

## PHOTOLYSIS OF PERFLUOROGLUTARIC ANHYDRIDE VAPOR AT LOW PRESSURES: EFFECT OF WAVELENGTH ON THE PRODUCT RATIO

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### Summary

The photolysis of perfluoroglutaric anhydride vapor has been investigated in the pressure range 0.03 - 2 Torr using light of wavelength 270, 265, 254, 240 and 232 nm. The products were CO, CO<sub>2</sub>, C<sub>2</sub>F<sub>4</sub> and *c*-C<sub>3</sub>F<sub>6</sub>. The [C<sub>2</sub>F<sub>4</sub>]/[*c*-C<sub>3</sub>F<sub>6</sub>] ratio is directly proportional to the energy supplied but is inversely proportional to the pressure.

### 1. Introduction

We have previously reported that the photolysis of perfluoroglutaric anhydride (PFGA) vapor yields CO, CO<sub>2</sub>, C<sub>2</sub>F<sub>4</sub> and *c*-C<sub>3</sub>F<sub>6</sub> [1, 2]. The ratio of these two last products depends on the total pressure as well as on the nature of the inert gases added. In this previous work, PFGA was irradiated with a full arc mercury lamp at a constant pressure of 2 Torr and several inert gases were added to give different total pressures. The highest total pressure was 700 Torr. Plots of the Stern-Volmer type showed curvature and an intercept value could be obtained. The results were interpreted in terms of the formation of a vibrationally excited intermediate species leading to the formation either of C<sub>2</sub>F<sub>4</sub> by decomposition or of *c*-C<sub>3</sub>F<sub>6</sub> by collisional stabilization. The curvature may be due to the non-monochromaticity of the incident light.

In this paper we present results obtained at pressures lower than 2 Torr and at the wavelengths 270, 265, 254, 240 and 232 nm.

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## 2. Experimental details

The photolysis was run in a grease-free conventional vacuum system. PFGA was handled as previously described [2]. The reactant pressure was varied from 0.03 to 2 Torr and measured with a capacitance manometer to within  $\pm 0.001$  Torr. In most cases, the sample was photolyzed for 10 min at the wavelengths mentioned above. Several runs at a 1:104 ratio of PFGA in  $N_2$  were also performed using 265 nm light. A chromatograph with a flame ionization detector was used for quantitative analysis. Separation of the products was achieved with a 6 m Porapak Q-silica gel combined column. Monochromatic radiation was supplied by a grating monochromator.

## 3. Results

Table 1 shows the yields of  $c\text{-C}_3\text{F}_6$  and  $\text{C}_2\text{F}_4$  and the ratio  $[\text{C}_2\text{F}_4]/[c\text{-C}_3\text{F}_6]$  at the wavelengths 270, 265, 254, 240 and 232 nm for different pressures of PFGA. This wavelength range corresponds to the first  $n \rightarrow \pi^*$  PFGA absorption band from 200 to 290 nm with a maximum at 231 nm. The half-width of the bandpass in all runs was not more than 5 nm.

A plot of the ratio  $[\text{C}_2\text{F}_4]/[c\text{-C}_3\text{F}_6]$  vs. wavelength for different pressures of PFGA is shown in Fig. 1 and the ratio  $[c\text{-C}_3\text{F}_6]/[\text{C}_2\text{F}_4]$  vs. PFGA

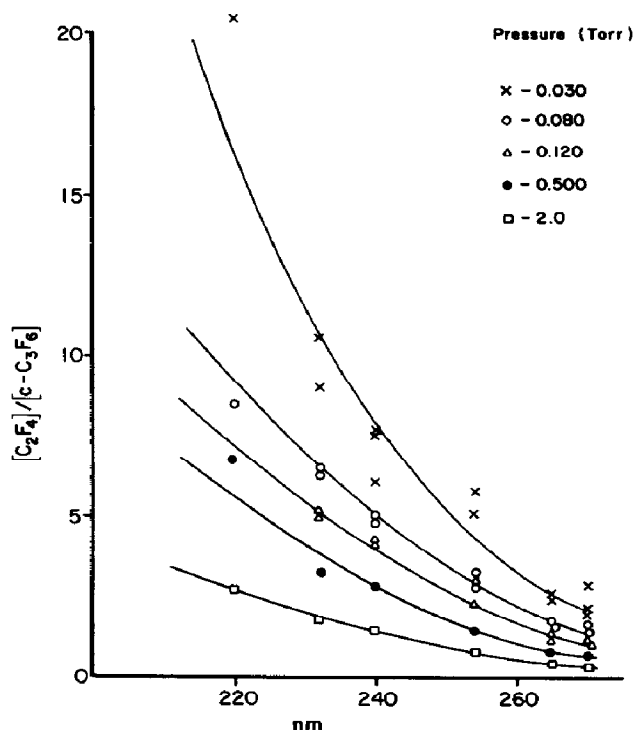


Fig. 1. The ratio  $[\text{C}_2\text{F}_4]/[c\text{-C}_3\text{F}_6]$  as a function of wavelength at different pressures in the photolysis of PFGA.

