

Reactions of Radicals containing Fluorine

Part 3.—Hydrogen and Deuterium Atom Abstraction from Dimethylamine, Dimethylamine-d, Trimethylamine and Ethyleneimine

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The reactions of trifluoromethyl radicals with dimethylamine, dimethylamine-d, trimethylamine and ethyleneimine have been studied in the temperature range 27–161°C. Arrhenius parameters (based upon a value of $10^{13.37}$ mole⁻¹ cm³ sec⁻¹ for the velocity constant for the combination of trifluoromethyl radicals) have been obtained for the reactions:

	$\log_{10} A(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1})$	$E(\text{kcal mole}^{-1})$
$\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + \text{C}_2\text{H}_6\text{N}$	11.45 ± 0.12	4.1 ± 0.2
$\text{CF}_3 + (\text{CH}_3)_2\text{ND} \rightarrow \text{CF}_3\text{D} + (\text{CH}_3)_2\text{N}$	10.88 ± 0.29	4.7 ± 0.5
$\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{N}$	10.5 ± 0.7	3.3 ± 1.0
$\text{CF}_3 + (\text{CH}_3)_2\text{ND} \rightarrow \text{CF}_3\text{H} + \text{CH}_3(\text{CH}_2)\text{ND}$	11.82 ± 0.51	5.1 ± 0.8
$\text{CF}_3 + (\text{CH}_3)_3\text{N} \rightarrow \text{CF}_3\text{H} + (\text{CH}_3)_2\text{NCH}_2$	11.82 ± 0.12	4.5 ± 0.2
$\text{CF}_3 + (\text{CH}_2)_2\text{NH} \rightarrow \text{CF}_3\text{H} + \text{C}_2\text{H}_4\text{N}$	11.00 ± 0.17	4.1 ± 0.3

With dimethylamine, radical attack is favoured, on a "per-atom basis," at the nitrogen atom but the difference in reactivities of the C—H and N—H bonds is much less marked than with methyl radicals. Assuming a zero secondary isotope effect, substitution of D for H in dimethylamine alters the reactivity of the amino group by an amount in accord with zero-point-energy difference.

The reactions of methyl radicals with a wide variety of nitrogen-containing compounds have been studied¹⁻⁵ and information obtained regarding the positions and rates of hydrogen atom abstraction from the substrates. Trifluoromethyl radicals also readily abstract hydrogen from such molecules and their reactions with trideuteromethylamine and methylamine have been examined.⁶ We have extended this investigation to dimethylamine, trimethylamine and ethyleneimine.

EXPERIMENTAL

The apparatus used and experimental technique employed have been described.⁷

MATERIALS. Dimethylamine, trimethylamine and ethyleneimine were commercial samples which were purified by low-temperature distillation on the vacuum line.

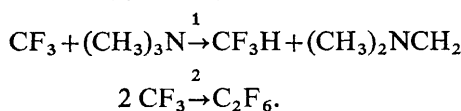
Dimethylamine-d was prepared by shaking dimethylamine with acidified D₂O at 25°C for 24 h followed by low-temperature distillation. This procedure was repeated and the extent of deuteration was followed by measuring the 730 cm⁻¹ band in the infra-red spectrum which shifts to 587 cm⁻¹ on deuteration. The sample was dried by low-temperature bulb-to-bulb distillation before being stored on the vacuum line. The sample used contained 63 % dimethylamine-d₁.

RESULTS

Hexafluoroacetone is frequently used as a photochemical source of trifluoromethyl radicals; however, it reacts to form a white involatile solid with amines. We have chosen the photolysis of trifluoromethyl iodide (TFMI) as the source of free radicals since no reaction (as evidenced by there being no pressure change) occurred when this was mixed with any of the compounds used in this investigation.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF TRIMETHYLAMINE

When TFMI is photolyzed in the presence of trimethylamine the reaction products observed and analyzed for were CF_3H and C_2F_6 . Their formation and distribution are accounted for by reactions (1) and (2):



The following relationship may be derived:

$$R_{\text{CF}_3\text{H}}/R_{\text{C}_2\text{F}_6}[(\text{CH}_3)_3\text{N}] = k_1/k_2^{\frac{1}{2}},$$

where R_X refers to the rate of formation of X and $[(\text{CH}_3)_3\text{N}]$ is the mean concentration of trimethylamine. Our experimental data are shown in table 1.

