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Kinetics of the Hydrogen Abstraction from Hydrogen Cyanide by Trifluoromethyl Radicals

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Freie Radikale / Gase / Reaktionskinetik

The reaction of CF_3 radicals with HCN in the gas phase has been studied in the temperature range 573 – 673 K using CF_3 radicals generated by thermal decomposition of CF_3I. Arrhenius parameters for the reaction:

$$CF_3 + HCN \longrightarrow CF_3H + CN \qquad (1)$$

relative to CF_3 recombination:

$$2\,CF_3 \xrightarrow{k_c} C_2F_6 \qquad (2)$$

are given by:

$$\log\,[(k_1/k_c^{1/2})/\mathrm{cm^{3/2}\,mol^{-1/2}\,s^{-1/2}}] = 5.50\,(\pm 0.26) - 57.65\,(\pm 3.14)\ \mathrm{kJ\,mol^{-1}}/4.576\,T\,.$$

Rate parameters are compared with those for other reactions of CF_3 with polar and non-polar substrates.

Introduction

A considerable amount of data has been accumulated over the years concerning reactions of CF_3 radicals. However, very few quantitative kinetic data are available on reactions of atoms or radicals with cyano-compounds [1 – 3]. The reactions of CF_3 [4] and C_2F_5 [5] with ClCN have been studied in this laboratory, with abstraction of chlorine atom taking place at the highest temperatures of the covered range. On account of this and our interest in expanding our knowledge on reactions of this type of substrates, we undertook the present work.

Experimental

Trifluoromethyl iodide from a cylinder (PCR Research Chemicals) was twice distilled at 143 K under vacuum and a middle cut retained. Hydrogen cyanide was prepared by dropwise addition of H_2SO_4 to KCN free from carbonate. The gas evolved was frozen in a liquid air trap and was purified by vacuum distillation at low temperature. In some cases, it was further purified by gas chromatography using a 3.0 m column of Triacetin at room temperature. Nitrogen (99.99%) was used without further purification. Perfluorocyclobutane (Pierce Chemical Company) was bulb to bulb distilled from 213 K to 77 K.

Reactants were stored and measured out in a mercury-free and grease-free static vacuum system. Mixtures of CF_3I and HCN were heated in a cylindrical quartz reaction vessel, volume 109 cm³, located in a horizontal electric metal block furnace. Temperature was controlled to ±0.3 °C by a Lauda Electronic regulator type PTR 50 and was uniform in both space and time to within ±1 °C. The temperature was measured with a chromel-alumel thermocouple.

At the end of each experiment, the total content of the cell was frozen out and analyzed by gas chromatography using a Varian 200 chromatograph equipped with a Gow Mac density balance detector. Products were separated on a 2.4 m column packed with silica gel. Retention times were compared with authentic samples run under identical conditions. Qualitative identification of the products was achieved by infrared and mass spectrometry.

Results

The thermal decomposition of trifluoromethyl iodide, CF_3I, seems to be a convenient way of generating CF_3 radicals [6], the relevant reactions being:

$$CF_3I + \emptyset \longrightarrow CF_3 + I$$

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

$$I + I + CF_3I \longrightarrow I_2 + CF_3I$$

$$I_2 + CF_3 \longrightarrow I + CF_3I\,.$$

When CF_3 radicals are caused to react with HCN, CF_3H, C_2F_6, CF_3CN and I_2 are obtained as products.

Runs were carried out over the temperature range 573 – 673 K. The rate of formation of CF_3H relative to C_2F_6 was measured for different pressures of HCN at any given temperature. In most of our experiments, not more than 2% of the HCN was consumed (calculated from the yield of CF_3H). Results for the complete temperature range are shown in Table 1.

Addition of inert gases such as N_2 and c – C_4F_8 did not substantially modify the ratio $R_{CF_3H}/R_{C_2F_6}^{1/2}$ [HCN].

