Addition of Free Radicals to Unsaturated Systems. Part 24.[1] Kinetics and Mechanism of the Gas-phase Thermal Reactions of Trifluoroiodomethane with Propene

Robert N. Haszeldine, David W. Keen, and Peter J. Robinson *†
Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The gas-thermal addition of trifluoroiodomethane to propene, at temperatures of 533—583 K, reactant ratios from 1 : 1 to 4 : 1, and total pressures of 100—300 mmHg, is shown to be a free-radical chain reaction with the kinetic equation as shown below. It is concluded that initiation is by the reaction of

$$\frac{d[\text{adduct}]}{dt} = k_8[I_2]^{0.25}[CF_3I]^{1.09}[C_3H_6]^{0.41}$$

iodine atoms, in thermal equilibrium with molecular iodine, with trifluoroiodomethane, and termination is predominantly by reactions involving trifluorobutyl radicals. The Arrhenius parameters found for k_8 are discussed in terms of those for the elementary reactions involved on the basis of the proposed mechanism.

This paper describes a kinetic investigation of the thermally initiated reactions of trifluoroiodomethane with propene. The major reaction occurring is the addition reaction (1),

$$CF_3I + C_3H_6 \longrightarrow CF_3CH_2CHIMe \qquad (1)$$

which is typical of a very important class of synthetic processes in which a saturated compound, usually with a relatively weak bond (CF_3–I), adds across the double bond of an olefin ($CH_3CH{=}CH_2$). There is a large volume of literature on the synthetic aspects of such addition reactions;[2] the majority proceed by free-radical chain mechanisms, which may be initiated thermally, catalytically, or photochemically. Photolytic, and to a lesser extent catalytic, additions have been widely studied as a source of kinetic data on the elementary reactions of the free radicals involved,[3] and there have thus been many detailed kinetic and mechanistic studies of these processes. By contrast, there is relatively little literature on the kinetics of thermally initiated addition reactions. Such reactions tend to behave less systematically, and are also more complex because the higher temperatures frequently result in enhanced side reactions and other complications.

The title reaction has been investigated qualitatively by Haszeldine *et al.*;[4] a 3 : 1 molar mixture of trifluoroiodomethane and propene heated for 18.5 h at 200 °C and *ca.* 6 atm pressure afforded a 99% yield of 1 : 1 adduct, comprising 89% of 1,1,1-trifluoro-3-iodobutane (reaction 1) and 11% of 1-iodo-2-trifluoromethylpropane (reaction 2). At 250 °C the

$$CF_3I + C_3H_6 \longrightarrow CF_3CHMeCH_2I \qquad (2)$$

major products were 4,4,4-trifluorobut-1-ene, 1,1,1-trifluorobutane, and iodine, presumed to have been formed by thermal decomposition of the adducts initially produced. In view of the overall importance of addition reactions, and the general lack of kinetic data on thermally initiated additions, a detailed kinetic investigation has now been carried out on the thermal reactions of trifluoroiodomethane and propene.

Experimental

The apparatus was similar to those described previously,[5] using Pyrex reaction vessels (26 × 3.2 cm i.d.), pressure measurement by a glass spiral gauge (sensitivity 4.4 mm deflection of the reflected light spot per mmHg), temperature control to ±0.3 K, and a dead-space factor *a* of 0.973.[6] Reactants were stored in blackened bulbs, with the trifluoroiodomethane normally kept at 77 K, and were pre-mixed in a 1 dm^3 blackened bulb before admission to the reaction vessel. Reaction mixtures for analysis were condensed from the reaction vessel into a 250 cm^3 bulb forming part of a gas-sampling system, evaporated and allowed to become homogeneous, then injected into a Pye Unicam Model 104 g.l.c. with dual flame-ionisation detectors. Complete separation of all reactants and products was obtained with a composite column consisting of 16 cm of 20% dodecyl phthalate on Chromasorb P at room temperature followed by 85 cm of 4% Apiezon L on alumina and 35 cm of 3% Kel-F 10 on alumina, both at 367 K. Quantitative analysis for all the components was precluded by problems of condensation and adsorption of the high-molecular-weight compounds, but good calibrations were obtained for the two fluorohydrocarbons, 1,1,1-trifluorobutane and 4,4,4-trifluorobutene.

