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# The Gas-phase Reaction of CF<sub>3</sub> Radicals with HCN in the Temperature Range 333-523 K

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> The reaction of  $CF_3$  radicals produced by photolysis of  $CF_3I$  with HCN has been investigated in the temperature range 333-523 K. The radicals react with HCN by addition followed by a sequence of reactions of which the most important are:

> > $CF_3 + HCN \Leftrightarrow CF_3 HCN$  (1, -1)

$$CF_3 + CF_3HCN \rightarrow HCF_3C = NCF_3$$
 (2)

 $CF_3 + CF_3HCN \rightarrow CF_3H + CF_3CN$  (3)

$$I + CF_3HCN \rightarrow HI + CF_3CN$$
 (4)

$$2CF_3 \xrightarrow{\kappa_c} C_2F_6.$$

Arrhenius parameters for the addition reaction relative to radical recombination were estimated from experiments at conversions  $\Rightarrow 3\%$  in the temperature range 333-453 K. The best fit to our experimental results gave log  $[(A_1/A_c^{1/2}) \text{ cm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}] = 4.97$  and  $E_1 - \frac{1}{2}E_c = 30.9 \text{ kJ mol}^{-1}$ , with systematic estimated errors of up to 0.3 and 2.4 kJ mol<sup>-1</sup>, respectively. These parameters are compared with those obtained for other addition reactions of these radicals to substrates with a triple bond.

The gas-phase reaction of CF<sub>3</sub> radicals with HCN in the temperature range 523-673 K has been examined in our laboratory with CF<sub>3</sub> radicals generated by thermal decomposition<sup>1</sup> or photolysis<sup>2</sup> of CF<sub>3</sub>I at  $\lambda > 290$  nm under various conditions. CF<sub>3</sub>H, CF<sub>3</sub>CN, C<sub>2</sub>F<sub>6</sub> and I<sub>2</sub> were the main reaction products, while HCF<sub>3</sub>C=NCF<sub>3</sub> and HI were detected in very small amounts.

Conversion effects, through a significant increase of the ratio  $R_{CF_3H}/R_{C_2F_6}^{1/2}$  [HCN], were observed, especially when CF<sub>3</sub> radicals were obtained from the ultraviolet irradiation of CF<sub>3</sub>I. This was accounted for by the participation of iodine in the formation of CF<sub>3</sub>H through a complex reaction scheme.

Arrhenius parameters for the hydrogen abstraction reaction:

$$CF_3 + HCN \xrightarrow{k_H} CF_3H + CN$$

relative to CF<sub>3</sub> recombination:

$$2CF_3 \xrightarrow{k_c} C_2F_6$$

were obtained from results up to 2% conversion:

 $\log \left[ (k_{\rm H}/k_{\rm c}^{1/2}) \, {\rm cm}^{3/2} \, {\rm mol}^{-1/2} \, {\rm s}^{-1/2} \right] = 5.50(\pm 0.26) - 57.65(\pm 3.14) \, {\rm kJ} \, {\rm mol}^{-1}/2.303 \, {\it RT}.$ 

The reaction of  $CF_3$  radicals with  $ClCN^{3,4}$  has also been studied in this laboratory over a wide temperature range, 268-693 K, and a strongly curved Arrhenius plot was

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obtained for the ratio  $R_{CF_3Cl}/R_{C_2F_6}^{1/2}$  [ClCN]. The curvature was interpreted in terms of a chlorine-atom abstraction at high temperatures and the addition of the CF<sub>3</sub> radical to the C $\equiv$ N triple bond at low temperatures. Similar behaviour was observed for the reactions of C<sub>2</sub>F<sub>5</sub>, n-C<sub>3</sub>F<sub>7</sub> and i-C<sub>3</sub>F<sub>7</sub> with ClCN.<sup>5-7</sup> We now present results for the reaction of CF<sub>3</sub> radicals generated by photolysis of CF<sub>3</sub>I with HCN in the temperature range 333-523 K.