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Table 1
Results for CF_3 radical-HCN reaction[a)]

		reactant pressure/Torr					
T/K	time/s	CF_3I	HCN	R_{CF_3H}	$R_{C_2F_6}$	R_{CF_3CN}	$R_{CF_3H}/R^{1/2}_{C_2F_6}$ [HCN][b)]
573	21600	104.0	15.6	0.308	0.116	0.213	2.08
573	21600	101.4	30.7	0.491	0.105	0.335	1.77
573	21600	102.6	25.4	0.463	0.113	0.312	1.96
573	19800	102.4	15.6	0.301	0.128	0.186	1.94
573	28800	100.8	20.7	0.356	0.0944	0.249	2.02
593	14460	49.1	20.0	0.620	0.165	0.308	2.85
593	14400	49.0	30.5	0.795	0.163	0.457	2.41
593	10800	101.7	33.5	1.46	0.414	0.932	2.54
593	14400	52.9	23.6	0.697	0.203	0.384	2.44
593	10800	101.7	14.9	0.743	0.511	0.503	2.61
613	7200	30.0	10.5	0.875	0.423	0.405	4.95
613	7200	33.0	20.6	1.42	0.465	0.630	3.89
613	7200	50.2	40.8	2.79	0.622	1.58	3.34
613	7200	30.0	30.0	1.75	0.366	0.746	3.70
613	7200	25.6	40.0	2.04	0.317	0.866	3.48
633	3600	29.4	30.0	4.53	1.26	2.42	5.37
633	3600	52.1	40.6	7.61	2.02	4.78	5.28
633	3600	30.1	11.3	2.21	1.71	1.33	5.98
633	3000	25.5	35.0	5.04	1.12	2.65	5.42
633	1800	32.0	17.3	4.02	2.31		6.08
633	2400	30.2	23.3	4.63	1.76		5.96
653	1200	27.8	29.0	11.5	5.15	5.64	7.20
653	1200	26.8	24.1	9.07	5.47	4.97	6.60
653	600	30.3	15.2	9.53	9.49	4.15	8.36
653	600	28.5	14.6	6.62	8.33	3.37	6.43
653	600	29.8	20.0	11.4	9.21		7.68
653	1200	26.6	39.5	15.5	5.20	8.20	7.09
653	720	30.6	10.0	6.18	8.72	3.35	8.59
653	1200	28.8	38.1	10.0	2.59	3.89	6.68[c)]
653	1200	26.9	40.3	10.8	2.09		7.62[d)]
653	1200	25.7	40.5	8.56	1.48		7.11[e)]
673	300	31.3	15.8	19.4	24.8	8.37	10.4
673	300	29.2	15.4	21.7	27.2	8.43	11.5
673	300	30.6	19.5	25.4	29.2	10.4	10.2
673	300	31.3	33.5	45.0	25.5	21.3	11.3
673	300	31.7	24.4	35.7	27.1	16.4	11.9
673	300	29.1	33.5	42.1	24.1	16.6	10.8

[a)] The volume of reaction vessel was 109 cm^3. Rates of formation of products, R, in units of 10^{-12} mol cm^{-3} s^{-1}; – [b)] Units of $cm^{3/2}$ $mol^{-1/2}$ $s^{-1/2}$; – [c)] With the addition of 256 Torr of N_2; – [d)] 260 Torr of c-C_4F_8; – [e)] 260 Torr of c-C_4F_8.

