

Photolyses of Perfluoroacetic Anhydride and Perfluoropropionic Anhydride Vapours. New Sources of CF₃ and C₂F₅ Radicals

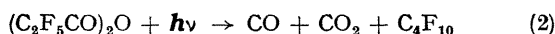
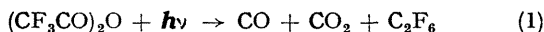
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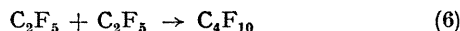
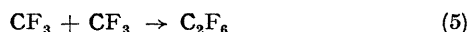
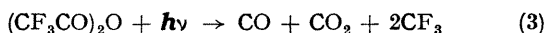
Summary CF₃ and C₂F₅ radicals are conveniently produced by photolysis of perfluoroacetic and perfluoropropionic anhydrides respectively.

Few sources of CF₃ radicals exist that are free of complications and there are even fewer such sources of C₂F₅ radicals. We now report on new sources of these radicals.

The photolyses of the vapours of (CF₃CO)₂O and (C₂F₅CO)₂O in the range 20–220 °C are quantitatively described by the overall equations (1) and (2). The addition of



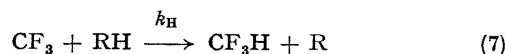
radical scavengers such as NO, isobutene, or cyclohexene to either system did not affect the yields of CO or CO₂ but reduced the respective yields of C₂F₆ and C₄F₁₀ to zero. We conclude that the effective primary processes are described by equations (3) and (4), followed by (5) and (6).



Thus the anhydrides are convenient sources of CF₃ and C₂F₅ radicals, the only limitation to their use being that wavelengths < 290 nm are needed for photolysis (λ_{max} ca. 240 nm). The yield of CO or CO₂ is a direct measure of the number of radicals produced since equations (1)–(4) are obeyed quantitatively. Above 220 °C, thermal decomposition of (CF₃CO)₂O occurs¹ but CF₃ radicals are not produced. (C₂F₅CO)₂O is also stable up to 220 °C.

To test the behaviour of (CF₃CO)₂O as a source of CF₃ radicals, it was photolysed with methane and with cyclohexane where H-abstraction can occur as shown in equation

(7). Values of $k_{\text{H}}/k_5^{\ddagger}$ and the corresponding Arrhenius



parameters are shown in the Table together with results obtained using other sources of CF₃ radicals. The present results agree with previous work within experimental error.

TABLE

RH	$k_{\text{H}}/k_5^{\ddagger}$ * at 400 K	$\log(A_{\text{H}}/A_5^{\ddagger})$ *	$E_{\text{H}} - \frac{1}{2}E_5^{\ddagger}$ †	Ref.
CH ₄	0.16	5.93 ± 0.32	12.5 ± 0.7	a
	0.19	5.40 ± 0.14	11.2 ± 0.2	2
cyclo-C ₆ H ₁₂	132	5.18 ± 0.15	5.6 ± 0.2	a
	100	5.44 ± 0.20	6.3 ± 0.4	3

* Units, cm^{3/2} mol^{-1/2} s^{-1/2}. † Units, kcal mol⁻¹. a This work; ref. 2, radicals produced by photolysis of CF₃COCF₃; ref. 3, radicals produced by photolyses of CF₃COCF₃ and CF₃I

Perfluoropropionic anhydride was photolysed with cyclohexene where C₂F₅ radicals can either abstract H (rate constant k_{H}) or add to the double bond. Assuming that the rate of addition is given by the "missing" C₂F₅ radicals, calculated from equation (8) we obtain equations (9) and (10).

$$R(\text{Add}) = R(\text{CO}) + R(\text{CO}_2) - R(\text{C}_2\text{F}_5\text{H}) \quad (8)$$

$$E_{\text{H}} - E_{\text{Add}} = 2.53 \pm 0.12 \text{ kcal mol}^{-1} \quad (9)$$

$$\log A_{\text{H}}/A_{\text{Add}} = 0.67 \pm 0.07 \quad (10)$$

When (C₂F₅CO)₂O is photolysed with benzene vapour, the C₂F₅ radicals add to the ring with the addition becoming reversible above 110 °C. This behaviour parallels the reactions of CF₃ radicals with benzene.⁴

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