## Experimental

Materials were obtained and purified as described previously.<sup>1</sup> The apparatus, procedure and product analysis described in ref. (2) were also used for this work.

## **Results and Discussion**

In the temperature range 333-523 K the reaction products were the same as before,<sup>2</sup> and experiments were performed under similar conditions of reactant concentrations; however, a significant difference in product yield was observed.

From the data in table 1, the ratio  $R_{CF_3CN}/R_{CF_3H}$  is temperature-dependent, practically independent of HCN concentration, greater than unity at low temperatures and less than unity above 573 K.

In the temperature range 333-453 K with results obtained at conversions  $\geq 3\%$ ,  $R_{CF_3CN}/R_{C_2F_6}^{1/2}$  [HCN] is constant and independent of HCN concentration at each temperature. At higher temperatures, however, this ratio increases with conversion, as shown by the results above 523 K included in table 1 for comparison.

On account of these facts we suggest that, at low temperatures, the formation of  $CF_3CN$  and  $CF_3H$  occurs through a reaction scheme different from that proposed in ref. (1).

The addition of the  $CF_3$  radical would be the main step, as for  $CF_3$  with  $ClCN^4$ , followed by a series of reactions of the adduct such as

$$CF_3I + h\nu \rightarrow CF_3 + I$$

$$CF_3 + HCN \Leftrightarrow CF_3 HCN$$
 (1, -1)

$$CF_3 + CF_3 HCN \rightarrow HCF_3 C = NCF_3$$
<sup>(2)</sup>

$$CF_3 + CF_3HCN \rightarrow CF_3H + CF_3CN$$
 (3)

$$I + CF_3HCN \rightarrow HI + CF_3CN$$
 (4)

$$CF_3 + HI \rightarrow CF_3H + I$$
 (5)

$$2CF_3HCN \rightarrow \text{products}$$
 (6)

in addition to

$$2CF_3 \xrightarrow{\kappa_c} C_2F_6$$
$$I+I+M \rightarrow I_2+M.$$

We have not included in this reaction sequence the unimolecular decomposition of the adduct radical, CF<sub>3</sub>HCN, to produce CF<sub>3</sub>H+CN, as in ref. (4) for CF<sub>3</sub>ClCN. In spite of the uncertainties associated with the thermochemistry of the CF<sub>3</sub>HCN radical, we can estimate  $\Delta H$  for the decomposition reaction to be *ca*. 205 kJ mol<sup>-1</sup>, which sets a lower limit for the critical energy of decomposition. This value, together with an estimated log A = 13.1, indicate that the decomposition to CF<sub>3</sub>H+CN should be negligible in this temperature range. However, there is still the possibility that CF<sub>3</sub>HCN