At selected temperatures, several runs were done using, at each temperature, approximately constant pressures of CF_3I and HCN but with various reaction times. In these experiments the ratio $R_{CF_3H}/R^{1/2}_{C_2F_6}$ [HCN] was not constant. The results of these studies of time dependence, given in Fig. 1 show that as the temperature increases the slope of

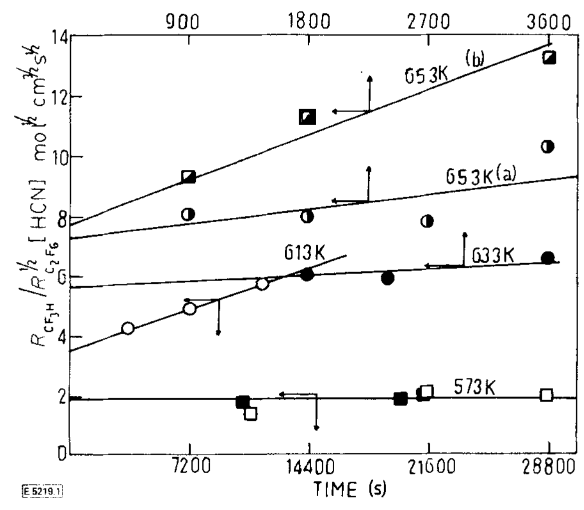

Fig. 1

Plot of $R_{CF_3H}/R^{1/2}_{C_2F_6}$ (HCN) versus time at different temperatures.
(◑): With 32 Torr of CF_3I – (a); (◪): With 50 Torr of CF_3I – (b);
(□): With 20 Torr of HCN; (■): With 15 Torr of HCN

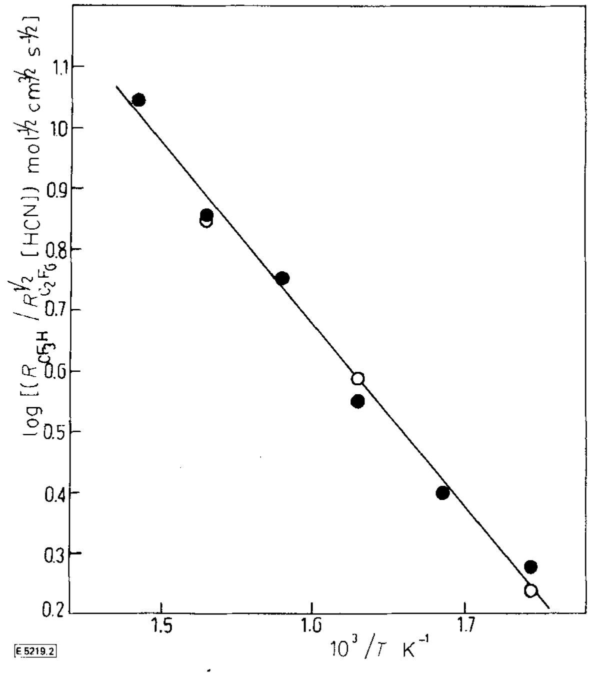

Fig. 2

Arrhenius plot for reaction of CF_3 radicals with HCN.
(○): Results obtained from rates of formation of products at zero time

the ratio $R_{CF_3H}/R^{1/2}_{C_2F_6}$ [HCN] versus time increases. Moreover at 653 K for different pressures of CF_3I, the slope is greater for a larger concentration of CF_3I; the intercepts being approximately the same within experimental error.

The temperature dependence of the ratio $R_{CF_3H}/R^{1/2}_{C_2F_6}$ [HCN] taking the results of Table 1 is a good straight line (Fig. 2) which corresponds to the following expression calculated by the least squares method:

$$\log [(R_{CF_3H}/R^{1/2}_{C_2F_6}[\mathrm{HCN}])/\mathrm{cm}^{3/2}\,\mathrm{mol}^{-1/2}\,\mathrm{s}^{-1/2}] = 5.50\,(\pm 0.26) - 57.65\,(\pm 3.14)\,\mathrm{kJ\,mol}^{-1}/4.576\,T\,. \tag{I}$$

Error limits are standard deviations. In this figure we have included results obtained from rates of formation of products at zero time calculated from the slopes of the plots of concentration of products versus time. These data, however, were not used in deriving the result in Eq. (I); they were only meant as evidence that the above Arrhenius parameters are reliable up to 2% conversion.

