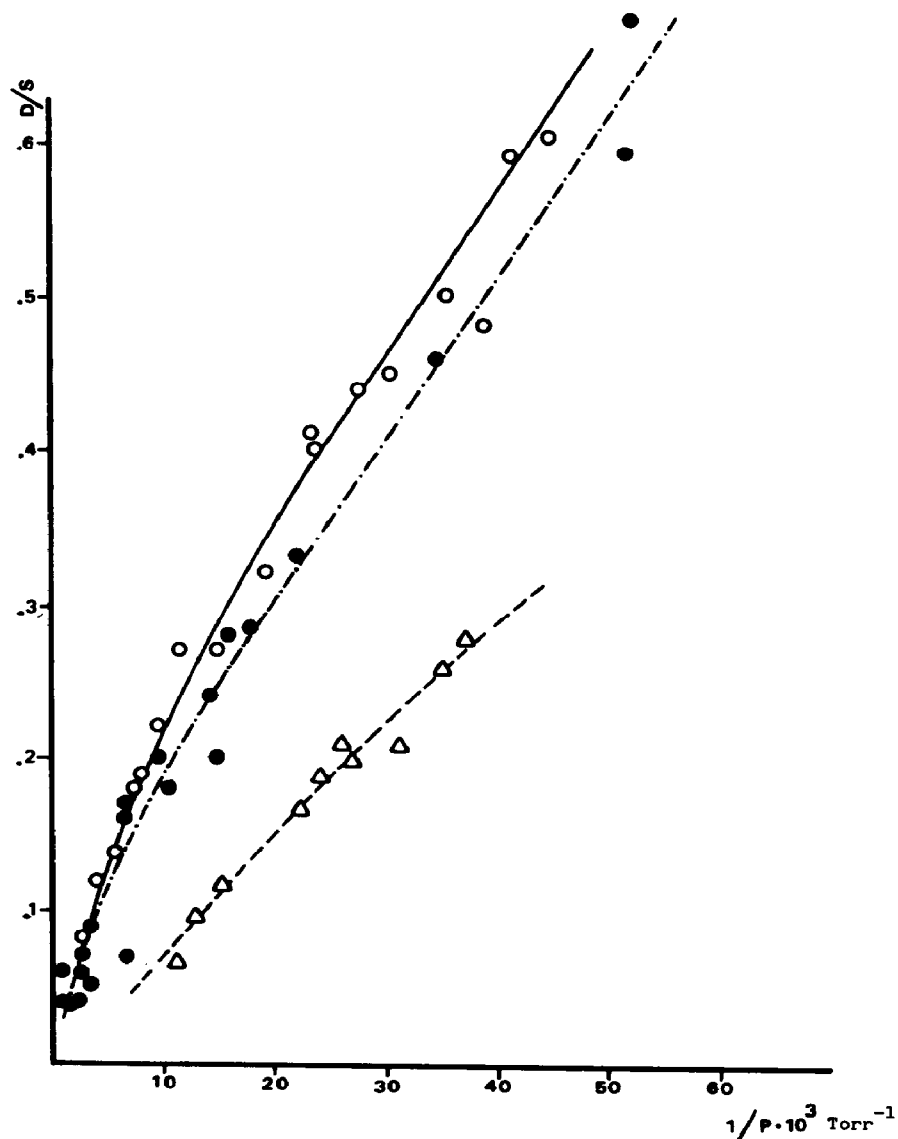


Fig. 3. Variation of the $[D]/[S]$ ratio as a function of $1/P$ for added inert gases in the photolysis of PFGA: \circ —, argon; \bullet - · -, nitrogen; \triangle - - -, CCl_2F_2 .