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		reac pressur	ctant re/Torr			D	$R_{\rm CF_3CN}$	
T/K	time/s	CF <sub>3</sub> I	HCN	R <sub>CF3CN</sub>	$R_{C_2F_6}$	$R_{CF_3CN}$ / $R_{CF_3H}$	$(\mathrm{HCN})^{b}$	sion (%) <sup>c</sup>
333	18 000	91.0	29.0	0.401	0.305	1.20	0.520	0.5
	18 000	94.0	44.5	0.511	0.274	1.05	0.455	0.4
	18 120	82.0	44.0	0.487	0.273	1.10	0.440	0.4
	18 000	87.0	66.5	0.804	0.262	1.14	0.490	0.5
	14 538	147.0	76.5	0.973	0.293	1.18	0.488	0.4
353	14 400	95.5	50.0	0.739	0.106	1.39	1.00	0.5
	21 600	96.3	48.8	0.681	0.103	1.20	0.960	0.7
	14 400	88.5	65.0	1.24	0.194	1.20	0.953	0.6
	14 400	81.0	78.0	1.31	0.159	1.34	0.930	0.5
403	21 600	103.5	5.0	0.169	0.0503	1.45	3.83	1.8
	21 600	100.3	10.7	0.202	0.0160	1.40	3.75	1.0
433	14 640	100.5	5.0	0.346	0.0562	1.75	7.98	2.8
	18 000	101.5	10.0	0.564	0.0342	1.79	8.35	2.7
453	11 700	102.0	5.0	0.454	0.0556	1.42	11.0	3.0
	18 000	102.0	10.0	0.730	0.0377	1.44	10.8	2.7
	18 000	100.5	16.0	0.870	0.0272	1.54	9.45	2.8
473	10 800	110.0	3.0	0.535	0.103	1.21	16.6	2.9
	10 800	110.0	5.0	0.812	0.079	1.32	17.5	5.2
	10 800	118.5	9.5	1.12	0.0473	1.45	16.3	3.7
	10 800	110.0	15.5	1.64	0.0434	1.34	15.2	3.4
493	10 800	103.0	4.0	0.710	0.169	0.92	13.6	5.9
	10 800	102.0	7.0	0.883	0.125	0.96	11.2	4.2
	10 800	102.0	12.0	1.02	0.081	1.03	9.31	2.6
523	10 800	103.5	7.0	0.983	0.246	1.31	9.45	4.9
	10 800	103.5	14.0	2.12	0.193	1.04	11.5	5.3
	900	52.0	19.7	1.64	0.265	1.06	5.27	0.2
	1 800	51.1	19.9	2.21	0.267	0.96	7.00	0.6
573 <sup>d</sup>	1 800	101.1	19.1	4.83	2.82	0.93	5.42	1.6
	3 600	101.8	19.2	5.39	1.97	0.91	7.27	3.6
613	3 600	31.3	9.9	1.23	1.59	0.67	3.79	1.7
	7 200	30.9	10.7	1.73	1.10	0.80	6.01	4.4
653	900	50.0	20.4	9.79	15.5	0.65	5.03	1.8
	1 800	50.3	20.0	12.0	10.2	0.71	7.83	4.4
	3 600	51.4	19.9	13.1	7.06	0.76	10.6	9.6

Table 1. Reaction of CF<sub>3</sub> radicals with HCN<sup>a</sup>

<sup>*a*</sup> Volume of the reaction vessel 109 cm<sup>3</sup>; rate of formation of products, R, in units of  $10^{12}$  mol cm<sup>-3</sup> s<sup>-1</sup>. <sup>*b*</sup> Units of cm<sup>3/2</sup> mol<sup>-1/2</sup> s<sup>-1/2</sup>. <sup>*c*</sup> Conversion calculated from the yield of CF<sub>3</sub>CN. <sup>*d*</sup> From ref. (2).

is produced with some excess energy above threshold. In this respect, considering the thermochemistry of the CF<sub>3</sub>HCN radical formation and decomposition reactions this excess energy would, at most, be *ca.* 16 kJ mol<sup>-1</sup>. We estimated the relative importance of the decomposition process with respect to collisional stabilization (D/S) using RRKM theory and a stepladder model for deactivation, with 8 kJ mol<sup>-1</sup> of energy transferred in each collision. The results obtained indicate that D/S is always  $<1 \times 10^{-3}$ , whereas for CF<sub>3</sub>ClCN it is always larger than this value, even when the critical and excitation energies are varied within reasonable limits. Thus the decomposition of the adduct radical to CF<sub>3</sub>H+CN can be safely ignored under our experimental conditions.

Mass spectral analysis of the reaction products confirmed CF<sub>3</sub>CN and CF<sub>3</sub>H as the main products, while the relative intensities of peaks at m/e = 146 and 96 assigned to

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 $HCF_3C=NCF_3$  and m/e = 128 to HI at 333 K were higher than at 573 K.<sup>2</sup> This accounts for the importance of the addition step at low temperatures.