Discussion

Possible reactions of the CF_3 radicals generated by thermal decomposition of CF_3I are:

$$CF_3 + HCN \longrightarrow CF_3H + CN \tag{1}$$

$$2\,CF_3 \longrightarrow C_2F_6\,. \tag{2}$$

If these reactions are the sole sources of CF_3H and C_2F_6, respectively, then the following rate relation is obtained:

$$R_{CF_3H}/R^{1/2}_{C_2F_6}[\mathrm{HCN}] = k_1/k_c^{1/2}$$

where R denotes rate of formation, [HCN] is the mean substrate concentration and k_1 and k_c are the rate constants for reactions (1) and (2) respectively.

Results given in Table 1 can be interpreted in terms of these reactions, thus a plot of $R_{CF_3H}/R^{1/2}_{C_2F_6}$ versus [HCN] at each temperature is a straight line of zero intercept and slope $k_1/k_c^{1/2}$. At higher conversions, however, there is an additional source of CF_3H other than the abstraction reaction itself. The fact that the slopes of the time-dependence plot increase with temperature and that for a given temperature and two different concentrations of CF_3I the slope of $k_1/k_c^{1/2}$ versus time is larger for the larger concentration suggests that the "extra" CF_3H may arise from a reaction in which iodine and/or the iodine atom are involved. Despite the fact that we were unable to find any iodine containing products under our present analysis conditions, we think that feasible reactions leading to CF_3H formation could be:

$$I + HCN \rightleftharpoons IHCN \tag{3),(-3}$$

$$CF_3 + IHCN \longrightarrow CF_3H + ICN \tag{4}$$

and/or:

$$I + IHCN \longrightarrow IH + ICN \tag{5}$$

$$CF_3 + IH \longrightarrow CF_3H + I\,. \tag{6}$$

The occurrence of reactions (3) and (5) would be supported by the dependence of $k_1/k_c^{1/2}$ with time since IH would accumulate as reaction proceeds. Amphlett and Whittle [7] have found that reaction (6) is very fast and have assigned 2.1 kJ mol^{-1} to its activation energy.

In an attempt to provide evidence regarding the reaction between iodine and HCN, approximately 35 Torr of HCN and bisublimated iodine were heated at 673 K for about 1 hour. C_2N_2 was identified by gas chromatography.

The occurrence of the above processes does not seem improbable in view of previous work on the addition of iodine to unsaturated compounds such as acetylene [8]. Walton and coworkers [9] have studied the addition of CF_3 radicals to fluorosubstituted olefins and have included in their mechanism a reversible addition of iodine to the olefin.

When the reaction was carried out under ultra-violet irradiation at 573 K, the conversion effect was remarkably enhanced. The presence of a silver vane which produces fixation of iodine as silver iodide or a filter to prevent light absorption by I_2 minimizes this conversion effect. Although these facts are not as yet fully understood, further experiments are being performed and results will be reported. Notwithstanding, we conclude that iodine plays an important part in this system and we stress that at his stage no further attemps were made to clarify the mechanism through which the formation of additional CF_3H may be explained. Use of an alternative source of radicals lacking iodine will probably provide definite evidence.

CF_3CN formation can be explained by the following reaction:

$$CF_3 + CN \longrightarrow CF_3CN\,. \tag{7}$$

If all the CN radicals formed in reaction (1) are trapped by CF_3, then the ratio R_{CF_3CN}/R_{CF_3H} should be equal to one. Our data show, however, that the ratio is always less than unity and approximately constant in this temperature range. We interpret this by assuming that CN radicals are being removed by self-combination or by reaction with HCN [10] as follows:

$$CN + HCN \longrightarrow H + C_2N_2 \tag{8}$$

$$H + I_2 \longrightarrow HI + I\,. \tag{9}$$

These reactions could also account for the observed conversion effect on $k_1/k_c^{1/2}$. We were unable to detect C_2N_2 in this case due to interference from a large excess of unreacted CF_3I when products were analyzed on a chromatographic column.