**TABLE 1**  
**PFGA photolysis product distribution**

[PFGA] (Torr)	[C <sub>2</sub> F <sub>4</sub> ] (× 10 <sup>-7</sup> mol l <sup>-1</sup> )	[c-C <sub>3</sub> F <sub>6</sub> ] (× 10 <sup>-7</sup> mol l <sup>-1</sup> )	[C <sub>2</sub> F <sub>4</sub> ]/[c-C <sub>3</sub> F <sub>6</sub> ]
<i>270 nm</i>			
0.030	1.74	0.85	2.05
0.080	2.64	1.66	1.58
0.079	3.38	2.41	1.40
0.119	2.26	1.92	1.18
0.118	2.52	2.13	1.18
0.498	10.61	17.60	0.60
2.000 <sup>a</sup>	0.52	2.27	0.34
2.000	0.57	2.47	0.35
<i>265 nm</i>			
0.032	2.71	1.11	2.44
0.031	3.01	1.18	2.56
0.030	3.64	1.47	2.48
0.079	2.99	2.11	1.42
0.080	3.37	2.11	1.60
0.120	2.51	1.73	1.45
0.120	2.31	1.68	1.38
0.502	10.64	14.85	0.72
2.000	1.24	5.05	0.37
2.000	1.01	4.14	0.37
<i>254 nm</i>			
0.029	3.43	0.68	5.01
0.030	3.44	0.60	5.78
0.081	6.28	2.05	3.06
0.080	6.29	2.25	2.80
0.120	12.70	4.10	3.10
0.122	10.16	4.58	2.22
0.500	16.22	11.07	1.46
2.000	1.61	3.21	0.75
<i>240 nm</i>			
0.031	2.22	0.35	6.30
0.030	2.97	0.40	7.52
0.030	3.74	0.62	6.03
0.080	5.45	1.30	4.20
0.080	5.51	1.16	4.76
0.121	8.12	1.91	4.26
0.119	9.35	2.15	4.34
0.502	14.52	5.17	2.80
2.000	1.15	1.23	1.40
2.000	1.15	1.24	1.39
<i>232 nm</i>			
0.029	1.93	0.18	10.5
0.030	2.23	2.49	8.97
0.081	2.04	0.32	6.39
0.080	2.06	0.33	6.25
0.119	3.13	0.64	4.86
0.120	3.15	0.61	5.17
0.495	8.36	2.66	3.14
1.002	6.32	1.92	3.29
2.000	0.83	0.71	1.74
2.000	0.69	0.61	1.70

<sup>a</sup>Runs at 2.000 Torr were carried out for different photolysis times.

