Attack of Trifluoromethyl Radicals on Ammonia and Ammonia-d3

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Hydrogen abstraction by trifluoromethyl radicals from ammonia and ammonia-d_3 has been studied in the temperature range 113-240°C. The Arrhenius parameters, based on Ayscough's value of $10^{13\cdot36}$ cm^3 $mole^{-1}$ sec^{-1} for the combination of trifluoromethyl radicals, are:

	log (A/cm^3 $mole^{-1}$ sec^{-1})	(E/kcal $mole^{-1}$)
$CF_3+NH_3 \rightarrow CF_3H+NH_2$	$10\cdot55\pm0\cdot07$	$8\cdot29\pm0\cdot14$
$CF_3+ND_3 \rightarrow CF_3D+ND_2$	$10\cdot47\pm0\cdot20$	$9\cdot35\pm0\cdot40$

Comparison of the relative reactivities of methyl and trifluoromethyl radicals in their attack on ammonia and ammonia-d_3 has been made; apparently both polar character and bond energy considerations have to be invoked to account for the observed enhanced reactivity of CF_3 over CH_3 radical attack. The isotope effect for the N—H bond has been measured and is in agreement with zero-point energy differences for the stretching of one N—H bond.

Hydrogen abstraction by methyl radicals from ammonia and ammonia-d_3 has been previously studied,[1-3] but no results have been reported for abstraction by trifluoromethyl radicals; in fact no kinetic studies of reactions of trifluoromethyl radicals with nitrogen-containing compounds* have been reported.[4] It is particularly desirable to determine whether ammonia is more readily attacked by trifluoromethyl than by methyl radicals, or whether inter-molecular polar repulsion between CF_3 and NH_3 decreases reactivity. Isotope effects in hydrogen abstraction are known for the methyl radical+ammonia system; the corresponding study of trifluoromethyl with ammonia-d_3 will increase the knowledge of the abstraction mechanism. Consequently, the rates of attack of trifluoromethyl radicals on ammonia and ammonia-d_3 and the isotope effect for the N—H bond were measured.

This paper also describes experiments on the hydrogen abstraction from hydrazine and hydrazine-d_4 which were attempted to extend the comparison between CH_3 and CF_3 radical attack on ammonia, to hydrazine.

EXPERIMENTAL

MATERIALS

TRIFLUOROMETHYL IODIDE (K & K Laboratories, Inc.) was passed successively through traps at −96, −150 and −196°C. The fraction condensing at −150°C was collected, thoroughly degassed, and stored in a blackened bulb. AMMONIA (Matheson Co. Inc.) was passed through traps at −96, −150 and −196°C, and the contents of the last trap were degassed and stored. AMMONIA-d_3 (Merck, Sharp & Dohme of Canada Ltd.) was treated as for ammonia; it had an isotopic purity greater than 98 %. HYDRAZINE (Eastman Organic Chemicals) was dried and distilled from barium oxide. The fraction boiling between 110 and 112°C was collected, thoroughly degassed and stored on the vacuum line.

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* Since the present work was completed, the reaction of CF_3 radicals with methylamine has been reported.[26]

APPARATUS AND PROCEDURE

Reactions were carried out in a 123 ml quartz reaction vessel, contained in an electrically heated aluminium block furnace controlled to better than $\pm 1\,^\circ C$. Reactant pressures were measured by means of a spiral gauge in conjunction with a mercury manometer. Radiation from a 250 W Mazda lamp was limited to wavelengths > 3000 Å by means of a Pyrex plate and a Chance-Pilkington OX9A filter.

Trifluoromethyl iodide was used as the source of CF_3 radicals for the ammonia system, because ammonia reacts with hexafluoroacetone. The relevant products—fluoroform and hexafluoroethane—were separated by a method similar to that [5] described previously, except that in the separation from the unreacted starting materials, the products were passed through an alumina column only. The CF_3H and C_2F_6 were then separated on a 4ft alumina column at room temperature. Authentic pure samples were used to identify products and to calibrate the thermal conductivity detector.

Attempts to find a suitable source of trifluoromethyl radicals for reaction with hydrazine were unsuccessful. Both hexafluoroacetone and perfluoroazomethane condensed with hydrazine, while mixing of hydrazine and trifluoromethyl iodide reduced the iodide and produced large amounts of fluoroform.

