# Isotope Effects in Reactions of Trifluoromethyl Radicals with Hydrogen Chloride and Hydrogen Sulphide

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Rate constants, Arrhenius parameters and primary kinetic isotope effects have been measured for the reactions of trifluoromethyl radicals with  $H_2S$ ,  $D_2S$ , HCl and DCl:

$\log (A/cm^3 mole^{-1} sec^{-1})$	(E/kcal mole <sup>-1</sup> )		
$11.81 \pm 0.05$	4·19±0·12		
$11.90 \pm 0.02$	4·93±0·07		
11·38±0·01	$5.33 \pm 0.03$		
$11.41 \pm 0.03$	$6.11 \pm 0.06$		
	$\begin{array}{c} \log \left( 4/\mathrm{cm^3 \ mole^{-1} \ sec^{-1}} \right) \\ 11\cdot81 \pm 0\cdot05 \\ 11\cdot90 \pm 0\cdot02 \\ 11\cdot38 \pm 0\cdot01 \\ 11\cdot41 \pm 0\cdot03 \end{array}$		

Quotients of A-factors do not differ significantly from unity, but values for  $(E_D - E_H)$  are significantly less than the respective zero-point-energy differences  $\Delta E_0$  of 1.1 kcal mole<sup>-1</sup>. The reactivity of CF<sub>3</sub> radicals towards the two substances is markedly less than that of CH<sub>3</sub> radicals; the differences reside in the higher activation energies and may be attributed to the polar character of CF<sub>3</sub>.

In recent years, kinetic isotope effects have been studied in hydrogen- and deuterium-abstraction reactions by methyl or trifluoromethyl radicals from a number <sup>1-7</sup> of C—H, N—H and O—H bonds. In a number of systems, Arrhenius parameters have been determined and activation energy differences  $(E_D - E_H)$  correlated with the zero-point-energy differences  $\Delta E_0$  for each bond. For C—H and C—D bonds,  $(A_H/A_D)$  is close to unity but values for  $(E_D - E_H)$  exceed  $\Delta E_0$  both in attack by CH<sub>3</sub> radicals,<sup>1</sup> and by CF<sub>3</sub> radicals.<sup>2</sup> For N—H and N—D bonds <sup>4-6</sup> attacked by methyl radicals,  $(A_H/A_D)$  is close to unity—the quotient does not fall outside the range 0.7-1.4 —while values for  $(E_D - E_H)$ , ranging from 0.8-1.7 kcal mole<sup>-1</sup>, sometimes exceed and sometimes fall below  $\Delta E_0$ , characteristically *ca*. 1.3 kcal mole<sup>-1</sup>.

No measurements have been reported on isotope effects in the reactions between trifluoromethyl radicals and either H<sub>2</sub>S or HCl although both parent molecules <sup>8, 9</sup> have been investigated, and accordingly it was decided to study the reactivity of D<sub>2</sub>S and DCl. The photolysis of hexafluoracetone is a convenient source of CF<sub>3</sub> radicals in these systems and to assess the validity of the procedure the reactions with H<sub>2</sub>S and HCl may be re-investigated in the same apparatus. Since the free-radical thermochemistry and values for thermodynamic properties generally of the trifluoromethyl radical depends on the value of the activation energy of its reaction with hydrogen chloride, re-determination may narrow the limit of uncertainty in the values <sup>11-13</sup> for  $D(CF_3-H)$ ,  $\Delta H_{f}^{\circ}(CF_3)$  and  $S_{298}^{\circ}(CF_3)$ .

#### **EXPERIMENTAL**

## MATERIALS

HEXAFLUOROACETONE (a gift from DuPont) was fractionated through traps at -78, -96, -150 and  $-196^{\circ}$ C. The fraction which collected at  $-150^{\circ}$ C was degassed and stored in a blackened bulb. Hydrogen sulphide from a cylinder (Matheson Co.) was fractionated as

above. The fraction which collected at  $-150^{\circ}$  was degassed and stored in a blackened bulb. DEUTERIUM SULPHIDE was used as supplied by Merck, Sharp and Dohme. The isotopic purity was stated to be greater than 98 %. HYDROGEN CHLORIDE from a cylinder (Matheson Co.) was fractionated and stored as for hydrogen sulphide. DEUTERIUM CHLORIDE was used as supplied by Merck, Sharp and Dohme. The isotopic purity was stated to be greater than 99 %.