According to the above reaction scheme

$$[CF_{3}HCN] = \frac{k_{1}[CF_{3}][HCN]}{k_{-1} + k_{2}[CF_{3}] + k_{3}[CF_{3}] + k_{4}[I] + k_{6}[CF_{3}HCN]}.$$
 (7)

In an attempt to find an equation for the rate of formation of  $CF_3CN$  compatible with the experimental results, a few approximations to eqn (7) can be made. Assuming the reversibility of reaction (1), at low temperatures, reaction (-1) would probably be negligible, becoming more important as the temperature increases. The reversibility of the addition step was also included for the reaction of  $CF_3$  with  $ClCN^{3,4}$  and with other perfluoroalkyl radicals,<sup>5-7</sup> as well as for the reactions of  $CF_3$  and  $C_2F_5$  with other non-saturated substrates such as benzene.<sup>8,9</sup>

The remaining terms of the denominator correspond to mutual terminations or cross-reactions between CF<sub>3</sub>HCN, I and CF<sub>3</sub>. An analysis of the data in table 1 for the rate of formation of CF<sub>3</sub>CN and C<sub>2</sub>F<sub>6</sub> in the temperature range of interest, 333-453 K, suggests that CF<sub>3</sub> and CF<sub>3</sub>HCN radical concentrations are comparable, and unless  $k_6$  is very low,  $k_6$  [CF<sub>6</sub>HCN] should be taken into account. Under our experimental conditions, however, no heavy products [such as a dimer of CF<sub>3</sub>HCN from reaction (6)] were found. Thus reaction (6) was included in our mechanism for completeness, but not considered for our kinetic analysis, so that eqn (7) becomes

$$[CF_{3}HCN] \approx \frac{k_{1}[CF_{3}][HCN]}{k_{2}[CF_{3}] + k_{3}[CF_{3}] + k_{4}[I]}$$
(8)

so that

$$\frac{R_{\rm CF_3CN}(1+\alpha+\beta)}{R_{\rm C,F_a}^{1/2}(1+\alpha)} = \frac{k_1[\rm HCN]}{k_{\rm c}^{1/2}}$$
(9)

with

$$\alpha = R_4 / R_3 = k_4 [I] / k_3 [CF_3]$$
$$\beta = k_2 / k_3$$

and R the rate of formation. If the mechanism is accepted and the formation of CF<sub>3</sub>H through reaction (5) is not important at low conversion,  $\alpha$  is related to the measured ratio [CF<sub>3</sub>CN]/[CF<sub>3</sub>H] and could be estimated as  $(R_{CF_3CN}/R_{CF_3H}) - 1$ .

Unfortunately, we could not determine the rate of formation of the imine from its measured concentration by gas chromatography, since a satisfactory separation from the unreacted CF<sub>3</sub>I could not be achieved, even upon trying several different columns. This means that  $\beta$  could not be evaluated from our experimental results; however, taking account of the nature of steps (2) and (3),  $k_2$  could easily differ from  $k_3$  by a factor of two or three.

We have plotted in Arrhenius form the left-hand side of eqn (9) assuming that  $\beta$  is independent of temperature and takes different values between 0.1 and 10 in the temperature range 333-453 K with experiments at conversions  $\Rightarrow 3\%$ . The best fit to our experimental data was obtained for  $\beta = 2$ , and the following activation parameters result: log  $(A_1/A_c^{1/2}) = 4.97$  and  $E_1 - \frac{1}{2}E_c = 30.9$  kJ mol<sup>-1</sup> (fig. 1).

The deviations in the assigned values of log  $(A_1/A_c^{1/2})$  and  $E_1 - \frac{1}{2}E_c$  are determined mainly by the approximation in the value of  $\beta$ . According to our estimation a systematic error of up to 0.3 in log  $(A_1/A_c^{1/2})$  and 2.4 kJ mol<sup>-1</sup> in  $E_1 - \frac{1}{2}E_c$  may be considered. At temperatures >453 K, log  $[R_{CF_3CN}(1 + \alpha + \beta)/R_{C_2F_0}^{1/2}[HCN](1 + \alpha)]$  goes through