TABLE 1.—HYDROGEN AND DEUTERIUM ABSTRACTION BY TRIFLUOROMETHYL RADICALS FROM AMMONIA AND AMMONIA-d_3.

AMMONIA

$T\,^\circ C$	$[NH_3]$ (mm)	$[CF_3I]$ (mm)	$[NH_3]$ (10^{-6} mole cm^{-3})	R_{CF_3H}*	$R_{C_2F_6}$*	$k_2/k_1^{\frac{1}{2}}$
112·8	72·2	46·8	3·00	0·248	0·272	0·158
112·8	74·9	42·9	3·11	0·267	0·327	0·150
133·4	76·7	44·9	3·03	0·555	0·453	0·273
143·2	64·7	43·2	2·49	0·446	0·278	0·340
143·2	65·5	40·7	2·52	0·450	0·283	0·335
164·0	80·6	45·0	2·96	0·845	0·283	0·537
167·6	78·1	41·0	2·84	1·80	1·02	0·626
185·2	76·5	38·3	2·67	2·84	1·73	0·807
188·8	78·5	40·6	2·72	1·51	0·620	0·706
202·8	71·0	42·0	2·39	2·78	0·990	1·17
208·2	82·3	37·6	2·74	2·47	0·490	1·28
233·8	77·3	49·4	2·45	1·70	0·118	2·02
235·4	78·6	41·1	2·48	2·55	0·248	2·06
239·6	71·9	37·4	2·25	2·07	0·148	2·39

AMMONIA-d_3

$T\,^\circ C$	$[ND_3]$ (mm)	$[CF_3I]$ (mm)	$[ND_3]$ (10^{-6} mole cm^{-3})	R_{CF_3D}*	$R_{C_2F_6}$*	$k_3/k_1^{\frac{1}{2}}$
123·2	92·7	55·0	3·75	0·132	0·439	0·0532
126·7	90·5	53·2	3·63	0·0958	0·411	0·0412
145·2	78·9	47·2	3·02	0·138	0·333	0·0791
147·0	74·2	78·1	2·83	0·177	0·649	0·0777
165·2	80·8	45·6	2·95	0·286	0·494	0·137
168·4	77·5	67·4	2·81	0·376	0·756	0·154
186·4	76·8	46·1	2·68	0·346	0·359	0·216
206·1	79·3	46·7	2·66	0·565	0·296	0·390
213·2	79·3	47·3	2·61	0·487	0·262	0·364
235·8	76·9	48·2	2·42	0·703	0·304	0·526
237·8	76·0	50·9	2·39	0·846	0·432	0·540
240·4	79·9	59·0	2·49	1·50	0·524	0·833

* rates of formation of products: 10^{-12} mole cm^{-3} sec^{-1}.

RESULTS

Previous studies [6, 7] of the photolysis of trifluoromethyl iodide showed that CF_3 radicals and hexafluoroethane were produced by the reaction

$$\begin{gathered} CF_3I + h\nu \rightarrow CF_3 + I \\ 2CF_3 \rightarrow C_2F_6 \end{gathered} \tag{1}$$

In the presence of ammonia, fluoroform is produced,

$$CF_3 + NH_3 \rightarrow CF_3H + NH_2 \tag{2}$$

Blank runs showed that the contribution of products resulting from the thermal decomposition of the iodide were negligible under the experimental conditions employed.

The following expression may be derived:

$$(k_2/k_1^{\frac{1}{2}}) = R_{CF_3H}/R^{\frac{1}{2}}_{C_2F_6}[NH_3].$$

The reaction was studied over the temperature range 113-240°C, and the following rate expression was obtained (taking $k_1 = 10^{13\cdot 36}$ cm^3 mole^{-1} sec^{-1}):[8]

$$\log (k_2/\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (10{\cdot}55 \pm 0{\cdot}07) - (8290 \pm 140)/2{\cdot}303\ RT. \tag{2A}$$

Likewise, for ammonia-d_3,

$$CF_3 + ND_3 \rightarrow CF_3D + ND_2, \tag{3}$$

the rate constant k_3 derived from a study over the temperature range 123-240°C was

$$\log (k_3/\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (10{\cdot}47 \pm 0{\cdot}20) - (9350 \pm 400)/2{\cdot}303\ RT. \tag{3A}$$

These values were obtained by the method of least squares and the errors quoted are standard deviations. The results are given in Table 1.

