979. *Mechanism of the Addition of Trifluoroiodomethane to Ethylene.*

By T. N. BELL.

The thermal reaction between trifluoroiodomethane and ethylene yields addition products $CF_3 \cdot [CH_2 \cdot CH_2]_n \cdot I$; the main product being 1,1,1-trifluoro-3-iodopropane ($n = 1$). The rate of the addition is given by two limiting rate equations which arise from two propagating steps, each of which can be made rate-controlling depending on the reactant ratio CF_3I/C_2H_4. A mechanism is suggested which satisfactorily accounts for the dependence of the rate of addition on the reactant concentration.

THE thermally or photochemically initiated reaction in which trifluoroiodomethane adds to olefins has been used to prepare fluoroalkyl derivatives.[1] In the present case 1,1,1-trifluoro-3-iodopropane is the main product; however, at low trifluoroiodomethane : ethylene ratios some telomers $CF_3 \cdot [C_2H_4]_n \cdot I$, where $n > 1$, are formed. As these additions have only been investigated qualitatively it was decided to study kinetically the reaction between trifluoroiodomethane and ethylene with a view to establishing the mechanism.

EXPERIMENTAL

Materials.—Ethylene was obtained from a cylinder (C.I.G. brand) and purified by fractionation through traps cooled to −72°, −95°, −129°, and liquid-air temperature. The fraction collecting in liquid air was shown to contain no detectable impurity (by molecular weight determination and gas chromatography).

Trifluoroiodomethane was prepared by heating silver trifluoroacetate with iodine.[2] The

[1] Haszeldine, *J.*, 1949, 2856; 1953, 3761.
[2] Haszeldine, *J.*, 1951, 584.

impure gas was washed with sodium hydroxide solution and dried (P_2O_5), then fractionated as above. The fraction collected at −129° contained no detectable impurity (molecular weight determination and gas chromatography). The purified product was stored at liquid-air temperature.

Apparatus.—A conventional static high-vacuum apparatus was used. The Pyrex-glass vessel (81 ml.) was fitted with a thermocouple well, and was embedded in a tubular furnace, the temperature being controlled to within 0·5° with a Sunvic RT2 temperature controller. Pressures were measured with a constant-volume manometer similar to that described by Dodd and Robinson;[3] this was modified by using air pressure and suction to raise and lower the mercury in the manometer limbs, thereby eliminating a manually operated mercury reservoir connected by rubber tubing, and preventing contamination of the mercury. The modified manometer is shown in Fig. 1. Pressure readings were obtained by using two cathetometers, focused on the manometer limbs.

It was found impossible to make and store mixtures of the two gases, as reaction was initiated in the mixing vessel by sun and fluorescent light. The two gases were therefore admitted separately to the vessel through a two-way capillary tap, the time interval between successive additions being less than 5 sec.

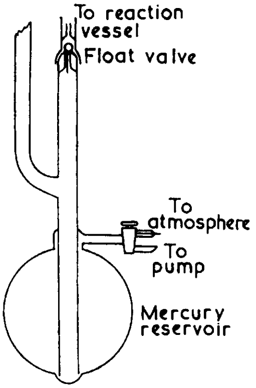

FIG. 1. Constant-volume manometer.

The stoicheiometry of the reaction was determined by use of gas chromatography (Perkin-Elmer model 154 C). The procedure adopted was to empty the contents of the vessel after a given heating time through a trap cooled to −78° in order to removal all products; the residual starting materials were then condensed into a liquid-air trap. This trap, of standard volume, was then warmed to 20° and attached to the gas-sampling device on the gas chromatograph where the contents were equilibrated with a standard 1-ml. sampling volume; the total pressure could be read on a manometer incorporated in the system. Separation was achieved on a 2-m. column containing di-isodecyl phthalate as the liquid phase, and the partial pressure of each component was determined from the recorded peaks.