Materials.—Trifluoroiodomethane[7] and propene, purified by low-temperature distillation, were spectroscopically and chromatographically pure. 1,1,1-Trifluoro-3-iodobutane and 1-iodo-2-trifluoromethylpropane were prepared by addition of trifluoroiodomethane to propene; 1,1,1-trifluorobutane was obtained by reduction of the former with hydrogen iodide, and 4,4,4-trifluorobutene was prepared by zinc dehalogenation of 4-chloro-3-iodo-1,1,1-trifluorobutane.[8]

Results

Preliminary investigations were carried out using 3 : 1 trifluoroiodomethane to propene mixtures, at around 300 mmHg total initial pressure, in the temperature range 520—580 K. As in sealed-tube reactions at 473 K and *ca.* 6 atm total pressure, the major product was found to be the 1 : 1 adduct 1,1,1-trifluoro-3-iodobutane (*ca.* 90%) together with a smaller amount of its isomer 1-iodo-2-trifluoromethylpropane (*ca.* 10%). In this paper, ' adduct ' refers to this mixture unless otherwise stated, but the reactions will in general be discussed in terms of the predominant isomer. However, in contrast to the clean 1 : 1 addition observed in the sealed-tube reactions, the pressure measurements indicated a more complex reac-

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† *Present address*: Department of Chemistry, Manchester Polytechnic, Manchester MA 5GD.

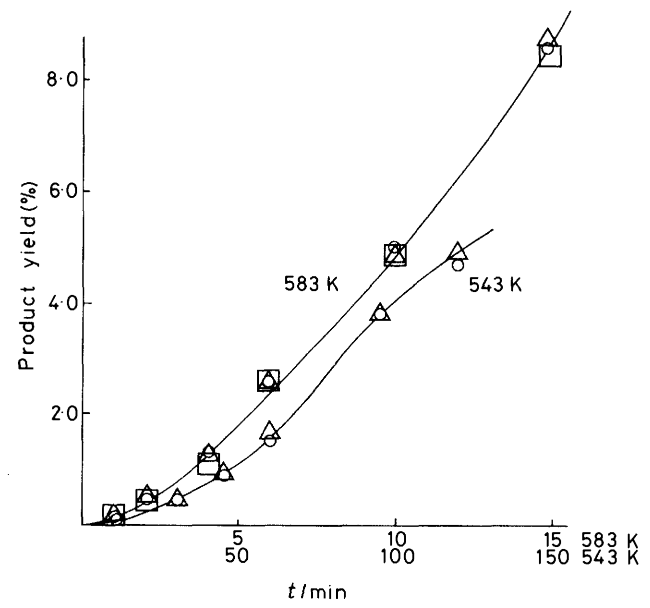

Figure 1. Appearance curves for secondary products: ○ = iodine, △ = 1,1,1-trifluorobutane, □ = 4,4,4-trifluorobutene; % yields based on initial propene and equations (1) and (3)

tion, since (a) the pressure change accelerated during the earlier part of the reaction, and (b) the pressure never fell to the value expected for 1 : 1 addition, and after reaching its lowest value began to rise again. It was further observed that iodine, 1,1,1-trifluorobutane and 4,4,4-trifluorobutene were formed in the reaction (Figure 1), to the extent of 5—9% of the product at 40% reaction, and that added iodine increased the overall rate of addition. These observations suggested that the initially formed adducts were unstable under the conditions used, decomposing to provide iodine, which acted as an autocatalyst for the addition reaction. Traces of trifluoromethane were also found (*ca.* 5% of the addition product at 520 K); this was not quantified, but probably arose from allylic hydrogen abstraction.[9]

Pyrolysis of the adduct alone at 583 K for 12 h gave equimolar amounts of iodine, 1,1,1-trifluorobutane, and 4,4,4-trifluorobutene, in accordance with equation (3). The ratio of final to initial pressure was 1.41, in good agreement with the predicted value of 1.48 (allowing for dead-space [6]), the discrepancy being attributed to condensation or adsorption of iodine in the dead-space.

$$2CF_3CH_2CHIMe \longrightarrow CF_3CH_2CH_2Me + CF_3CH_2CH{=}CH_2 + I_2 \quad (3)$$

The products of reaction (3) were similarly found in the products of the addition reaction (see Figure 1); they were again formed in equimolar quantities and the appearance curves demonstrate that they were (at least predominantly) secondary products, formed by decomposition of the primary adduct. The mechanism of this decomposition may be proposed as four-centre elimination of hydrogen iodide to give the olefin, and reduction of a second adduct molecule by the hydrogen iodide to give iodine and the alkane.