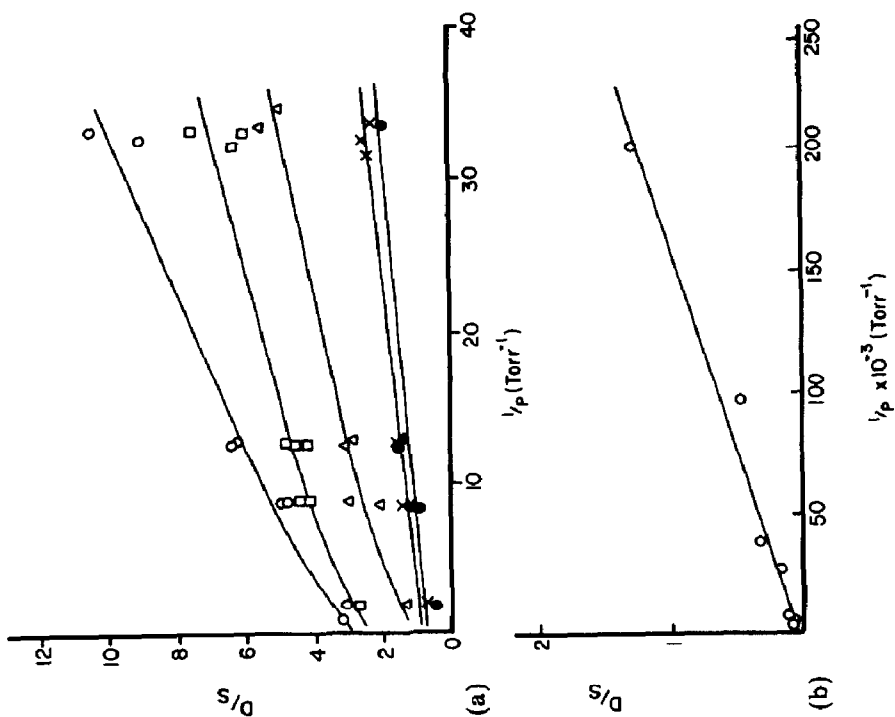
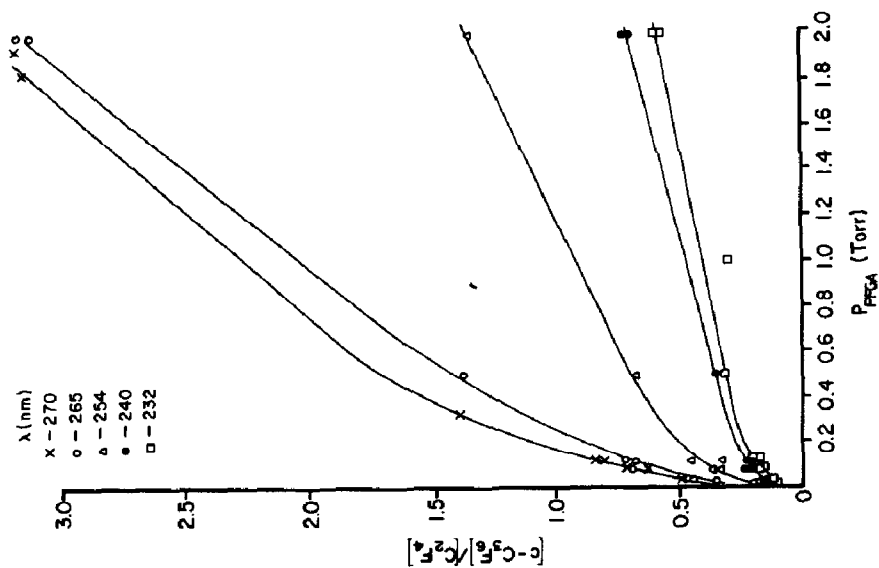


Fig. 2. The ratio  $[c\text{-C}_3\text{F}_6]/[C_2F_4]$  as a function of pressure at different wavelengths in the photolysis of PFGA.

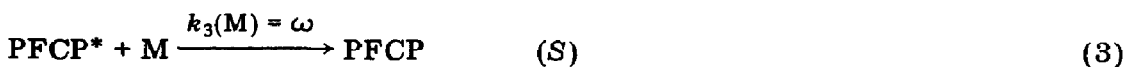
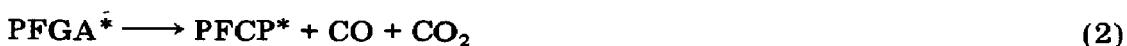
Fig. 3. The ratio  $[C_2F_4]/[c\text{-C}_3F_6]$  ( $D/S$ ) as a function of  $1/P$ . (a)  $\circ$ ,  $\lambda = 232$  nm;  $\square$ ,  $\lambda = 254$  nm;  $\times$ ,  $\lambda = 265$  nm;  $\bullet$ ,  $\lambda = 270$  nm. (b)  $\lambda = 265$  nm. ( $P$  is the total pressure of the PFGA: $N_2$  (1:104) mixture.)



pressure at different wavelengths is plotted in Fig. 2. The ratio  $[C_2F_4]/[c-C_3F_6]$  is directly proportional to the supplied energy but is inversely proportional to the pressure of PFGA. A straight line with its intercept at zero is obtained for the ratio  $[C_2F_4]/[c-C_3F_6]$  vs.  $1/P$ , where  $P$  stands for the total pressure of a mixture of PFGA: $N_2$  (1:104) at 265 nm (Fig. 3(b)).

#### 4. Discussion

The following mechanism has been previously proposed for the photolysis of PFGA [2]:



According to the above mechanism, perfluorocyclopropane (PFCP) and perfluoroethylene both come from the same intermediate species, namely  $PFCP^*$ , which may be either the activated cyclopropane or the perfluoromethylene biradical or both in equilibrium.  $PFCP^*$  can either stabilize by collision ( $S$ ) or decompose ( $D$ ) according to steps (3) and (4) respectively.

The results shown in Figs. 1 and 2 support the validity of a mechanism which involves an intermediate activated species which will decompose to a greater extent as the supplied energy increases and at lower pressures where the probability of deactivation is lower.

Figure 3(b) also confirms this mechanism and shows that, at a given wavelength,  $[C_2F_4]$  tends to zero at high pressures.