The kinetics of the reaction were followed by measuring the rate of change of pressure with time; initial rates were determined from the pressure–time curves.

RESULTS

Stoicheiometry.—A number of runs at 309° with the same initial reactant composition but different heating times were analysed for residual trifluoroiodomethane and ethylene by gas chromatography. The process was repeated for several series of runs, each series differing in the trifluoroiodomethane : ethylene ratio. At pressure ratio trifluoroiodomethane : ethylene = 1·9 and 3·0, corresponding to total reactant pressures of 135 and 172 mm., the rate of consumption of ethylene and trifluoroiodomethane was the same. When the pressure ratio was reduced to 1·3 at a total pressure of 107 mm. the amount of ethylene consumed was slightly greater than the amount of trifluoroiodomethane consumed. It being assumed that the excess of ethylene was used in the formation of a dimer adduct the increased consumption of ethylene corresponded to 5% of telomer in the total product.

[3] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

The stoicheiometry can then be expressed by equations (*a*) and (*b*).

$$CF_3I + C_2H_4 \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

$$CF_3I + nC_2H_4 \longrightarrow CF_3{\cdot}[C_2H_4]_n{\cdot}I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

At reactant ratios $CF_3I/C_2H_4 > 1{\cdot}9$, eqn. (*a*) may be considered to be solely operative, while below this ratio both eqns. (*a*) and (*b*) are operative, the extent of eqn. (*b*) increasing with a decreasing trifluoroiodomethane : ethylene ratio.

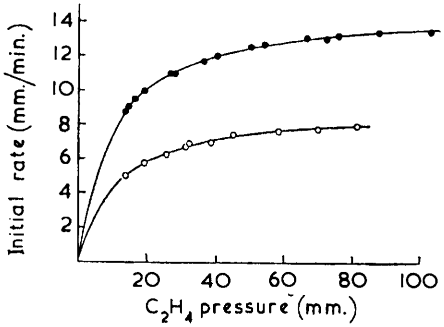

FIG. 2. Variation of initial rate with ethylene pressure. ○ p_{CF_3I} constant at 130 mm. ● p_{CF_3I} constant at 187 mm.

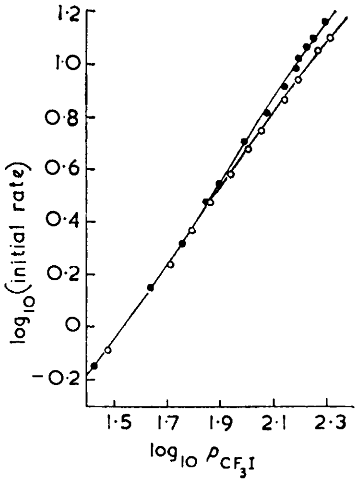

FIG. 4. Variation of log (initial rate) with log (trifluoroiodomethane pressure). ○ $p_{C_2H_4}$ constant at 31·5 mm. ● $p_{C_2H_4}$ constant at 55·5 mm.

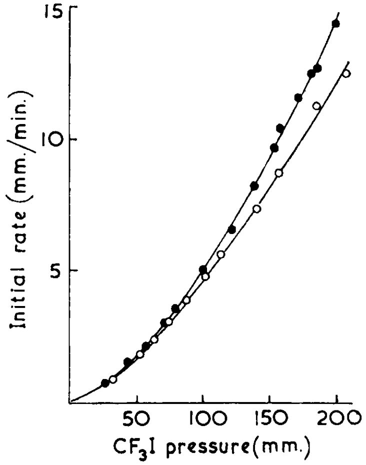

FIG. 3. Variation of initial rate with trifluoroiodomethane pressure. ○ $p_{C_2H_4}$ constant at 31·5 mm. ● $p_{C_2H_4}$ constant at 55·5 mm.

