The Photolysis of Trifluoroacetaldehyde at 313 nm

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Summary The quantum yield of the molecular split is shown to be zero at 313 nm and at temperatures up to 150 °C; Arrhenius parameters are reported for abstraction of the hydrogen atom from the parent molecule by CF_3.

THE photolysis of trifluoroacetaldehyde has been used extensively as a source of CF_3 radicals to investigate the abstraction of hydrogen atoms, equation (1), from various substrate molecules.[1] Doubts were expressed[2] about the

$$CF_3 + RH \rightarrow CF_3H + R \qquad (1)$$

validity of the kinetic data obtained from this system when photolysis of the aldehyde in the presence of nitric oxide as a free radical trap resulted in the production of appreciable amounts of CF_3H. It was concluded that the molecular split equation (2) is an important complicating feature of this system.

$$CF_3CHO + h\nu \rightarrow CF_3H + CO \qquad (2)$$

We have studied the photolysis of trifluoroacetaldehyde at 313 nm at temperatures up to 150 °C†. The reaction mechanism includes the equations[3] (3)—(6). The formyl

$$CF_3CHO + h\nu \rightarrow CF_3 + CHO \qquad (3)$$

$$CF_3 + CF_3CHO \rightarrow CF_3H + CF_3CO \qquad (4)$$

$$CF_3CO \rightarrow CF_3 + CO \qquad (5)$$

$$2CF_3 \rightarrow C_2F_6 \qquad (6)$$

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† Apparatus and procedures were almost identical with those used previously.[11] The incident intensity was varied in the range 5×10^{14}—5×10^{13} quanta s^{-1} using wire gauze screens and silica plates. The decadic molar extinction coefficient of the aldehyde at 313 nm was 6·94 and was approximately independent of temperature.

radical formed in reaction (3) may decompose, particularly at higher temperatures, yielding a further source of CF_3 radicals. The reaction sequence (3) to (6) predicts that

$$HCO \rightarrow H + CO \qquad (7)$$

$$H + CF_3CHO \rightarrow H_2 + CF_3CO \qquad (8)$$

$\phi C_2F_6 = 0{\cdot}5$, while if reactions (7) and (8) are included, $\phi C_2F_6 = 1{\cdot}0$. Measured quantum yields of C_2F_6 had a maximum value of *ca.* 0·35 at the highest temperature of 150 °C and ϕC_2F_6 decreased with increase in pressure and with decrease in temperature, indicating that considerable deactivation of excited states occurs in the system. However, at any one temperature and pressure, ϕC_2F_6 was independent of a ten-fold variation in incident light intensity which provides confidence that the yield of C_2F_6 is a true measure of the CF_3 radical concentration in this system.

It can be shown that the above mechanism leads to equation (9), where R (C_2F_6) is the rate of formation of hexafluoroethane and I_{abs} is the rate of absorption of light.

$$\phi CF_3H = (k_4/k_6^{\frac{1}{2}})\{R(C_2F_6)\}^{\frac{1}{2}}[CF_3CHO]/I_{abs} \qquad (9)$$

On the other hand, if reaction (2) is a source of CF_3H, then equation (10) holds. It is also possible in principle, particularly at low temperature and at high intensity, that the

$$\phi CF_3H = \phi_2 + (k_4/k_6^{\frac{1}{2}})\{R(C_2F_6)\}^{\frac{1}{2}}[CF_3CHO]/I_{abs} \qquad (10)$$

$$CF_3 + CHO \rightarrow CF_3H + CO \qquad (11)$$

reaction (11) might provide an additional source of CF_3H. However, the lack of any variation in $k_4/k_6^{\frac{1}{2}}$ with variation in light intensity suggests that reaction (11) cannot be a significant source of CF_3H. Thus, from equation (10), a plot of ϕCF_3H against the function $\{R(C_2F_6)\}^{\frac{1}{2}}/I_{abs}$ will have a non-zero intercept of ϕ_2 if the molecular split is important.

The results obtained at 70 °C, where the incident intensity was varied by a factor of eight, are shown in the Figure.