If a value of $10^{13.37}$ ($\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}$) is used for the rate constant for the combination of trifluoromethyl radicals,⁸ our results are expressed by the equation:

$$\log k_1(\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}) = 11.85 \pm 0.12 - (4460 \pm 190)/2.303 RT,$$

where the error limits represent the standard deviation of a least-mean-squares computer treatment. The uncertainty in k_2 ($\sim 10^{\pm 0.2}$) has not been included in the error limits quoted in this paper.

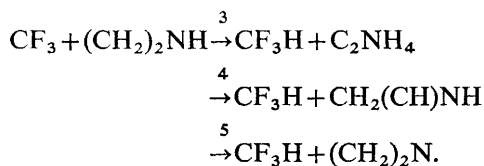
TABLE 1.—HYDROGEN ATOM ABSTRACTION FROM TRIMETHYLAMINE BY TRIFLUOROMETHYL RADICALS

$T(^{\circ}\text{K})$	$t(\text{sec})$	$[(\text{CH}_3)_3\text{N}]$	$[\text{CF}_3\text{I}]$	$[\text{CF}_3\text{H}]$	$[\text{C}_2\text{F}_6]$	$k_1/k_2^{\frac{1}{2}}$
303.0	100	0.175	1.761	67.1	18.8	88.6
303.3	45	1.008	1.003	390.2	21.6	83.3
322.5	100	0.164	1.651	93.9	14.6	150
344.8	100	0.174	1.759	150.4	14.0	230
370.3	45	1.117	1.110	1008	10.6	277
400.0	120	0.221	1.192	350.8	12.5	448
400.0	45	0.305	1.248	720.5	17.3	568
434.8	30	0.387	1.586	1215	12.7	879
434.8	60	0.266	1.091	683.5	9.95	813

$(\text{CH}_3)_3\text{N}$ and CF_3I in $10^6 \text{ mole cm}^{-3}$; CF_3H and C_2F_6 in $10^{12} \text{ mole cm}^{-3} \text{sec}^{-1}$; $k_1/k_2^{\frac{1}{2}}$ in $\text{mole}^{-\frac{1}{2}} \text{cm}^{\frac{3}{2}} \text{sec}^{-\frac{1}{2}}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF ETHYLENEIMINE

Since in ethyleneimine hydrogen atoms are attached to the carbon and also to the nitrogen atoms, it is probable that CF_3H formation can occur by trifluoromethyl radical attack at both sites, i.e., reaction (3) represents the sum of the contributions from reactions (4) and (5).



Gray and Jones have⁴ studied the reaction of methyl radicals with ethyleneimine and, using a deuterium-labelling technique, have concluded that at 150°C the hydrogen

atom attached to the nitrogen atom is about 160 times more reactive than the corresponding hydrogen atom linked to the carbon atom. We have assumed that a similar situation exists for trifluoromethyl radicals and that data obtained for the overall-reaction represents closely the abstraction from the N—H bond, i.e., that $k_3 = k_5$.

Our experimental data are recorded in table 2 and are represented by the expression:

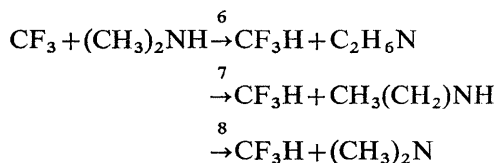
$$\log k_3(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.03 \pm 0.17 - (4140 \pm 270)/2.303 RT.$$