The smooth curvature of the Stern-Volmer plot (Figs. 3 and 4) indicates that there must be a step which depends on the energy of the species involved. The following mechanism could take this fact into account:



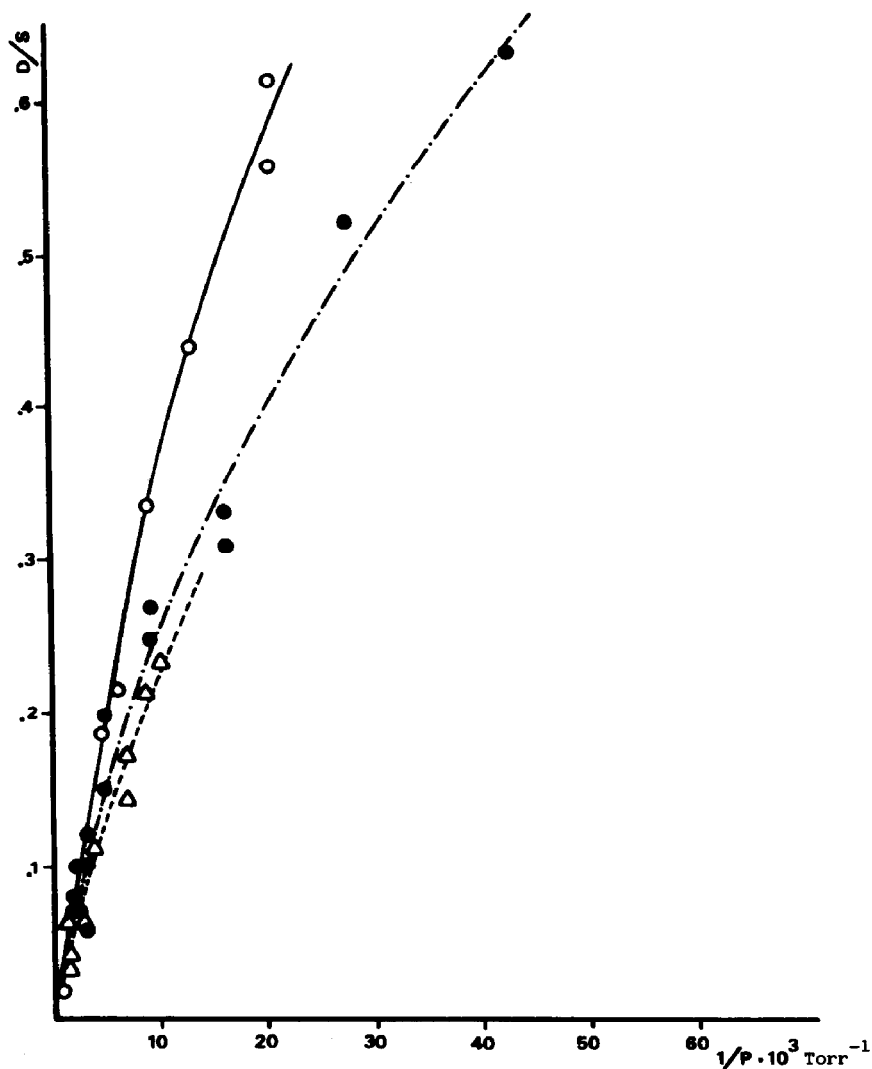


Fig. 4. Variation of the $[D]/[S]$ ratio as a function of $1/P$ for added inert gases in the photolysis of PFGA: Δ — — —, helium; \bullet - · - ·, oxygen; \circ — — —, PFGA.

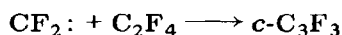


This mechanism suggests that perfluorocyclopropane (PFCP) and perfluoroethylene may arise from the same vibrationally excited intermediate (PFCP*) which may be either excited perfluorocyclopropane or perfluoro-trimethylene. PFCP* may stabilize (S) or decompose (D) according to steps (6) and (7) respectively. The constant in step (6), if strong collision frequencies are assumed, is $k_6[M] = \omega$, where M represents either PFGA or any other inert gas. Step (7) could produce the curvature in the Stern-Volmer plots

which might imply that PFCP* molecules are initially formed with varying amounts of excess vibrational energy.

The absorption band of the first excited singlet of PFGA is in the range 200 - 290 nm [6]; therefore when the sample is illuminated using a full mercury arc lamp without filtration PFGA would absorb lines at 232 nm, 254 nm and 265 nm whose relative intensities are approximately 1, 3 and 3.5 respectively. In runs where a PGFA pressure of 2 Torr was used, the absorption was 14%, 10% and 5% respectively; this means that the three lines contribute to the photolysis. PFGA is then produced in step (4) within an energy range of 123 - 108 kcal mol⁻¹ when it absorbs radiation of wavelength 232 nm or 265 nm. This means that there is a distribution of energy between the reaction products and, although there may be other explanations for the curvature in this type of plot, we believe that the effect of the distribution of energy is the main reason in this case.