#### APPARATUS AND PROCEDURE

Photolysis experiments were carried out in a silica reaction vessel (illuminated volume, 123 ml) fitted with plane parallel windows. It was suspended in an aluminium block furnace fitted with quartz end-windows. The temperature of the furnace was controlled by a platinum element relay unit and was measured by three chromel+alumel thermocouples. The vessel was illuminated by a Mazda, medium-pressure mercury lamp, and radiation was limited to > 3000 Å by a Chance-Pilkington OX9A filter.

In the experiments with  $H_2S$  and  $D_2S$ , mixtures of either gas with hexafluoroacetone were used; with HCl and DCl, the reactants were admitted separately into the reaction vessel. Before a deuterated substrate was used, a sample was allowed to stand overnight in the vacuum line in order to "deuterate" the surface. This sample was then pumped away and fresh gas admitted for use in the experiments.

The reaction products were analyzed by the method of Arthur and Bell.<sup>8</sup> This involved collecting the condensable products in a U-trap cooled to  $-190^{\circ}$ C, allowing them to warm up, and then sweeping them with nitrogen carrier at a flow rate of between 30 and 50 ml/min on to a  $\frac{1}{4}$ in. absorption column containing 40 cm of alumina (60-80 mesh). The eluent was collected, for periods between 15 and 25 min depending on the activity of the alumina, in a trap packed with glass wool and cooled in liquid nitrogen. This trap was then evacuated and the eluent transferred to a side-arm which could be sealed off for gas chromatographic analysis. All the reactants and products except CF<sub>3</sub>H and C<sub>2</sub>F<sub>6</sub> were absorbed. The CF<sub>3</sub>H and C<sub>2</sub>F<sub>6</sub> were analyzed on a 3-ft alumina column with hydrogen carrier, flow rate 70-80 ml/min, at room temperature. It was assumed that the calibration for CF<sub>3</sub>H was applicable to CF<sub>3</sub>D. In experiments with HCl and DCl, CF<sub>3</sub>Cl was produced and was collected together with CF<sub>3</sub>H and C<sub>2</sub>F<sub>6</sub> in the procedure described above. Analysis of the products on the alumina column gave the following order of elution; C<sub>2</sub>F<sub>6</sub>, CF<sub>3</sub>Cl, CF<sub>3</sub>H.

All velocity constants were determined relative to Ayscough's value <sup>14</sup> of  $10^{13\cdot36}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> for the recombination of trifluoromethyl radicals. A least-mean-squares treatment was carried out to estimate "best" values and standard deviations for the parameters of the Arrhenius equations.

#### RESULTS

## PHOTOLYSIS OF HEXAFLUOROACETONE WITH $H_2S$ and $D_2S$

The photolysis of hexafluoroacetone gives carbon monoxide and hexafluoroethane in amounts approximating closely to the stoichiometry,

$$CF_3COCF_3 \rightarrow C_2F_6 + CO.$$

When hexafluoroacetone is photolyzed with  $H_2S$ ,  $CF_3H$  is produced by hydrogen abstraction by trifluoromethyl radicals, and the production of  $CF_3H$  and  $C_2F_6$  can be described by the following reactions :

$$CF_3COCF_3 \rightarrow 2CF_3 + CO$$
 (1)

 $CF_3 + H_2S \rightarrow CF_3H + SH \tag{2}$ 

$$2CF_3 \rightarrow C_2F_6. \tag{3}$$

According to Darwent and Roberts,<sup>15</sup> the hydrosulphide radicals may recombine in two ways, represented by reactions (4*a*) and (4*b*),  $(k_{4a}/k_{4b})$  being approximately 0.15:

$$2SH \rightarrow H_2 + S_2 \tag{4a}$$

$$2SH \rightarrow H_2S + S. \tag{4b}$$

# CF<sub>3</sub> PLUS HCl, DCl, H<sub>2</sub>S AND D<sub>2</sub>S

Some CF<sub>3</sub> and SH radicals associate to CF<sub>3</sub>SH:

$$CF_3 + SH \rightarrow CF_3SH.$$
 (5*a*)

From measurements on the material balance  $(n_{\rm CO} - n_{\rm C_2F_6} - 0.5n_{\rm CF_3H})$ , Arthur and Bell <sup>8</sup> concluded that some 18 % of  $CF_3$  radicals reacted in this way.