TABLE 2.—HYDROGEN ATOM ABSTRACTION FROM ETHYLENEIMINE BY TRIFLUOROMETHYL RADICALS

$T(^{\circ}\text{K})$	$t(\text{sec})$	$[(\text{CH}_2)_2\text{NH}]$	$[\text{CF}_3\text{I}]$	$[\text{CF}_3\text{H}]$	$[\text{C}_2\text{F}_6]$	$k_3/k_2^{\frac{1}{2}}$
303.1	45	0.429	1.758	57.3	40.6	20.9
322.5	45	1.951	0.771	110.2	3.94	28.5
344.8	45	0.252	1.003	59.7	21.1	51.4
370.3	45	0.384	1.575	135.7	26.9	68.0
400.0	90	1.536	0.607	206.1	2.42	86.3
434.8	45	0.387	1.588	470.0	55.2	163
434.8	90	0.540	1.032	296.5	9.19	180

$(\text{CH}_2)_2\text{NH}$ and CF_3I in $10^6 \text{ mole cm}^{-3}$; CF_3H and C_2F_6 in $10^{12} \text{ mole cm}^{-3} \text{ sec}^{-1}$; $k_3/k_2^{\frac{1}{2}}$ in $\text{mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}$.

PHOTOLYSIS OF TFMI IN THE PRESENCE OF DIMETHYLAMINE

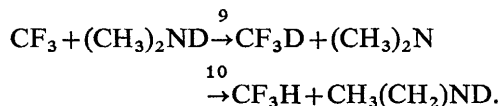


Hydrogen atom abstraction occur from both the C—H and N—H bonds, so that reaction (6) represents the overall sum of the contributions of reactions (7) and (8). Our results for the overall abstraction are given in table 3 and are expressed by

$$\log k_6(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.48 \pm 0.12 - (4140 \pm 180)/2.303 RT.$$

A study of the reaction of methyl radicals with dimethylamine³ has shown that, unlike for ethyleneimine, there is not such a large difference between the reactivity of the hydrogen atoms attached to the carbon and nitrogen atoms. Consequently, the individual contributions of reactions (7) and (8) may only be assessed by suitable labelling of dimethylamine.

We have investigated the reaction of CF_3 radicals with dimethylamine- d_1 containing 37 % $(\text{CH}_3)_2\text{NH}$, and measured the CF_3H and CF_3D produced by reactions (9) and (10):



A correction was made for the CF_3H formed by reaction with the unlabelled amine (reaction (6)) before a comparison may be made between reactions (9) and (10).

This correction, together with the facts that the yield of CF_3D is generally much less than that of CF_3H and that relatively small amounts of C_2F_6 are formed, results in our data being subject to a large experimental error. Our data are shown in table 4 and, after least-squares analysis, are expressed by the equations:

$$\log k_9(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 10.91 \pm 0.29 - (4710 \pm 460)/2.303 RT,$$

and

$$\log k_{10}(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 11.85 \pm 0.51 - (5060 \pm 820)/2.303 RT.$$

TABLE 3.—HYDROGEN ATOM ABSTRACTION FROM DIMETHYLAMINE BY TRIFLUOROMETHYL RADICALS

$T(^{\circ}\text{K})$	$t(\text{sec})$	$[(\text{CH}_3)_2\text{NH}]$	$[\text{CF}_3\text{I}]$	$[\text{CF}_3\text{H}]$	$[\text{C}_2\text{F}_6]$	$k_6/k_{\frac{1}{2}}$
370.3	90	0.295	0.767	228	14.5	211
370.3	45	0.554	0.794	357	8.53	224
357.1	90	0.694	0.690	44.1	0.14	170
344.8	300	0.183	1.83	25.8	0.84	156
344.8	900	0.187	1.87	28.6	1.28	145
333.3	150	1.25	1.26	193	2.12	107
333.3	45	0.481	1.25	328	40.6	108
333.3	45	0.902	1.29	490	27.1	106
322.6	1100	0.124	1.24	11.5	1.02	96.5
322.6	90	0.479	1.36	30.3	0.52	88.6
322.6	900	0.476	1.35	31.7	0.45	102
312.7	90	0.591	1.54	307	54.2	72.2
303.0	300	0.345	1.66	18.8	0.75	63.5
303.0	1500	0.359	1.73	13.8	0.39	63.5

$(\text{CH}_3)_2\text{NH}$ and CF_3I in $10^6 \text{ mole cm}^{-3}$; CF_3H and C_2F_6 in $10^{12} \text{ mole cm}^{-3} \text{ sec}^{-1}$; $k_6/k_{\frac{1}{2}}$ in $\text{mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}$.