In the mechanism given above the step



was not taken into account because at room temperature it is five orders slower than step (8) [8].

At low pressure limits, in the absence of collisions, all PFCP* will decompose into C₂F₄ according to step (7) and step (6) will not occur so that [S]/[D] will be zero. However, the curves in Figs. 1 and 2 show a non-zero value of [S]/[D] at the origin. This implies the presence of an additional amount of *c*-C₃F₆ that could be produced via the following mechanisms: (a) some *c*-C₃F₆ arises from a pressure-independent step, *i.e.*



where PFGA[#] is another excited state different from that of PFGA* and involves step (5'); (b) the excess energy available for distribution between the free groups is not enough to produce decomposition.

The formation of excited PFCP in this reaction allows the efficiencies of the relative vibrational deactivation of various added gases to be studied. Strong collisions were assumed and the parameter β_c [9] corresponding to each gas relative to the deactivation effect of PFGA was calculated at low pressures (β_c^o) and high pressures (β_c[∞]). The Lennard-Jones parameters σ(M) and ε/kM for PFCP, PFGA and C₂Cl₃F₃ were estimated [10] as 4.78, 5.11 and 6.5 and as 175.3, 320.35 and 209.9 respectively; these parameters for the rest of the gases were taken from the literature [11, 12]. The unimolecular rate constant for the decomposition of PFCP* to 3/2 C₂F₄ was calculated at the highest pressure studied (Table 3) from data for the collisional frequencies. The values found for the non-polar gases used indicate that the collisional efficiency increases linearly with the collision force and with the melting point [9, 13]. In general, the results obtained here show deactivation coefficients which agree with previously reported data for the transfer of vibrational energy.

TABLE 3

Rate constant for the decomposition of PF₂CP* and the collisional efficiencies β_c° and β_c^∞ for the various gases added

Gas	$k_a(M)_\infty$ ($\times 10^7 \text{ s}^{-1}$)	β_c^∞	β_c°
He	21.28	0.08	0.08
Ar	14.29	0.12	0.07
N ₂	15.87	0.11	0.06
O ₂	18.63	0.095	0.11
CCl ₂ F ₂	3.29	0.54	0.60
C ₂ Cl ₃ F ₃	1.43	1.23	0.39
PFGA	1.76	1	1

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References

- 1 G. A. Chamberlain and E. Whittle, *J. Chem. Soc., Faraday Trans. I*, 68 (1972) 88, 96.
- 2 G. A. Chamberlain and E. Whittle, *J. Chem. Soc., Faraday Trans. I*, 71 (1975) 1978.
- 3 C. Stock and E. Whittle, *J. Chem. Soc., Faraday Trans. I*, 76 (1980) 496.
- 4 A. Ortiz, E. R. de Staricco and E. H. Staricco, *An. Asoc. Quím. Argent.*, 68 (1980) 229.
- 5 P. E. Watkins and E. Whittle, *J. Chem. Soc., Faraday Trans. I*, 76 (1980) 503.
- 6 G. A. Argüello, E. R. de Staricco and E. H. Staricco, *An. Asoc. Quím. Argent.*, 70 (1982) 215.
- 7 G. A. Argüello, E. R. de Staricco and E. H. Staricco, unpublished work, 1981.
- 8 B. Atkinson and D. MacKeegan, *Chem. Commun.*, (1966) 189.
- 9 S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin and S. P. Paulov, *J. Phys. Chem.*, 74 (1970) 3160.
- 10 G. A. Argüello, *Tesis Doctoral*, Universidad Nacional de Córdoba, 1983.
- 11 J. O. Hirschfelder, C. F. Curtis and R. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964, p. 552.
- 12 R. C. Iretron and B. S. Rabinovitch, *J. Phys. Chem.*, 78 (1974) 1979.
- 13 M. Volpe and H. S. Johnston, *J. Am. Chem. Soc.*, 78 (1956) 3903.