When mixtures of D<sub>2</sub>S and hexafluoroacetone are photolyzed, CF<sub>3</sub>D is produced instead of CF<sub>3</sub>H (reaction (2D)), and the resultant SD radical will be involved in reactions analogous to (4) and (5).

Provided that (2) and (3) are the only significant sources of CF<sub>3</sub>H and C<sub>2</sub>F<sub>6</sub>,  $k_2$ can be obtained from the relationship:



FIG. 1.--Temperature dependence (Arrhenius plots) of rate constants  $k_2$ ,  $k_{2D}$ ,  $k_6$  and  $k_{6D}$ for hydrogen and deuterium atom abstraction by trifluoromethyl radicals. All graphs in the form log  $(k_n/k_3^{\frac{1}{3}})/(\text{mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}})$  against  $(^{\circ}K)/T$ 

Curve 2: hydrogen abstraction from hydrogen sulphide; curve 2D: deuterium abstraction from deuterium sulphide; curve 6: hydrogen abstraction from hydrogen chloride; curve 6D: deuterium abstraction from deuterium chloride.

For convenience of presentation, curve 2 has been displaced 0.2 unit downwards and curve 2D has been displaced 0.1 unit downward. The upper abscissa scale refers to curves 2 and 2D, and the lower scale to curves 6 and 6D.

As in the previous investigation,<sup>8</sup> it was found that (2) was so rapid that sufficient  $C_2F_6$  for analysis could be obtained only with low  $H_2S$  concentrations (approximately 1 mm in reaction volume of 123 ml), and by restricting the temperature range to less than 110°. The amount of  $H_2S$  reacted was always less than 10 %. Arrhenius plots for  $\log_{10} (k_2/k_3^{\frac{1}{3}})$  and  $\log_{10} (k_{2D}/k_3^{\frac{1}{3}})$  over the temperature range 60-101°, and the concentration range 4.7 to  $5.4 \times 10^{-8}$  mole cm<sup>-3</sup>, are included in fig. 1. The results, when combined with Ayscough's value <sup>12</sup> for  $k_3$  (10<sup>13.36</sup> cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>), and evaluated by the method of least squares, may be expressed in the form :

$$\log (k_2/\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}) = (11.81 \pm 0.05) - (4190 \pm 120)/2.303RT,$$
(2A)  
$$\log (k_{2D}/\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}) = (11.90 \pm 0.02) - (4930 \pm 70)/2.303RT.$$
(2D—A)

#### PHOTOLYSIS OF HEXAFLUOROACETONE WITH HCl AND DCl

When hexafluoroacetone is photolyzed with HCl, the products include  $CF_3H$ , CF<sub>3</sub>Cl and C<sub>2</sub>F<sub>6</sub>. Amphlett and Whittle <sup>9</sup> have advanced the following reaction scheme to account for their formation :

$$CF_3COCF_3 \rightarrow 2CF_3 + CO$$
 (1)

$$CF_3 + HCl \rightarrow CF_3H + Cl$$
 (6)

$$CF_3 + CI \rightarrow CF_3Cl$$
 (7)

$$Cl + Cl + M \rightarrow Cl_2 + M \tag{8}$$

$$CF_3 + Cl_2 \rightarrow CF_3Cl + Cl \tag{9}$$

$$2CF_3 \rightarrow C_2F_6. \tag{3}$$

Whittle <sup>9</sup> found that the ratio  $(R_{CF_3Cl}/R_{CF_3H})$  was always less than unity, from which they argued that the source of CF<sub>3</sub>Cl was almost exclusively reaction (9).