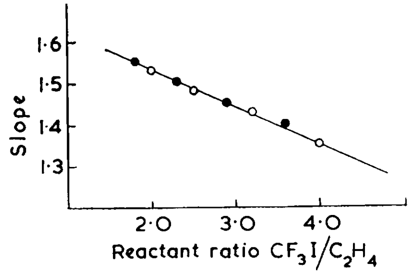

FIG. 5. Variation of slope of curves in Fig. 4 with reactant ratio.

Rate Equation.—The influence of the reactant concentrations on the rate of the reaction was investigated at one temperature, 309°. Here the initial rates of reaction were determined for a series of runs in which the pressure of one reactant was varied with respect to a fixed pressure of the other. In Fig. 2 is shown the variation of rate with pressure of ethylene, with respect to two different fixed pressures of trifluoroiodomethane. Fig. 3 shows the results where the pressure of ethylene is fixed and that of trifluoroiodomethane is varied. From Fig. 2 it is apparent that the rate of addition is markedly dependent on the pressure of ethylene when this is low, while at higher pressures the rate is almost independent of the pressure of ethylene. On the other hand, the rate of reaction is very dependent on the pressure of trifluoroiodomethane throughout the whole of the range investigated (Fig. 3).

From the results shown in Figs. 2 and 3, the empirical rate equation can be written in the form

$$\text{Rate} = k[CF_3I]^x[C_2H_4]^y$$

The question arises as to whether x and y are primarily pressure dependent, or are primarily dependent on the ratio, CF_3I/C_2H_4. If the former is the case the slope of the plot of log (trifluoroiodomethane pressure) against log (rate of reaction) should be equal to the order of reaction with respect to trifluoroiodomethane. Thus, for different fixed pressures of ethylene a series of parallel curves should result. Fig. 4 shows the data from Fig. 3 plotted in this manner; here coincidence of the two curves occurs up to about 68 mm. pressure of trifluoroiodomethane, above this pressure a marked divergence is seen. Thus, the order of reaction cannot be primarily dependent on pressure. If the reactant ratio is the controlling factor the slopes of the curves in Fig. 4 should be similar for the same pressure ratios. That this is so can be seen from Fig. 5 where the slopes, taken from Fig. 4 at various points, are plotted against the corresponding reactant ratio. The coincidence of the lower points in Fig. 4 is inevitable, for here the ratio of trifluoroiodomethane to ethylene is low, and it can be seen from Fig. 2 that the rate is almost independent of the pressure of ethylene and can be considered to be wholly dependent on the pressure of trifluoroiodomethane, at the ratios where coincidence occurs.

Two limiting cases for reaction exist, (1) where the ratio of trifluoroiodomethane to ethylene tends to infinity, and (2) where this ratio tends to zero. The latter case is of theoretical interest only because of telomer formation at low trifluoroiodomethane to ethylene ratios. It is of interest to consider how the empirical rate equation behaves as the reactant ratio varies, and an indication of this can be had from the experimental results. From Fig. 2 it is apparent that the rate of reaction becomes more dependent on the ethylene as the ratio trifluoroiodomethane to ethylene increases, and if the extrapolation of the curve to zero pressure of ethylene is considered to approach a straight-line relationship as the ethylene pressure tends to zero, then the empirical rate equation can be written in the form

$$\text{Rate} = k[CF_3I]^x[C_2H_4]^1.$$

This equation can be considered to operate under the first limiting condition, *i.e.*, where the trifluoroiodomethane to ethylene ratio tends to infinity. Because of the approximate nature of the extrapolation in Fig. 2, a determination of the order, with respect to trifluoroiodomethane, which can be had by equating the two slopes at $p_{C_2H_4} = 0$, is not a justifiable calculation. However, if the rate equation assumes the above form as the ratio of trifluoroiodomethane to ethylene becomes high it is obvious that the slope of the plot of log (rate) against log p_{CF_3I} will equal x, the order with respect to trifluoroiodomethane at the limiting condition. In Fig. 5, it is seen that, as the ratio of trifluoroiodomethane to ethylene increases, so the slopes of the curves in Fig. 4 decrease; thus, it can be presumed that the order with respect to trifluoroiodomethane will be less than 1·35 at very high ratios.