DISCUSSION

Hexafluoroacetone condensed with ammonia and was also unsuitable as a radical source for reaction with hydrazine. The difficulty with the CF_3I + hydrazine system has a parallel in the reaction between methyl iodide and hydrazine.[9] The formation of large amounts of fluoroform in the system was caused by the characteristic replacement of the halide in CF_3I by a hydrogen atom from hydrazine.[10]

RELATIVE REACTIVITY OF CF_3 AND CH_3 RADICALS

The rates of hydrogen abstraction by trifluoromethyl radicals are usually greater than the rates of abstraction by methyl radicals for most organic compounds; however, for polar molecules such as hydrogen halides,[13, 14] hydrogen sulphide [15] and trifluoroacetaldehyde,[16] this trend is reversed. This change is usually attributed to activation energy differences (E_{CH_3}—E_{CF_3}), since the ratios of A factors (A_{CF_3}/A_{CH_3}) are generally close to unity.

The present work shows that (k_{CF_3}/k_{CH_3}) = 3·3 at 164°C and the superiority in abstraction by CF_3 radicals is due wholly to an activation energy difference (E_{CH_3}—E_{CF_3}) of 1·7 kcal mole^{-1}, because the ratio of A factors does not differ significantly from unity. This is substantiated by the data for attack on ND_3 where (k_{CF_3}/k_{CH_3}) = 1·7 is also caused by an activation energy difference. Thus, ammonia and ammonia-d_3, although classed as polar molecules, do not behave in the same way as the examples given above, and their reactivities are intermediate between polar and non-polar substrates.

Trotman-Dickenson [19] suggests that the difference in reactivity between CF_3 and CH_3 radicals will be most significant for compounds with strong X—H bonds (e.g., paraffins) while Thynne [16] has correlated reactivity differences with the strengths of the bonds being broken and formed. The present results do not exhibit a marked enhanced reactivity of CF_3 over CH_3 radicals and they may suggest that reactivity differences expected to be large on bond energy considerations are largely compensated by intermolecular polar repulsion between the CF_3 radical and the ammonia molecule. Work by Thynne [26] indicates that methylamine and dimethylamine show the same type of reactivity towards CF_3 radical attack as do the ammonias.

It can be concluded that both bond energy and polar character of the substrate participate in determining the relative rates of methyl and trifluoromethyl hydrogen abstraction reactions.

TABLE 2.—RELATIVE REACTIVITIES OF CH_3 AND CF_3 RADICALS

	CH_4	NH_3	ND_3	$CD_3N\underline{H_2}$	$(CH_3)_2N\underline{H}$
E_{CH_3}	14·7	10·0	10·9	6·0	6·4
E_{CF_3}	10·3	8·3	9·35	4·4	3·3
ΔE	4·4	1·7	1·55	1·6	3·1
A_{CF_3}/A_{CH_3}	0·77	0·45	0·30	1·5	0·5
k_{CF_3}/k_{CH_3} (164°C)	118	3·3	1·7	9·3	18
D(X—H)[a]	104	103	103	92	86
dipole moment ($\times 10^{18}$ e.s.u.)	0	1·47	1·51	1·25	1·03
ref.	23, 24	1, this work	3, this work	25, 26	26, 27

[a] taken from ref. (20)

TABLE 3.—COMPARISON OF OBSERVED AND PREDICTED ISOTOPE EFFECTS

attacking radical	substrate	predicted $(k_H/k_D)_{150}$	predicted ΔE_0	predicted A_H/A_D	observed $(k_H/k_D)_{150}$	observed $E_D—E_H$	observed A_H/A_D	ref.
CF_3	H_2/D_2	9·3	1·9	1	4·4	1·0	1·35	11
CF_3	HCl/DCl	3·8	1·1	1	2·2	0·7	0·9	5
CF_3	H_2S/D_2S	3·8	1·1	1	1·9	0·7	0·8	5
CF_3	CH_4/CD_4	4·2	1·2	1	6·7	1·6	1·0	18
CF_3	NH_3/ND_3	4·7	1·3	1	4·3	1·1	1·2	this work
CF_3	$(CH_3)_2N\underline{H}/(CH_3)_2N\underline{D}$	4·7	1·3	1	2·2	1·4	0·42	26
CH_3	NH_3/ND_3	4·7	1·3	1	2·6	1·1	0·7	3
CH_3	$(CH_3)_2N\underline{H}/(CH_3)_2N\underline{D}$	4·7	1·3	1	7·9	1·4	0·69	27
CH_3	N_2H_4/N_2D_4	5·3	1·4	1	7·0	1·4	1·4	12

ISOTOPE EFFECTS

The studies [1, 2, 3] of hydrogen abstraction by methyl radicals from ammonia show general agreement, while there has been only one determination [3] for ammonia-d_3. The present results permit comparison of the isotope effect for the N—H bond, obtained from CF_3 and CH_3 hydrogen abstractions.