If  $CF_3H$  and  $C_2F_6$  are formed only by reactions (6) and (3) respectively, then

$$(k_6/k_3^{\frac{1}{2}}) = (R_{CF_3H}/R_{C_2F_6}^{\frac{1}{2}}[HCl]).$$

The validity of this equation was tested by varying the initial concentration of HCl between 90 and  $130 \times 10^{-8}$  mole cm<sup>-3</sup>. The amount of HCl consumed was always less than 5 %. An Arrhenius plot of the data is shown in fig. 1 : the values of  $(k_6/k_3^{\pm})$  are independent of the HCl concentration, in accordance with the results of the previous work.<sup>9</sup> A least-mean-squares treatment of the data obtained in the present work over the temperature range 40-205°, together with Ayscough's value of  $10^{13.36}$  for  $k_3$ , gives

$$\log (k_6/\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}) = (11.38 \pm 0.01) - (5380 \pm 30)/2.303 RT,$$
(6A)

 $\log (k_{6D}/\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}) = (11.41 \pm 0.03) - (6110 \pm 60)/2.303 \text{RT}.$ (6D--A)

## DISCUSSION

There have been no previous determinations of rate parameters for abstraction of deuterium from deuterium sulphide and deuterium chloride by free radicals. The results reported here for hydrogen abstraction by trifluoromethyl radicals from H<sub>2</sub>S and HCl are in general agreement with those of Arthur and Bell<sup>8</sup> for H<sub>2</sub>S and Amphlett and Whittle<sup>9</sup> for HCl. The velocity constants at 100°C are in excellent agreement but the A-factors and activation energies in this work are slightly higher than those obtained in the earlier work; thus  $k_2 = 10^{9\cdot35}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> at 100°C,  $A_2 = 10^{11\cdot81}$ cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> and  $E_2 = 4\cdot19$  kcal mole<sup>-1</sup>, and  $k_6 = 10^{8\cdot23}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>,  $A_6 = 10^{11\cdot38}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> and  $E_6 = 5\cdot38$  kcal mole<sup>-1</sup>, whereas Arthur and Bell found  $k_2 = 10^{9\cdot37}$ ,  $A_2 = 10^{11\cdot22}$  and  $E_6 = 5\cdot07$ .

By carrying out a series of competitive experiments in which pairs of reactants were photolyzed with hexafluoracetone, Amphlett and Whittle <sup>9,11</sup> obtained Arrhenius parameters for CF<sub>3</sub> attack on HCl, HBr, HI, Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>. Their values ultimately depend on the Arrhenius parameters for the attack of CF<sub>3</sub> on HCl since only in this reaction was sufficient  $C_2F_6$  formed for analysis. If the results for abstraction from HCl obtained in the present work are used, recalculation of Amphlett and Whittle's data yields different values of improved accuracy for the Arrhenius parameters for the other reactions. These are listed in table 1. For each reaction the errors quoted are the sum of the standard deviations obtained by leastmean-squares treatment of each set of contributory data, making the usual assumption that the reference reaction (combination of CF<sub>3</sub> radicals) is not subject to appreciable error.

# $CF_3$ plus HCl, DCl, $H_2S$ and $D_2S$

From the Arrhenius parameters for (6), (-6), (10), (-10),

$$CF_3 + HCl \rightleftharpoons CF_3H + Cl \tag{6}$$

$$CF_3 + HBr \rightleftharpoons CF_3H + Br, \tag{10}$$

Coomber and Whittle <sup>12, 13</sup> have calculated values for  $D(CF_3 - H)$  of 106.3 kcal mole<sup>-1</sup>, for  $\Delta H_f^{\circ}(CF_3)$  of -112.6 kcal mole<sup>-1</sup> at 25°C, and for  $S_{CF_3}^{\circ}$  of 66.9 cal mole<sup>-1</sup> deg<sup>-1</sup>. at 177°C. If the variation of  $S_{CF_3}^{\circ}$  with temperature given in the JANAF tables<sup>16</sup> is assumed, at 25°C,  $S_{CF_3}^{\circ} = 59.8$  cal deg.<sup>-1</sup> mole<sup>-1</sup>. The new values obtained for