Again from Fig. 2, as the ratio falls, independence of the ethylene pressure is approached; the rate is therefore mainly dependent on the pressure of trifluoroiodomethane in this region. The empirical rate equation governing the reaction when the ratio tends to zero is therefore of the form

$$\text{Rate} = k[CF_3I]^x$$

From Fig. 5 it is seen that the slope of the plot of log (rate) against log p_{CF_3I} increases as the ratio of trifluoroiodomethane to ethylene falls, and for the second limiting case cited above, x will be greater than 1·55.

Thus the rate of reaction is governed by two limiting rate equations, each singly operative where the ratio of trifluoroiodomethane to ethylene approaches the limiting conditions of zero and infinity.

DISCUSSION

The form of the rate equation is complex and on this basis the direct bimolecular reaction,

$$CF_3I + C_2H_4 \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2I,$$

is discounted. Thus a radical chain mechanism appears most likely, the mode of initiation of the chain being through the thermal decomposition of trifluoroiodomethane. Besides activation through like collisions, activation through collisions of trifluoroiodomethane with ethylene must be postulated, for it is well known that foreign molecules can be quite efficient in promoting thermal decompositions.[4]

$$CF_3I + CF_3I \longrightarrow CF_3I^* + CF_3I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CF_3I + CF_3I^* \longrightarrow CF_3I + CF_3I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CF_3I + C_2H_4 \longrightarrow CF_3I^* + C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CF_3I^* + C_2H_4 \longrightarrow CF_3I + C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$CF_3I^* \longrightarrow \bullet CF_3 + I\bullet \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Steps (3) and (4) appear of little importance when the dependence of rate on the ethylene pressure is considered. Fig. 2 shows that there is very little dependence of the rate on the ethylene pressure when the pressure is appreciable; thus for the sake of simplicity steps (3) and (4) are considered small enough to be neglected.

Propagation *via* steps (6) and (7) is suggested, while telomer formation can be considered to arise through step (8). Since this discussion is concerned with the formation of the 1 : 1-adducts, step (8) can be discounted.

$$\bullet CF_3 + C_2H_4 \longrightarrow CF_3\cdot CH_2\cdot CH_2\bullet \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$CF_3\cdot CH_2\cdot CH_2\bullet + CF_3I \longrightarrow CF_3\cdot CH_2\cdot CH_2I + \bullet CF_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$CF_3\cdot CH_2\cdot CH_2\bullet + C_2H_4 \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\bullet \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

Three termination steps are obviously possible: (9), (10), and (11).

$$\bullet CF_3 + \bullet CF_3 \longrightarrow C_2F_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$CF_3\cdot CH_2\cdot CH_2\bullet + CF_3\cdot CH_2\cdot CH_2\bullet \longrightarrow [CF_3\cdot CH_2\cdot CH_2]_2 \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

$$\bullet CF_3 + CF_3\cdot CH_2\cdot CH_2\bullet \longrightarrow CF_3\cdot CH_2\cdot CH_2\cdot CF_3 \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

Steps 1, 2, 5, 6, 7, 9, 10, and 11 being assumed the important steps controlling the reaction scheme, the following theoretical rate equation is derived.

$$-\mathrm{d}p/\mathrm{d}t = \mathrm{d}[CF_3\cdot CH_2\cdot CH_2I]/\mathrm{d}t = k_7[CF_3\cdot CH_2\cdot CH_2\cdot][CF_3I] \quad . \; . \quad (12)$$

Long chains being assumed, there will be a balance between the propagating steps (6) and (7), at the stationary-state condition.

$$\text{Thus,} \qquad k_7[CF_3\cdot CH_2\cdot CH_2\cdot][CF_3I] = k_6[\cdot CF_3][C_2H_4] \; . \; . \; . \; . \; . \; . \quad (13)$$