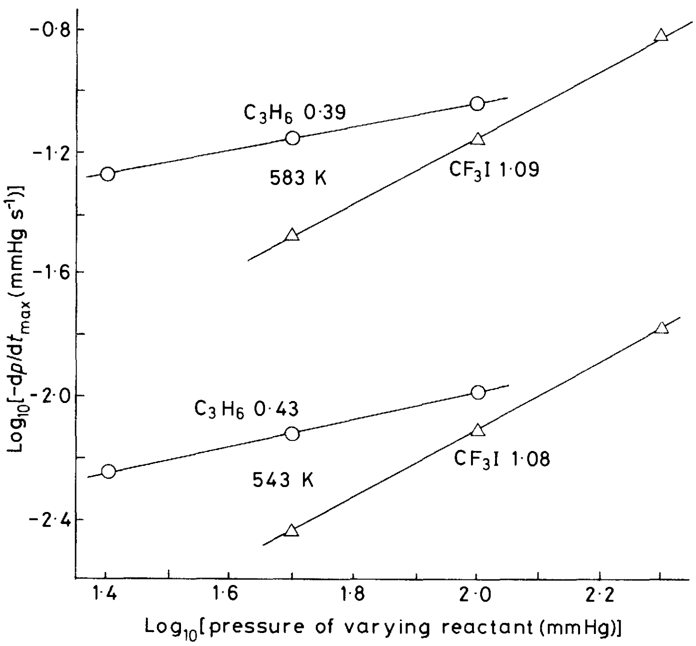

Figure 2. Kinetic orders of addition reaction from rate of pressure change: ○, 100 mmHg of trifluoroiodomethane with 25—100 mmHg of propene; △, 50 mmHg of propene with 50—200 mmHg of trifluoriodomethane. Figures on lines give derived orders

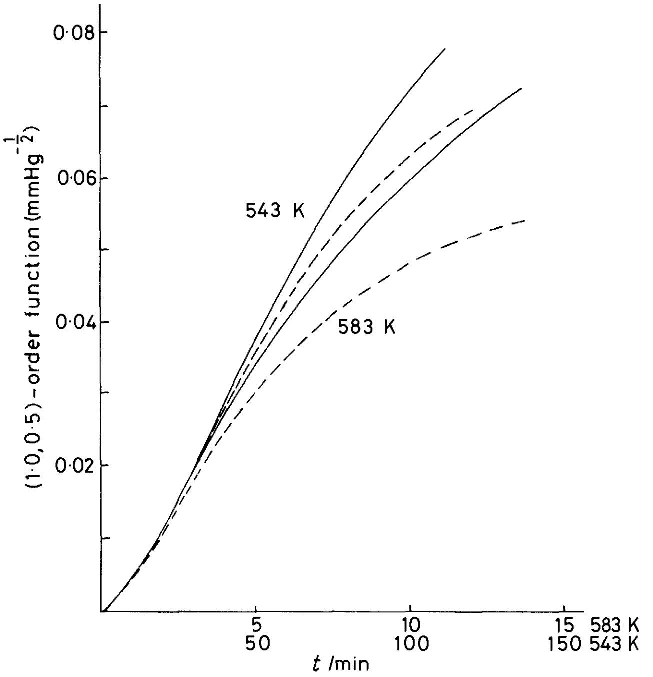

Figure 3. Integrated function plots, equation (6), for 100 mmHg CF$_3$I plus 50 mmHg propene: broken lines represent ' raw ' data, while solid lines are corrected for pressure change due to adduct decomposition. Ordinate = 0.007 for 10% addition, 0.025 for 30%, 0.063 for 60%