Table 2
Arrhenius parameters for some reactions of CF_3 radicals
$CF_3 + RH \rightarrow CF_3H + R$

Substrate	log (A_1/cm^3 mol^{-1} s^{-1})	E_1/kJ mol^{-1}	Ref.
HCl	11.23	21.3	[12]
	11.38	22.5	[13]
	11.44	23.0	[14]
H_2S	11.65	16.2	[15]
	11.81	17.5	[13]
	11.20	5.0	[16]
H_2	12.45	44.6	[17]
	13.40	51.5	[14]
CH_4	12.61	52.3	[18]
	12.08	46.8	[19]
HCN	12.19	57.7	this work

In Table 2, we compare our Arrhenius parameters A_1 and E_1 for attack of CF_3 on HCN with published data of other reactions of CF_3 with polar and non-polar substrates. The absolute A_1, and E_1 were all obtained assuming that, for CF_3 combination, $E_c = 0$ and $\log A_c = 13.36$ (Ref. [11]).

Table 2 shows that our values of A_1 and E_1 are closer to those for a non-polar molecule which would probably seem unexpected if we think of CN as having a behaviour similar to that of a halogen atom. The polar effect is therefore off-set by the energetics factor which appears to be the driving force in this case. The H – C bond in HCN is anomalously high compared to the same bond in CF_3H and this would account for the low reactivity of HCN towards CF_3 attack.

The heat of formation of CN has been the subject of a great deal of research effort and a considerable amount of data has been accumulated over the years ranging from 372 to 456 kJ mol^{-1} [20]. These values lead to $D(H-CN)$ between 455 and 539 kJ mol^{-1}. Taking 502 kJ mol^{-1}, in accordance with the latest determinations, reaction (1) would be endothermic in 58 kJ mol^{-1}, which allows us to set a lower limit for the activation energy of the abstraction reaction. Our value of E_1 = 57.7 kJ mol^{-1} corresponds to this limit within experimental error.

Unfortunately, we are not aware of the existence of any quantitative studies of endothermic hydrogen abstraction reactions by CF_3 radicals except for the work of Whittle and coworkers [21] on the hydrogen transfer from benzene. This prevents us from drawing any conclusion as to the relationship between endothermicity and activation energy any further than we have stated above. A determination of kinetic parameters of the reaction of CN radicals with CF_3H would be helpful to settle the question.

A_1 was also calculated from the evaluation of $\Delta S_1^{\ddagger}$ by the method of Benson [22]. A linear configuration, $CF_3 \ldots H \ldots C \overset{\cdots}{=} N$, was assumed for the activated complex. A value of $A_1 = 1.21 \cdot 10^{11}$ $cm^3\,mol^{-1}\,s^{-1}$ was obtained; which agrees with the experimental value within the error limits of this method and bearing in mind that the method provides a lower limit for the pre-exponential factor.

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Theory of Thermal Unimolecular Reactions in the Fall-off Range. I. Strong Collision Rate Constants

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Reaktionskinetik

(k_0/k_∞)-reduced strong collision fall-off curves of thermal unimolecular reactions are analyzed. They are represented by the Lindemann-Hinshelwood expression multiplied by strong collision broadening factors F^{SC}. The factors F^{SC} are approximated by fully empirical representations of RRKM theory. Compact expressions suitable for modeling are proposed. Their quality is demonstrated by comparison with exact RRKM calculations for 20 molecular systems.

1. Introduction

Thermal unimolecular reactions, as well as the related radical recombination reactions, play an important role in many complex reaction systems such as atmospheric chemical kinetics or combustion. A major practical problem of these reactions is their complicated pressure and temperature dependence which makes modeling a difficult task. Often these reactions are treated as simple first or second order processes. Sometimes,

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