Also the rate of formation of radicals will be equal to their rate of disappearance.

$$\text{Thus, } k_5[CF_3I^*] = k_9[\cdot CF_3]^2 + 2k_{11}[\cdot CF_3][CF_3\cdot CH_2\cdot CH_2\cdot] + k_{10}[CF_3\cdot CH_2\cdot CH_2\cdot]^2 \quad (14)$$

The plausible assumption being made that $k_9k_{10} \simeq k_{11}^2$, this can be substituted into eqn. (14) and the root taken.

$$\text{Thus,} \qquad (k_5[CF_3I^*])^{\frac{1}{2}} = k_9^{\frac{1}{2}}[\cdot CF_3] + k_{10}^{\frac{1}{2}}[CF_3\bullet CH_2\cdot CH_2\cdot] \quad . \; . \; . \; . \; . \quad (15)$$

From eqn. (13) we have

$$[CF_3\cdot CH_2\cdot CH_2\cdot] = k_6[\bullet CF_3][C_2H_4]/k_7[CF_3I] \quad . \; . \; . \; . \; . \; . \quad (16)$$

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[4] Bell, Robinson, and Trenwith, *J.*, 1957, 1474; Lindars and Hinshelwood, *Proc. Roy. Soc.*, 1955, *A*, **231**, 162; Volpe and Johnston, *J. Amer. Chem. Soc.*, 1956, **78**, 3903.

By substitution of $[CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}]$ from eqn. (16) into eqn. (15) we have,

$$(k_5[CF_3I^*])^{\frac{1}{2}} = k_9^{\frac{1}{2}}[{\cdot}CF_3] + k_{10}^{\frac{1}{2}}k_6[{\cdot}CF_3][C_2H_4]/k_7[CF_3I] \quad . \quad . \quad . \quad . \quad (17)$$

Now, $\quad d[CF_3I^*]/dt = 0 = k_1[CF_3I]^2 - k_2[CF_3I][CF_3I^*] - k_5[CF_3I^*] \quad . \quad . \quad . \quad . \quad (18)$

Thus,

$$(k_5[CF_3I^*])^{\frac{1}{2}} = [CF_3I]\left(\frac{k_5k_1}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (19)$$

Combination of equations (17) and (19) gives

$$[CF_3I]\left(\frac{k_5k_1}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} = [{\cdot}CF_3]\left(k_9^{\frac{1}{2}} + \frac{k_{10}^{\frac{1}{2}}k_6[C_2H_4]}{k_7[CF_3I]}\right) \quad . \quad . \quad . \quad (20$$

Hence,

$$[{\cdot}CF_3] = \frac{k_7[CF_3I]^2}{k_9^{\frac{1}{2}}k_7[CF_3I] + k_{10}^{\frac{1}{2}}k_6[C_2H_4]}\left(\frac{k_1k_5}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} \quad . \quad . \quad (21)$$

Now, from eqns. (12) and (13), the rate of reaction may be written:

$$-dp/dt = k_6[{\cdot}CF_3][C_2H_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and substituting for $[{\cdot}CF_3]$ from eqn. (21) we obtain

$$\text{Rate} = -\frac{dp}{dt} = \frac{k_6k_7[CF_3I]^2[C_2H_4]}{k_9^{\frac{1}{2}}k_7[CF_3I] + k_{10}^{\frac{1}{2}}k_6[C_2H_4]}\left(\frac{k_1k_5}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} \quad . \quad . \quad (23)$$

It is obvious that eqn. (23) may be written in two limiting forms, *i.e.* where the ratio $[CF_3I]/[C_2H_4]$ is high or low.

