Photolyses of Perfluoroacetic Anhydride and Perfluoropropionic Anhydride Vapours. New Sources of CF_3 and C_2F_5 Radicals

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Summary CF_3 and C_2F_5 radicals are conveniently produced by photolysis of perfluoroacetic and perfluoropropionic anhydrides respectively.

FEW sources of CF_3 radicals exist that are free of complications and there are even fewer such sources of C_2F_5 radicals. We now report on new sources of these radicals.

The photolyses of the vapours of $(CF_3CO)_2O$ and $(C_2F_5CO)_2O$ in the range 20—220 °C are quantitatively described by the overall equations (1) and (2). The addition of

$$(CF_3CO)_2O + h\nu \rightarrow CO + CO_2 + C_2F_6 \tag{1}$$

$$(C_2F_5CO)_2O + h\nu \rightarrow CO + CO_2 + C_4F_{10} \tag{2}$$

radical scavengers such as NO, isobutene, or cyclohexene to either system did not affect the yields of CO or CO_2 but reduced the respective yields of C_2F_6 and C_4F_{10} to zero. We conclude that the effective primary processes are described by equations (3) and (4), followed by (5) and (6).

$$(CF_3CO)_2O + h\nu \rightarrow CO + CO_2 + 2CF_3 \tag{3}$$

$$(C_2F_5CO)_2O + h\nu \rightarrow CO + CO_2 + 2C_2F_5 \tag{4}$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \tag{5}$$

$$C_2F_5 + C_2F_5 \rightarrow C_4F_{10} \tag{6}$$

Thus the anhydrides are convenient sources of CF_3 and C_2F_5 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 CO_2 is a direct measure of the number of radicals produced since equations (1)—(4) are obeyed quantitatively. Above 220 °C, thermal decomposition of $(CF_3CO)_2O$ occurs[1] but CF_3 radicals are not produced. $(C_2F_5CO)_2O$ is also stable up to 220 °C.

To test the behaviour of $(CF_3CO)_2O$ as a source of CF_3 radicals, it was photolysed with methane and with cyclohexane where H-abstraction can occur as shown in equation (7). Values of $k_H/k_5^{\frac{1}{2}}$ and the corresponding Arrhenius

$$CF_3 + RH \xrightarrow{k_H} CF_3H + R \tag{7}$$

parameters are shown in the Table together with results obtained using other sources of CF_3 radicals. The present results agree with previous work within experimental error.

TABLE

RH	$k_H/k_5^{\frac{1}{2}}$* at 400 K	$\log (A_H/A_5^{\frac{1}{2}}$*)	$E_H - \frac{1}{2}E_5$†	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_6H_{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 CF_3COCF_3; ref. 3, radicals produced by photolyses of CF_3COCF_3 and CF_3I

Perfluoropropionic anhydride was photolysed with cyclohexene where C_2F_5 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" C_2F_5 radicals, calculated from equation (8) we obtain equations (9) and (10).

$$R(\text{Add}) = R(CO) + R(CO_2) - R(C_2F_5H) \tag{8}$$

$$E_H - E_{Add} = 2{\cdot}53 \pm 0{\cdot}12 \text{ kcal mol}^{-1} \tag{9}$$

$$\log A_H/A_{Add} = 0{\cdot}67 \pm 0{\cdot}07 \tag{10}$$

When $(C_2F_5CO)_2O$ is photolysed with benzene vapour, the C_2F_5 radicals add to the ring with the addition becoming reversible above 110 °C. This behaviour parallels the reactions of CF_3 radicals with benzene.[4]

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