Complete quantitative analysis of reaction mixtures was not possible with the apparatus available, but since the stoicheiometry of the reaction has been established, it was possible to study the kinetics of the reaction by observing the pressure changes in a constant-volume system (with correction if necessary for decomposition of the adduct; see later). Attention was focused first on the maximum rate of pressure change during each run; these rates were measured and plotted logarithmically against initial reactant pressures in runs at 543 and 583 K, varying each reactant pressure in turn with the other held constant. The results (Figure 2) show a very good fit to the rate equation (4). Correspondingly, integrated function plots were constructed for the aproximate rate

$$-(\mathrm{d}p/\mathrm{d}t)_{\mathrm{max.}} = k_4[\mathrm{CF_3I}]^{1.09}[\mathrm{C_3H_6}]^{0.41} \tag{4}$$

$$-\mathrm{d}p/\mathrm{d}t = k_5[\mathrm{CF_3I}]^{1.00}[\mathrm{C_3H_6}]^{0.50} \tag{5}$$

$$(2/\Delta^{\frac{1}{2}})[\tan^{-1}([\mathrm{C_3H_6}]_t/\Delta)^{\frac{1}{2}}]_t^0 = k_5t \tag{6}$$

$$\text{where } \Delta = [\mathrm{CF_3I}]_0 - [\mathrm{C_3H_6}]_0$$

equation (5), *i.e.* plots of the left-hand side of equation (6) against time [10] using reactant pressures calculated from the pressure change with allowance for deadspace.[11] These plots were linear over a reasonable part of the reaction (Figure 3), although still showing the autocatalytic start. There are several reasons for the downward curvature towards the end of the reaction. One is the adduct decomposition which, as already noted, results in an eventual increase in pressure even after the addition is complete. This can be corrected for using the data of Figure 1, and it can be seen from Figure 3 that a substantial improvement in the function plots is obtained. The residual curvature may be partly due to the deviation of the reaction orders from 1.0 and 0.5, but a chemical cause will also be elucidated later.

The gradients k_5 of the linear parts of the integrated plots varied slightly from run to run, as expected from equation (4), but, when multiplied by the effectively constant ratio $([\mathrm{C_3H_6}]/[\mathrm{CF_3I}])^{0.09}$, provided rate-constants k_4 that were remarkably constant at a given temperature (Table 1). Addition runs over a wider range of temperatures similarly provided the rate constants in Table 2; the Arrhenius plot of these data was a good straight line corresponding to equation (7), in which the error limits are 95% confidence limits.

$$\log_{10}(k_4/\mathrm{dm^{3/2}\,mol^{-\frac{1}{2}}\,s^{-1}}) = (12.03 \pm 0.17) - (152.8 \pm 1.8)\ \mathrm{kJ\,mol^{-1}}/RT\ln 10 \tag{7}$$

Table 1. Addition rate constants from maximum rates and function plots

Initial pressure (mmHg)		10^5k_5/mmHg$^{-\frac{1}{2}}$ s^{-1}		10^5k_4/mmHg$^{-\frac{1}{2}}$ s^{-1}	
CF_3I	C_3H_6	543 K	583 K	543 K	583 K
50	50	1.36	11.6	1.36	11.6
100	50	1.42	12.5	1.34	11.7
200	50	1.52	13.3	1.34	11.7
100	25	1.47	13.8	1.30	12.2
100	50	1.42	12.5	1.34	11.7
100	100	1.40	12.0	1.40	12.0

Table 2. Variation of rate constant with temperature

Temperature (K)	No. of runs	10^3k_4/ dm$^{3/2}$ mol$^{-\frac{1}{2}}$ s^{-1}	$10^3\sigma(k)$ [a]
583.0	11	22.1	0.5
572.0	3	11.7	0.04
562.0	5	6.73	0.16
552.0	5	3.79	0.16
545.0	13	2.44	0.07
533.4	1	1.18	

[a] Estimated population standard deviation of k.

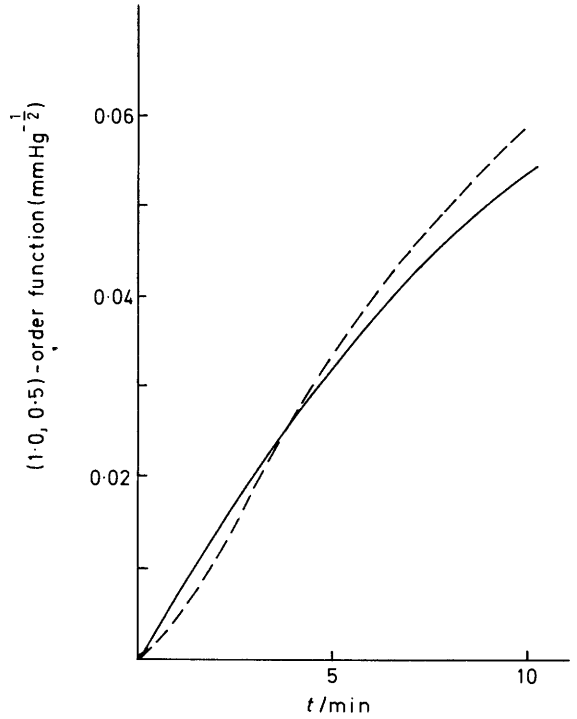

Figure 4. Effect of 1 mmHg iodine added to 100 mmHg CF_3I plus 50 mmHg propene at 583 K: broken line, without iodine; solid line, with iodine