If we apply a simple steady state treatment to this mechanism, assuming the approximation of strong collisions to be valid, we obtain

$$\frac{D}{S} = \frac{3}{2} k_a(E) \frac{1}{\omega}$$

According to the above equation, we obtained the  $k_a(E)$  from the slope of the plots  $D/S$  vs.  $1/P$  (or  $1/\omega$ ) as is shown in Fig. 3. The activation constant  $k_a(E)$  must increase with the photoexcitation energy and therefore the mean deactivation pressure should follow the same trend. Since the collision frequency is constant at a given pressure, the curves shown in Fig. 2 indicate the relative variation in the  $PFCP^*$  decomposition rate (step (4)). It can also be seen that a change of 17 kcal mol<sup>-1</sup> in the photoexcitation energy (from 270 to 232 nm) increases the value of the ratio  $[C_2F_4]/[c-C_3F_6]$  by a factor close to 6.

The Stern-Volmer plot in Fig. 2 shows curvature, as is also the case for other systems [3 - 9]. This curvature may be interpreted in terms of the fact that although in step (1) the PFGA\* can be monoenergetically excited, the PFCP\* species in steps (3) and (4) is not necessarily monoenergetically excited. In a previous paper [2], where pressures of above 2 Torr PFGA were used, a similar plot seemed to indicate an intercept value of  $S/D$  which could be interpreted as indicating the formation of PFCP\* with an energy lower than that necessary for decomposition regardless of the pressure. The result now obtained in the pressure range 0.03 - 2 Torr casts doubt upon the existence of this intercept value.

A plot of the  $[C_2F_4]/[c-C_3F_6]$  ratio *vs.* energy (Fig. 4) shows different straight lines converging to a limiting value of  $103 \text{ kcal mol}^{-1}$ . The  $\Delta H$  for the PFGA decomposition was estimated as  $60 \text{ kcal mol}^{-1}$ . ( $\Delta H_f$  for PFGA was estimated as  $-404 \text{ kcal mol}^{-1}$  from the group additivity rule [10], and  $\Delta H_f$  for PFCP was taken from ref. 11.) Assuming that the threshold energy for the photolytic reaction is  $103 \text{ kcal mol}^{-1}$ , PFGA would have approximately  $43 \text{ kcal mol}^{-1}$  left which would be distributed among the products of step (2). Thus, according to a statistical distribution, the  $c-C_3F_6$  would have about  $34 \text{ kcal mol}^{-1}$  in excess. It is well known that the  $c-C_3F_6$  decomposition into  $C_2F_4$  plus  $CF_2$  is endothermic by  $33 \text{ kcal mol}^{-1}$  [11, 12]. This

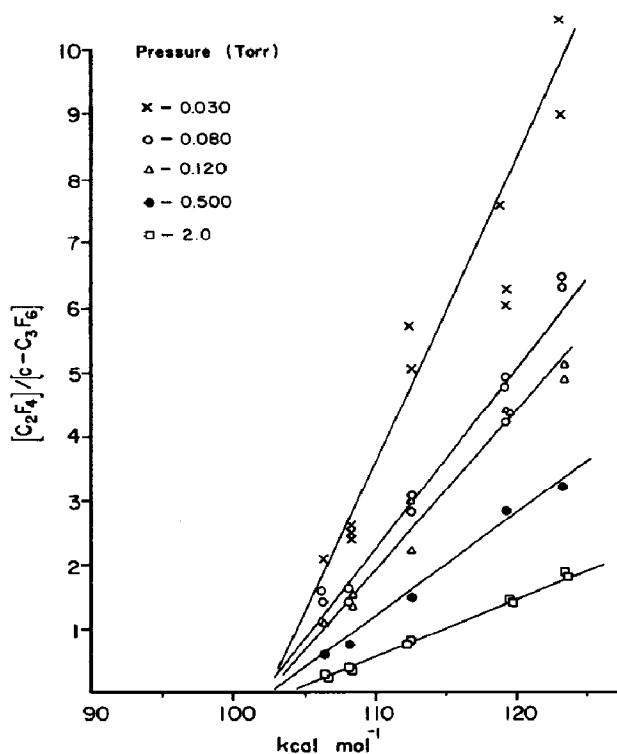


Fig. 4. Energy dependence of the  $[C_2F_4]/[c-C_3F_6]$  ratio at different pressures in the photolysis of PFGA.

would indicate, up to a point, that the  $[c\text{-C}_3\text{F}_6]/[\text{C}_2\text{F}_4]$  intercept found in the previous paper might be due to unfiltered light of wavelength longer than 270 nm. Photolysis would then lead to the formation of  $c\text{-C}_3\text{F}_6$  regardless of the pressure.

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