TABLE 4.—HYDROGEN AND DEUTERIUM ATOM ABSTRACTION FROM DIMETHYLAMINE- d_1 BY TRIFLUOROMETHYL RADICALS

$T(^{\circ}\text{K})$	$t(\text{sec})$	$[(\text{CH}_3)_2\text{ND}]$	$[\text{CF}_3\text{I}]$	$[\text{CF}_3\text{H}]$	$[\text{CF}_3\text{D}]$	$[\text{C}_2\text{F}_6]$	$k_{10}/k_{\frac{1}{2}}$	$k_9/k_{\frac{1}{2}}$
370.3	90	0.496	1.003	226	40.8	8.64	155	28.0
370.3	300	0.330	1.009	613	11.2	2.08	129	23.6
370.3	300	0.234	0.817	57	9.1	1.96	174	27.7
370.3	45	0.463	1.115	197	37.5	7.54	155	29.5
357.1	90	0.511	0.765	95	20.7	5.21	81.1	17.8
344.8	90	0.908	0.641	94	18.0	1.59	82.0	15.7
333.3	90	0.338	0.814	75	13.2	7.01	83.1	14.7
333.3	90	0.791	1.181	85	18.4	3.66	56.2	12.2
322.6	90	1.438	1.013	125	23.3	2.54	54.8	10.2

$(\text{CH}_3)_2\text{ND}$ and TFMI in $10^6 \text{ mole cm}^{-3}$; CF_3H , CF_3D and C_2F_6 in $10^{12} \text{ mole cm}^{-3} \text{ sec}^{-1}$; $k_4/k_{\frac{1}{2}}$ and $k_{10}/k_{\frac{1}{2}}$ in $\text{mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}$.

We can derive Arrhenius parameters for reaction (8) using our results for reactions (6) and (10) if we assume that secondary isotope effects^{1,9} are insignificant, i.e., $k_7 = k_{10}$. Our data indicate that the velocity constant, k_8 , is expressed by

$$\log k_8(\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}) = 10.5 \pm 0.7 - (3300 \pm 1000)/2.303 RT.$$

DISCUSSION

PRIMARY ISOTOPE EFFECT

Our results enable a primary isotope effect to be deduced for trifluoromethyl radical attack on the N—H and N—D bonds in dimethylamine and dimethylamine-d. Comparison of k_8 and k_9 indicates that hydrogen atom abstraction occurs more readily than that of a deuterium atom, the velocity constant ratio k_H/k_D having a value of approximately 3 at 77°C. Comparison of the Arrhenius parameters for reactions (8) and (9) indicate that, within the appreciable experimental error, the pre-exponential factors are similar. The difference in reactivity of the N—H and N—D arises mainly because of the difference in the activation energy requirements. This difference, although subject to a large experimental error, is comparable with the zero-point energy difference ΔE_0 of 1.3 kcal mole⁻¹, corresponding to a single N—H and N—D vibration. This observation is in accord with the primary isotope effects reported for several other systems involving methyl or trifluoromethyl radicals.^{1, 2, 6}

COMPARISON OF REACTIVITY OF METHYL AND AMINO GROUPS
IN DIMETHYLAMINE

Knowledge of the velocity constants for reactions (10) and (8) enable a quantitative comparison of the ease of hydrogen atom abstraction from the methyl and amino groups in dimethylamine. Attack on the N—H bond, which is weaker than the C—H bond, requires the lower activation energy by ~ 1.7 kcal mole⁻¹. The pre-exponential factors differ by about an order of magnitude being "normal" for abstraction from the alkyl group but lower for the amino group. Similar behaviour has been reported for methanol⁷ and methylamine⁶ and was interpreted in terms of the repulsion forces likely between the polar radical and the functional group of the molecule, thereby restricting the radical in its approach to the molecule for a reactive collision.