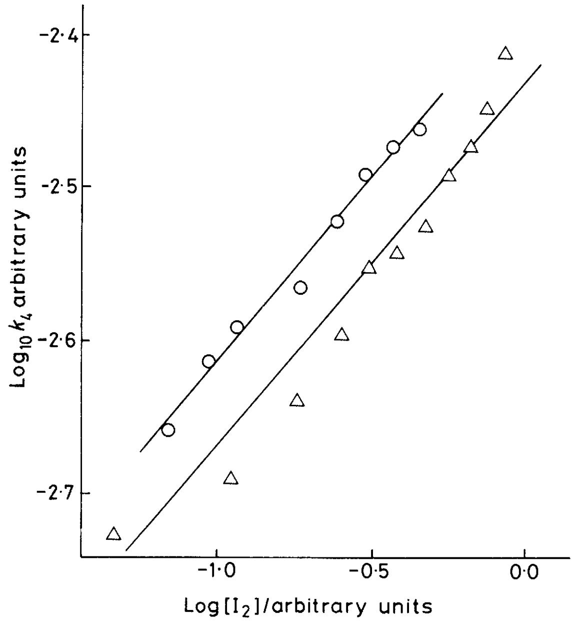

Figure 5. Variation of rate with iodine concentration during runs; ○, 583 K, △, 543 K. The solid lines have slope 0.25

It has already been suggested that the initial acceleration was due to iodine produced by the adduct decomposition, and this was confirmed by experiments with small amounts of initially added iodine, in which the function plots were linear from the start, with slope equal to the maximum slope observed in the corresponding experiments without added iodine (*e.g.* Figure 4). Conversely, addition of adducts to the initial reactant mixture had no immediate effect on the reaction. Since the concentration of iodine was not directly controllable, a comprehensive investigation of the kinetics with respect to iodine was not possible. However, an order of reaction could be determined from a log plot of the values of

Table 3. Arrhenius parameters for individual and composite rate/equilibrium constants

Constant	$\log_{10}\left(\dfrac{\text{pre-exponential factor}}{\text{units}^{a}}\right)$	$\dfrac{\text{' Activation energy '}}{\text{kJ mol}^{-1}}$	Ref.
k_{11}	10.9	75	14
K_{10}	4.2	151	*b*
k_{12}	8.0	2	3
k_{13}	7.5	45	estimated [c]
k_{15}	9.5	0	estimated [c]
k_8 (estimated)	9.5	99	equation (17)

[a] Units: $dm^3 mol^{-1} s^{-1}$ for k_{11}, k_{12}, k_{13}, k_{15}; $mol dm^{-3}$ for K_{10}; $dm^{9/4} mol^{-3/4} s^{-1}$ for k_8. [b] 'JANAF Thermochemical Tables,' ed. D. R. Stull and H. Prophet, NSRDS-NBS 37, NBS, Washington DC, 1971. [c] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1976, 2nd edn.

k_4 during the accelerating period against the pressure of iodine from Figure 1. Such plots are shown in Figure 5; although the points are somewhat scattered they demonstrate that the order of the addition reaction with respect to iodine is close to 0.25. Finally, equating the rate of pressure change to the rate of adduct formation, we obtain the overall kinetic equation (8). For the reasons just discussed, k_8 could not be determined as accurately as k_4, but the approximately known iodine concentration in the linear part of the reaction leads to equation (9). It would be erroneous to quote an Arrhenius equation for k_8, however, since the temperature variation of the effective iodine concentration cannot be defined with sufficient accuracy.

$$\frac{d[\text{adduct}]}{dt} = k_8[I_2]^{0.25}[CF_3I]^{1.09}[C_3H_6]^{0.41} \qquad (8)$$

$$k_8 \simeq k_4/0.08 \text{ mol}^{0.25} \text{ dm}^{-0.75} \qquad (9)$$

It was also noted that if larger amounts of iodine were present initially, the rate was actually depressed. This suggests that the build up of iodine in the later stages of the reaction may be responsible for the residual downward curvature of the function plots, after correction for adduct decomposition as already discussed. A mechanistic explanation will be given in the Discussion section.