TABLE 1.—ARRHENIUS PARAMETERS FOR REACTIONS OF  $CF_3$  radicals with hydrogen halides and halogens

reaction	$\log_{10} (A/cm^3 mole^{-1} sec^{-1})$	E (kcal mole <sup>-1</sup> )
CF <sub>3</sub> +HCl	$11.38 \pm 0.01$	5·33±0·03
CF <sub>3</sub> +HBr	11·94 ±0·15	$3.15 \pm 0.27$
CF₃+HI	11·90±0·23	0·68 ±0·45
$CF_3 + Cl_2$	$13.03 \pm 0.02$	3·89 ±0·05
$CF_3 + Br_2$	12·52 ±0·07	0·98±0·11
$CF_3+I_2$	$12.58\pm0.21$	0·17 ±0·39

these quantities are within the limits of experimental error given by Whittle *et al.* They are:  $D(CF_3 - H) = 106.0$  kcal mole<sup>-1</sup>,  $\Delta H_f^{\circ}(CF_3) = -112.9$  kcal mole<sup>-1</sup> at 25°C, and  $S_{CF_3}^{\circ} = 59.1$  cal deg.<sup>-1</sup> mole<sup>-1</sup> at 25°C. The revised data may be used to estimate the Arrhenius parameters for the reaction :

 $SH+CF_3H\rightarrow H_2S+CF_3$ .

They are  $A_{-2} \approx 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  and  $E_{-2} \approx 19.3 \text{ kcal mole}^{-1}$ .

It has been shown<sup>12</sup> by Amphlett and Whittle<sup>11</sup> that, for the series of reactions between CF<sub>3</sub> and hydrogen halides and H<sub>2</sub>S, a plot of *E* against  $\Delta H$  is a straight line which fits an Evans-Polanyi equation. If the values for activation energies listed in table 1 and the value for  $E_2$  reported here are plotted in this manner, *E* is given by the equation

$$E = 6.2 + 0.16 \Delta H^{\circ},$$

where E and  $\Delta H^{\circ}$  are in kcal mole.<sup>-1</sup>

Comparison of the rate parameters for CF<sub>3</sub> attack on H<sub>2</sub>S and HCl with those for the corresponding methyl radical reactions <sup>17, 18</sup> shows that with H<sub>2</sub>S and HCl as substrates, CF<sub>3</sub> radicals are less reactive than CH<sub>3</sub> radicals. Usually the reverse order of reactivity is observed. For hydrocarbons the A-factor ratio  $(A_{CF_3}/A_{CH_3})$  is usually nearly unity, and the difference in reactivity is due to an activation energy difference,  $(E_{CH_3} - E_{CF_3})$  of 3-4 kcal mole<sup>-1</sup>. For most other organic substrates  $(E_{CH_3} - E_{CF_3})$  is about 0-2 kcal mole<sup>-1.7</sup> Arrhenius parameters for CH<sub>3</sub> attack on H<sub>2</sub>S are  $A = 10^{11.4}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> and E = 2.6 kcal mole<sup>-1</sup>. Since the quotient  $(A_{CF_3}/A_{CH_3})$  is 0.95 for HCl and 2.5 for H<sub>2</sub>S, the greater reactivity of CH<sub>3</sub> radicals towards the substrates HCl and H<sub>2</sub>S is due to activation energy differences  $(E_{CH_3} - E_{CF_3})$  of -3.1 and -1.6 kcal mole<sup>-1</sup> respectively. This order of reactivity is also observed with HBr, <sup>10, 19</sup> HI <sup>11, 20</sup> and CF<sub>3</sub>CHO <sup>21, 22</sup>, and it has been postulated <sup>10</sup> that it is due to intermolecular repulsion between the highly polar substrates and the polar CF<sub>3</sub> radical.

#### **ISOTOPE EFFECTS**

The primary isotope effect for abstraction of hydrogen and deuterium atoms by CF<sub>3</sub> radicals from H<sub>2</sub>S and D<sub>2</sub>S is obtained by comparison of the Arrhenius parameters of reactions (2) and (2D). Thus,  $(k_{\rm H}/k_{\rm D}) = (k_2/k_{2\rm D}) = 2.18$  at 100°C,  $(A_{\rm H}/A_{\rm D}) = 0.81$ , and  $(E_{\rm D} - E_{\rm H}) = 0.74 \pm 0.19$  kcal mole<sup>-1</sup>. Similarly for H and D abstraction from HCl and DCl, comparison of reactions (6) and (6D) gives the isotope effect:  $(k_{\rm H}/k_{\rm D}) = 2.46$  at 100°,  $(A_{\rm H}/A_{\rm D}) = 0.93$ , and  $(E_{\rm D} - E_{\rm H}) = 0.73 \pm 0.09$  kcal mole.<sup>-1</sup> These appear to be the first isotope effects to be reported for hydrogen abstraction by free radicals from Cl—H and S—H bonds.