At 164°C the ratio of velocity constants k_{10}/k_8 is ~ 3 so that the methyl group is more reactive on an overall basis than is the amino group. On a per-hydrogen-atom-available basis, however, the hydrogen attached to the nitrogen is about twice as reactive as the hydrogen linked to the carbon atom. When methyl radicals are the abstracting species³ the ratio of velocity constants is about 18, the N—H bond being the more reactive. The trifluoromethyl radical is markedly less selective in abstracting hydrogen than is the methyl radical and this is in keeping with the greater reactivity of the trifluoromethyl radical.

REACTIVITY OF N—H BONDS IN CH₃NH₂, (CH₃)₂NH AND (CH₂)₂NH

In table 5 we have compared kinetic data for the abstraction of hydrogen from various substrates by methyl and trifluoromethyl radicals. In general, a similar pattern of reactivity is noted for both radicals, there being an increase in reactivity with decreasing bond strength, and activation energy requirements are *ca.* 1.5 kcal mole⁻¹ lower for the trifluoromethyl radical attack on the N—H bonds. With methylamine and dimethylamine, the introduction of a second methyl group has the effect of markedly increasing the reactivity of the N—H bond towards attack by both CH₃ and CF₃ radicals.

REACTIVITY OF C—H BONDS IN CH₃NH₂, (CH₃)₂NH AND (CH₃)₃N

The velocity constants for the abstraction of hydrogen attached to carbon increases as more hydrogen atoms are available in the molecule. For the series methylamine,

dimethylamine and trimethylamine, the velocity constants are in the ratio 1 : 4.5 : 10 for CF_3 attack and 1 : 3 : 6 for CH_3 attack. On a per-atom available basis the ratios are 1 : 2 : 3.5 and 1 : 1.5 : 2 respectively so that it appears that the $-\text{NH}_2$, $>\text{NH}$ and $>\text{N}$ groups do not have any marked difference in the activation of the $\text{C}-\text{H}$

TABLE 5.—HYDROGEN ATOM ABSTRACTION BY TRIFLUOROMETHYL AND METHYL RADICALS FROM AMINES AND RELATED COMPOUNDS

reaction	$\log A$ ($\text{mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$)	E (kcal mole^{-1})	overall	$\log k(164^\circ)$ per H-atom	ref.
$\text{CF}_3 + \text{CH}_3\text{NH}_2 \rightarrow \text{CF}_3\text{H}$	10.7	4.2	8.6	8.1	6
$\text{CH}_3\text{NH}_2 \rightarrow \text{CF}_3\text{H}$	9.9	4.4	7.7	7.4	6
$\text{CH}_3 + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_4$	11.0	8.7	6.7	6.2	1
$\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_4$	9.55	5.7	6.7	6.4	1
$\text{CF}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H}$	11.8	5.1	9.3	8.5	this work
$(\text{CH}_3)_2\text{NH} \rightarrow \text{CF}_3\text{H}$	10.5	3.3	8.9	8.9	this work
$\text{CH}_3 + (\text{CH}_3)_2\text{NH} \rightarrow \text{CH}_4$	11.5	8.7	7.2	6.4	3
$(\text{CH}_3)_2\text{NH} \rightarrow \text{CH}_4$	10.8	6.4	7.6	7.6	3
$\text{CF}_3 + (\text{CH}_3)_3\text{N} \rightarrow \text{CF}_3\text{H}$	11.8	4.5	9.6	8.7	this work
$\text{CH}_3 + (\text{CH}_3)_3\text{N} \rightarrow \text{CH}_4$	11.8	8.8	7.4	6.5	11
$\text{CF}_3 + (\text{CH}_2)_2\text{NH} \rightarrow \text{CF}_3\text{H}$	11.0	4.1	8.9	8.9	this work
$\text{CH}_3 + (\text{CH}_2)_2\text{NH} \rightarrow \text{CH}_4$	10.3	4.8	7.9	7.9	4

The hydrogen atom which is abstracted is underlined.

bonds. Within experimental error there is little difference in the activation energies; the activation energies for abstraction from $\text{C}-\text{H}$ bonds are about 4 kcal mole^{-1} lower for trifluoromethyl radicals than for methyl radicals. Pritchard *et al.*¹⁰ have reported that for abstraction from hydrocarbons there is an activation energy difference of about 3 kcal mole^{-1} .

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