Discussion

It is clear from the observed general features of the reaction that the addition is a free-radical chain reaction. Rate equation (8) applies over a large part of the reaction, and the 0.25 order with respect to I_2 suggests an initiation which is first-order in iodine atoms, the latter being in thermal equilibrium with molecular iodine. Equations (10)—(16) together with the overall secondary reaction (3) can, therefore, account for the observed products and kinetics of the reaction. On the basis

$$M + I_2 \rightleftharpoons 2I^{\cdot} + M \qquad (10)$$

$$I^{\cdot} + CF_3I \longrightarrow I_2 + CF_3^{\cdot} \qquad (11)$$

$$CF_3^{\cdot} + C_3H_6 \longrightarrow CF_3C_3H_6^{\cdot} \qquad (12)$$

$$CF_3C_3H_6^{\cdot} + CF_3I \longrightarrow CF_3C_3H_6I + CF_3^{\cdot} \qquad (13)$$

$$\left.\begin{array}{ll} 2CF_3C_3H_6^{\cdot} \longrightarrow & (14) \\ CF_3C_3H_6^{\cdot} + CF_3^{\cdot} \longrightarrow & (15) \\ 2CF_3^{\cdot} & (16) \end{array}\right\} \text{termination products}$$

of these equations, the orders with respect to trifluoroiodomethane and propene would be (1.5, 0), (1.0, 0.5), and (0.5, 1.0) for termination by reactions (14), (15), and (16) respectively. The observed orders of (1.09, 0.41) suggest that under the conditions used the termination is mainly by reactions (14) and (15); for example, termination by reaction (15) leads to the overall steady-state rate equation (17), which is close to the observed equation (8). Experimental rate/equilibrium

$$\frac{d[\text{adduct}]}{dt} = \left(\frac{k_{11}K_{10}^{\frac{1}{2}}k_{12}k_{13}}{k_{15}}\right)^{\frac{1}{2}} [I_2]^{0.25}[CF_3I]^{1.0}[C_3H_6]^{0.5} \qquad (17)$$

constants are available for k_{11}, K_{10}, and k_{12}, and reasonable estimates can be made for k_{13} and k_{15}, leading to the predicted Arrhenius parameters for k_8 given in Table 3. These parameters predict values for k_8 (see Table 4) which are satisfyingly close to the measured values [equations (7) and (9)] considering the nature of the estimations involved in making these predictions.

Table 4. Estimated and observed values for k_8

	$k_8/dm^{9/4} mol^{-3/4} s^{-1}$	
Temperature (K)	Estimated (Table 3)	Observed [equations (7) and (9)]
543	0.9	0.03
583	4.3	0.3

It should be noted that in principle there was no iodine present at the start of the reaction in our experiments, so that initiation by reactions (10) and (11) could not start until some iodine was formed. The thermal decomposition of trifluoroiodomethane (dissociation energy [12] *ca.* 220 kJ mol^{-1}) will be well in its fall-off region [13] and unlikely to produce iodine at a sufficient rate to account for the observed acceleration. Other reactions (molecular, heterogeneous or photochemical) may result in iodine formation, but a more likely rationalisation involves the presence of very small traces of iodine in the reactants. It is very difficult to obtain and maintain trifluoroiodomethane completely free of iodine, and because of the 0.25 order with respect to iodine, even 10^{-4} mmHg will give 10% of the ' steady-state ' initiation rate.

Previous studies [14] of the initiation reaction (11) have shown it to be reversible and the removal of propagating radicals by reaction (−11) could account both for the retarding effect of large amounts of iodine added initially, and for the falling-off of the integrated function plots at high extents of reaction. Assuming reaction (10) to be at equilibrium, the effective initiation rate is given by equation (18). Detailed calculations

$$R_i = k_{11}K_{10}[I_2]^{\frac{1}{2}}[CF_3I] - k_{-11}[I_2][CF_3^{\cdot}] \qquad (18)$$

show that as $[I_2]$ increases during the reaction, R_1 increases fairly rapidly to a shallow maximum, then falls off as reaction (−11) becomes increasingly important, and a semi-quantitative fit to the observed behaviour could be obtained.

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Received 14*th February* 1983; *Paper* 3/227