At temperatures >453 K,  $\log [R_{CF_3CN}(1 + \alpha + \beta)/R_{2F_6}^{1/2}[HCN](1 + \alpha)]$  goes through a maximum and then decreases even when the conversion has increased. This could be interpreted in terms of reaction (-1) becoming more important as the temperature



Fig. 1. Arrhenius plot of  $\log X$ .  $X = R_{CF_3CN}(1 + \alpha + \beta)/R_{C_2F_6}^{1/2}[HCN]$   $(1 + \alpha)$ .  $\bullet$ , Runs with conversion  $\geq 3\%$ ;  $\bigcirc$ , conversion 3.4%;  $\bullet$ , conversion 4.2%;  $\bullet$ , conversion 4.9%.

	$E/kJ mol^{-1}$	$\log{(A/\mathrm{cm}^3\mathrm{mol}^{-1}\mathrm{s}^{-1})}$	ref.
HC≡CH	20.92	12.44	11
$HC \equiv CCH_3$	14.43	12.37	11
$HC \equiv CCF_3$	21.34	12.18	11
CH <sub>3</sub> C≡CCH <sub>3</sub>	18.24	12.42	11
CF <sub>3</sub> C≡CH	27.65	11.87	11
$CF_3C \equiv CCF_3$	24.52	11.69	11
CICN	26.55	10.43	4
HCN	30.9	11.65	ь

Table 2. Arrhenius parameters for the addition reactions of CF<sub>3</sub> radicals<sup>a</sup>

<sup>*a*</sup>  $A_c = 2.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $E_c = 0 \text{ kJ mol}^{-1}$  from ref. (12). <sup>*b*</sup> This work.

increases and a change in mechanism for the formation of  $CF_3CN$  and  $CF_3H$  at high temperatures. In the present reaction scheme we have not included the interaction of the iodine atom with HCN as in ref. (2) since no conversion effect was observed at low conversion between 333-453 K. At high temperatures the concentration of iodine atoms must be larger than at the temperatures used in these experiments, since the thermal decomposition of  $CF_3I$  and  $I_2$  adds to the photolytic decomposition of both.

Apart from work by Szwarc<sup>10</sup> and Walton and coworkers<sup>11</sup> there are, as far as we are aware, no Arrhenius parameters for the addition of trifluoromethyl radicals to a triple bond. With respect to addition reactions of these radicals to  $C \equiv N$ , in particular, the only data we know of are for  $CF_3 + ClCN$ .<sup>4</sup>

In table 2 we compare these results with ours for HCN. The absolute Arrhenius parameters for the reactions of CF<sub>3</sub> with ClCN and HCN were determined using Ayscough's value<sup>12</sup> for the self-combination of CF<sub>3</sub> radicals, although more recent values<sup>13-18</sup> have been obtained for  $E_c$  and  $A_c$ . The absolute values of CF<sub>3</sub> addition to acetylene and substituted acetylenes given by Walton<sup>11</sup> are based on a value of  $3 \times 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the combination rate constant.<sup>19</sup> In order to compare results we

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have converted these determinations taking Ayscough's rate constant for CF<sub>3</sub> combination and these are the values shown in table 2. The Arrhenius parameters for HCN are about the same as for the other addition reactions, but if these values are compared with those obtained for ClCN it is clear that a compensation effect exists whereby the activation energy as well as the pre-exponential factor for HCN are higher so that  $k_{\rm H}/k_{\rm Cl}$ , the ratio of the rate constants for CF<sub>3</sub> addition to HCN and ClCN, is *ca.* 2 at 353 K. In contrast, the reactivity of CF<sub>3</sub> towards HCN is smaller by at least a factor of 10, at the same temperature, compared with the other substrates with a C $\equiv$ C triple bond.

Since the data reported for the kinetic parameters of this type of reaction are scarce, we are unable, at present, to obtain some correlation in order to provide a satisfactory explanation of the Arrhenius parameters for the addition reactions of  $CF_3$  to  $C \equiv N$  and the discrepancies observed for the addition of these radicals to the  $C \equiv C$  bond.

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