The simplest theory [28] of kinetic isotope effects assumes that only the zero-point energy associated with the stretching of the bond being attacked, is lost. Since the zero-point energy difference for the N—H and N—D bond is close to 1·3 kcal $mole^{-1}$, the theory predicts that $(A_H/A_D) = 1$, $(E_D—E_H) = 1·3$ kcal $mole^{-1}$ and at 150°C,

$(k_H/k_D) = 4{\cdot}7$. The results for CF_3 radical attack are $(A_H/A_D) = 1{\cdot}2$, $(E_D - E_H) = 1{\cdot}06$ kcal mole^{-1} and $(k_H/k_D) = 4{\cdot}3$ at 150°C. Simple theory predicts similar values, within experimental error. Thus, the results show no evidence to support effects such as quantum tunnelling; Gray and Thynne [3] reached the same conclusion from their methyl radical work.

Table 3 shows a comparison between predicted and observed isotope effects for a number of substrates. There is general agreement between the two sets of values in most cases, the variations being a reflection of the experimental errors involved. This agreement tends to support the general validity of the simple theory of kinetic isotope effects.

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[1] D. A. Edwards, J. A. Kerr, A. C. Lloyd and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 1966, 621.
[2] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Physics*, 1951, **19**, 329.
[3] P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 1964, **60**, 1047.
[4] A. F. Trotman-Dickenson and G. S. Milne, *Tables of Bimolecular Gas Reactions* NSRDS-NBS 9, 1967.
[5] N. L. Arthur and P. Gray, *Trans. Faraday Soc.*, in press.
[6] J. R. Dacey, *Disc. Faraday Soc.*, 1953, **14**, 84.
[7] J. Banus, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1950, 3041.
[8] P. B. Ayscough, *J. Chem. Physics*, 1956, **24**, 944.
[9] R. A. Hasty, *J. Chem. Eng. Data*, 1968, **13**, 134.
[10] C. C. Clark, *Hydrazine*, (Mathieson Chem. Co., 1953), p. 30.
[11] C. L. Kibby and R. E. Weston Jr., personal communication.
[12] P. Gray, A. A. Herod, A. Jones and J. C. J. Thynne, *Trans. Faraday Soc.*, 1966, **62**, 2774.
[13] J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1966, **62**, 1662.
[14] J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1967, **63**, 2695.
[15] N. L. Arthur and T. N. Bell, *Can. J. Chem.*, 1966, **44**, 1445.
[16] E. R. Morris and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2470.
[17] G. O. Pritchard and G. H. Miller, *J. Chem. Physics*, 1961, **35**, 1135.
[18] A. A. Herod, *Thesis*, (University of Leeds, 1967).
[19] A. F. Trotman-Dickenson, *Chem. and Ind.*, 1957, 1243.
[20] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.
[21] E. R. Morris and J. C. J. Thynne, *Trans. Faraday Soc.*, 1968, **64**, 414.
[22] P. Gray and A. A. Herod, *Trans. Faraday Soc.*, in press.
[23] F. S. Dainton, K. J. Ivin and F. Wilkinson, *Trans. Faraday Soc.*, 1959, **55**, 929.
[24] P. B. Ayscough, J. C. Polanyi and E. W. R. Steacie, *Can. J. Chem.*, 1955, **33**, 743.
[25] P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 1963, **59**, 2275.
[26] E. R. Morris and J. C. J. Thynne, *Trans. Faraday Soc.*, 1968, **64**, 2124.
[27] P. Gray, A. Jones and J. C. J. Thynne, *Trans. Faraday Soc.*, 1965, **61**, 474.
[28] L. Melander, *Isotope Effects on Reaction Rates* (Ronald Press, New York, 1960).