Case 1. *Ratio*$[CF_3I]/[C_2H_4]$*high.*—Obviously $k_9^{\frac{1}{2}}k_7[CF_3I] \gg k_{10}^{\frac{1}{2}}k_6[C_2H_4]$ and as the reactant ratio tends to infinity, so the rate equation can be written as

$$-\frac{dp}{dt} = \left(\frac{k_6[CF_3I][C_2H_4]}{k_9^{\frac{1}{2}}}\right)\left(\frac{k_1k_5}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Experimentally it has been shown that as the limiting condition is approached the empirical rate equation is of the form,

$$\text{Rate} = k[CF_3I]^x[C_2H_4]^1 \text{ where } x < 1{\cdot}35,$$

this is in excellent agreement with the limiting theoretical eqn. (24).

Case 2. *Ratio* $[CF_3I]/[C_2H_4]$ *low.*—Obviously $k_9^{\frac{1}{2}}k_7[CF_3I] \ll k_{10}^{\frac{1}{2}}k_6[C_2H_4]$ and as the reactant ratio tends to its limiting value so the rate eqn. (23) tends to

$$-\frac{dp}{dt} = \left(\frac{k_7[CF_3I]^2}{k_{10}^{\frac{1}{2}}}\right)\left(\frac{k_1k_5}{k_5 + k_2[CF_3I]}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Experimentally it has been shown that as the conditions for case 2 are approached the empirical rate equation is of the form

$$\text{Rate} = k[CF_3I]^x, \text{ where } x > 1{\cdot}55.$$

Again this is in agreement with the theoretical eqn. (25). The general equation for the rate of reaction, eqn. (23), can be rearranged in the forms (26) and (27), where κ, κ', and κ'' are combinations of velocity constants.

$$\frac{\text{Rate}}{\kappa} = \frac{[C_2H_4][CF_3I]^2}{([C_2H_4] + \kappa'[CF_3I])(1 + \kappa''[CF_2I])^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (26)$$

$$\frac{\kappa}{\text{Rate}} = \frac{(1 + \kappa''[CF_3I])^{\frac{1}{2}}}{[CF_3I]^2} + \frac{\kappa'(1 + \kappa''[CF_3I])^{\frac{1}{2}}}{[CF_3I]} \cdot \frac{1}{[C_2H_4]} \quad . \quad . \quad . \quad (27)$$

A plot of the results shown in Fig. 2, in the form 1/rate against $1/[C_2H_4]$, which corresponds to eqn. (27), is given in Fig. 6. The straight-line relationship as predicted by eqn. (27) is further evidence for the validity of the reaction mechanism suggested.

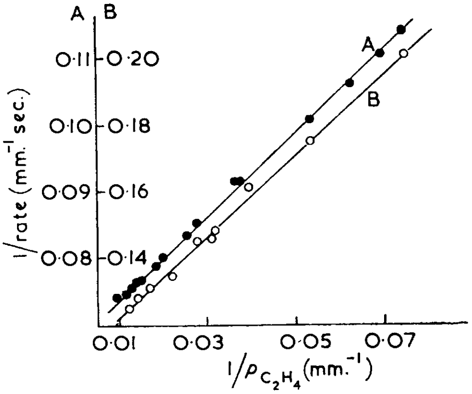

Fig. 6. Variation of 1/rate with $1/p_{C_2H_4}$ ○ p_{CF_3I} constant at 130 mm. ● p_{CF_3I} constant at 187 mm.

A series of experiments designed to measure accurately the initial slopes of the curves in Fig. 2 where the pressure of ethylene tends to zero would yield values corresponding to

$$\frac{k_6(k_5k_1)^{\frac{1}{2}}[CF_3I]}{k_9^{\frac{1}{2}}(k_5 + k_2[CF_3I])^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

By using different olefins a value corresponding to eqn. (28) could be obtained for each olefin. In these values the only uncommon velocity constant would be k_6, hence this method could be used to determine the differences in activation energy for the addition of trifluoromethyl radicals to various π bond systems.

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Department of Physical and Inorganic Chemistry,
The University of Adelaide, South Australia.

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