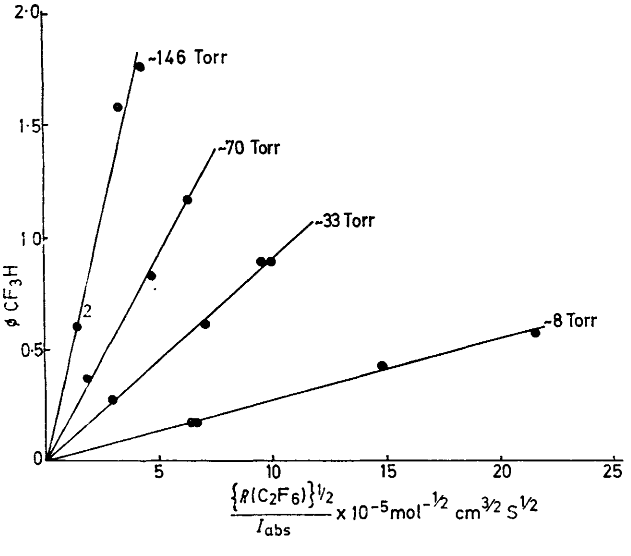

FIGURE. *ϕCF_3H values at four different pressures at* 70 °C, *with variable incident intensity within the range* 5×10^{14}—5×10^{13} quanta s^{-1}.

It can be seen that there is no evidence of any positive intercept, indicating that ϕ_2 must be very small or zero. The results in the Figure and comparable results obtained at 30 °C and 150 °C have been analysed by a least mean squares computer treatment (see Table) to obtain the best intercept. The results indicate that ϕ_2 is zero at 30 °C and 70 °C. The very high quantum yields ($\phi CF_3H > 20$) at 150 °C resulted in a large uncertainty in the intercepts at this temperature, but again there is no evidence that ϕ_2 is anything other than zero.

TABLE

Temperature (°C)	Pressure (Torr)	ϕ_2	$k_4/k_6^{\frac{1}{2}}(cm^{\frac{3}{2}}mol^{-\frac{1}{2}}s^{-\frac{1}{2}})$
30	8·6	0·000	0·157
30	33·0	−0·005	
30	70·0	−0·002	
30	146·0	+0·006	
70	8·7	−0·002	0·600
70	33·1	−0·008	
70	70·6	+0·010	
70	146·2	+0·008	
150	8·7	−0·068	4·617
150	33·0	−0·033	
150	70·5	+0·146	
150	145·2	−1·726	

This result is contrary to the report[3] that ϕ_2 has a value of 0·021 at room temperature and at pressures in the region 30 to 40 Torr. The value of ϕ_2 obtained depends intimately on the correct evaluation of I_{abs}. It is possible that the temperature of 125 °C used by Dodd and Smith[3] in their acetone actinometry experiments was too low, and may have introduced a slight error into the calculation of I_{abs}.[4] On the other hand, the difference may be explained by the larger wavelength spread of the light used in the previous study.[3] Presumably the molecular split can be important at other wavelengths. This explanation would also reconcile the assertion of Morris and Thynne[2] that ϕ_2 is important. It seems likely that they used the full mercury arc for illumination and there is evidence that the importance of the molecular split in aldehyde photolysis is very sensitive to wavelength.[5]

The implications of our results for the rate data reported for reactions of type (1), using CF_3CHO as the source of CF_3 radicals, are that they will not be in error if the light used is of wavelength 313 nm. Light of other wavelengths may give rise to an appreciable ϕ_2, but this will be swamped by the high quantum yields of CF_3H from the chain reaction at the temperatures normally employed in obtaining these rate data.[6] The effect of wavelength on ϕ_2 is now being investigated.

The results also allowed evaluation of $k_4/k_6^{\frac{1}{2}}$ for three temperatures used in this study. The average value of $k_4/k_6^{\frac{1}{2}}$ is shown in the Table, each value being the mean of 16 individual experimental values at that temperature. A least mean squares computer treatment of these results provides the Arrhenius equation

$$\log_{10}(k_4k_6^{\frac{1}{2}}) = (4{\cdot}38 \pm 0{\cdot}07) - (7200 \pm 120)/2{\cdot}303\,RT$$

Using the value of $\log_{10}k_6 = 13{\cdot}36$,[7] and assuming $E_6 = 0$, we obtain

$$\log_{10}k_4 = (11{\cdot}05 \pm 0{\cdot}07) - (7200 \pm 120)/2{\cdot}303\,RT$$

The A_4 and E_4 obtained here are smaller than those reported previously,[3,8] and they suggest that these inexplicably[8] high values are in error. Contrary to the previous work,[3] there was no variation in $k_4/k_6^{\frac{1}{2}}$ with either pressure or intensity in this work. In addition, the value of $E_{11} = 10{\cdot}4$ kcal mol^{-1} for reaction (12), which it was claimed[3] provided

$$CF_3 + CH_4 \rightarrow CF_3H + CH_3 \qquad (12)$$

support for the high value of E_4 is now thought to be in error.[9,10]

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