From the infra-red spectra <sup>23</sup> of H<sub>2</sub>S and D<sub>2</sub>S, the asymmetrical S—H stretching frequency is 2684 cm<sup>-1</sup>, and the corresponding S—D stretching frequency is 1892 cm<sup>-1</sup>. The corresponding zero-point energy difference is 1·13 kcal mole<sup>-1</sup>. The H—Cl stretching frequency <sup>24</sup> is 2886 cm<sup>-1</sup>, and that for D—Cl is 2092 cm<sup>-1</sup>, whence the zero-point energy difference is also 1·13 kcal mole<sup>-1</sup>. Simple theory, in which it is assumed that the formation of the transition state involves only the loss of one stretching vibration of the bond being attacked, predicts that  $(E_D - E_H) = 1·13$  kcal mole<sup>-1</sup>,  $(A_H/A_D) = 1$  and  $(k_H/k_D) = 4·59$  at 100°C. The experimentally determined isotope effects are considerably less than these. In particular,  $(E_D - E_H)$  is much less than the zero-point energy difference. The small value of  $(E_D - E_H)$  can be correlated with the slope of the plot of *E* against  $\Delta H$  referred to in the previous section, which showed <sup>11</sup> that *E* changed little for a large change in  $\Delta H$ . From this it might be expected that not all of the zero-point energy difference would be reflected in  $(E_D - E_H)$ .

TABLE 2.—KINETIC ISOTOPE EFFECTS IN HYDROGEN ABSTRACTION FROM HYDRIDES

	attacking radical	$A_{\rm H}/A_{\rm D}$	$E_{\rm D} - E_{\rm H}$	kн/kр (100°)	$\Delta E_0$	$k_{\rm H}/k_{\rm D}$ predicted	ref.
$H_2$	CF <sub>3</sub>	1.35	1.0	5.3	1.9	12.5	25
HCl	$CF_3$	0.9	0.7	2.5	1.1	4.6	this work
$H_2S$	$CF_3$	0.8	0.7	2.2	1.1	4.6	this work
$NH_3$	CH <sub>3</sub>	0.7	1.1	3.0	1.3	5.8	5
$N_2H_4$	CH <sub>3</sub>	1.4	1.4	8.9	1.4	6.6	6
CH₄	$CF_3$	1.0	1.6	8.7	1.2	5.0	7

The isotope effects obtained in this work are compared in table 2 with those for hydrogen abstraction from some other hydrides. Because values for  $(A_{\rm H}/A_{\rm D})$  for H<sub>2</sub>S, HCl, and NH<sub>3</sub> are close to unity, the low isotope effect is attributable to  $(E_{\rm D} - E_{\rm H})$  being less than  $\Delta E_0$ . The origin of low  $(k_{\rm H}/k_{\rm D})$  ratios has been attributed <sup>26</sup>

to the motion of the central atom in the symmetrical vibration  $[R \ldots H \ldots CF_3]$  of the activated complex. The more asymmetric the transition state, the greater the mass-dependence of this vibration and the closer the  $(k_H/k_D)$  ratio to unity. This provides an explanation of the low  $(k_H/k_D)$  values found for H<sub>2</sub>S and HCl since the transition states are both highly asymmetric.

The high values of  $(k_{\rm H}/k_{\rm D})$  for CH<sub>4</sub> and N<sub>2</sub>H<sub>4</sub> stem from the excess of  $(E_{\rm D}-E_{\rm H})$  over the difference in zero-point energy. Large  $(k_{\rm H}/k_{\rm D})$  ratios have been explained in terms of quantum-mechanical tunnelling <sup>2</sup> and loss of bending vibrations in the transition state.<sup>27</sup>

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## CF<sub>3</sub> PLUS HCl, DCl, H<sub>2</sub>S AND D<sub>2</sub>S

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