

# Kinetics and Isotope Effect of the Reaction of Methyl Radicals with Deuterium Chloride in Gas Phase

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Flash photolysis of acetone has been used as a source of  $\text{CH}_3$  radicals. The rate constant of a homogeneous gas phase reaction of deuterium chloride with methyl radicals has been measured between 298 and 473 K by monitoring the UV absorption of methyl radicals at 216 nm. The data can be fitted to the Arrhenius expression

$$\log(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (8.54 \pm 0.06) - (562 \pm 40) \text{ K}/T$$

Kinetic isotope effects were calculated by using previous values for the rate constant of the reaction between  $\text{CH}_3$  and HCl. The ratio of the second-order rate constants is

$$k_{\text{HCl}}/k_{\text{DCl}} = (1.23 \pm 0.06) \exp[(223 \pm 15) \text{ K}/T]$$

The observed isotope effects are compared with those calculated on the basis of three- and six-atom BEBO models for the activated complex.

In recent years, several studies have been carried out on the kinetic isotope effects in abstractions of hydrogen and deuterium by methyl or trifluoro-

methyl radicals from H–H, C–H and N–H bonds.<sup>1–5</sup> No measurements have been reported on isotope effects in the reactions of methyl radicals with HCl and DCl. In this study, values of the velocity constant and the appropriate Arrhenius parameters for deuterium abstraction by methyl radicals are reported and compared with isotope effects calculated on the basis of hypothetical transition state models.

## EXPERIMENTAL

*Materials.* Acetone was dried with anhydrous magnesium sulfate, distilled and degassed at liquid nitrogen temperature. Deuterium chloride was prepared from benzoyl chloride and deuterium oxide.<sup>6</sup> The isotopic purity was measured by mass spectrometry.

*Methods.* The apparatus and techniques employed were similar to those already described.<sup>7</sup> Before each experiment, the tube was treated with deuterated substrate overnight in order to deuterate the surface. Fresh gas was admitted for use in the experiments.

The methyl radical concentration was calculated using the value  $\varepsilon = 1010 \text{ m}^2 \text{ mol}^{-1}$  for the molar

Table 1. Rate constants of the reaction  $\text{CH}_3 + \text{DCl} \rightarrow \text{CH}_3\text{D} + \text{Cl}$  obtained at different acetone and DCl pressures.

| $T$<br>K | $P_{\text{acet}}$<br>Torr | $P_{\text{DCl}}$<br>Torr | Number of<br>experiments | $10^{-7} k$<br>$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|----------|---------------------------|--------------------------|--------------------------|--|
| 298      | 0.63–1.18                 | 3.93–48.3                | 9                        | $0.46 \pm 0.10$  |
| 373      | 0.53–1.20                 | 4.48–33.6                | 8                        | $1.04 \pm 0.20$  |
| 423      | 0.62–1.13                 | 4.45–22.9                | 9                        | $1.57 \pm 0.20$  |
| 473      | 0.66–1.15                 | 4.81–24.8                | 10                       | $2.33 \pm 0.20$  |

absorptivity.<sup>8</sup> The velocity constants were determined relative to our values of  $2.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the recombination of methyl radicals.<sup>8</sup> A least squares treatment was carried out to calculate the values and standard deviations for the parameters of the Arrhenius equation. The results are shown in Table 1 and Fig. 1.

### VIBRATIONAL FORCE FIELDS AND FREQUENCIES

The geometry and internal coordinates assumed for the complete six-atom activated complex are shown in Fig. 2. The linear configuration of the bonds Cl–H–CH<sub>3</sub> is based on the general prediction of semiempirical methods for three-atom transition states in hydrogen-abstraction reactions. The general valence force field which was used is

$$\begin{aligned}
 2V = & F_{\text{CH}}(\Delta R_{\text{CH}})^2 + F_{\text{HCl}}(\Delta R_{\text{HCl}})^2 \\
 & + 2F_{\text{int}}(\Delta R_{\text{CH}})(\Delta R_{\text{HCl}}) \\
 & + F_{\phi}[(\Delta\phi_1)^2 + (\Delta\phi_2)^2] \\
 & + F_d[(\Delta d_1)^2 + (\Delta d_2)^2 + (\Delta d_3)^2] \\
 & + 2F_{dd}[(\Delta d_1)(\Delta d_2 + \Delta d_3) + (\Delta d_2)(\Delta d_3)] \\
 & + F_{\alpha}[(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2 + (\Delta\alpha_3)^2] \\
 & + F_{\beta}[(\Delta\beta_1)^2 + (\Delta\beta_2)^2 + (\Delta\beta_3)^2] \\
 & + 2F_{\alpha\alpha}[(\Delta\alpha_1)(\Delta\alpha_2 + \Delta\alpha_3) + (\Delta\alpha_2)(\Delta\alpha_3)] \\
 & + 2F_{d\alpha}[(\Delta d_1)(\Delta\alpha_2 + \Delta\alpha_3) + (\Delta d_2)(\Delta\alpha_1 + \Delta\alpha_3) \\
 & + (\Delta d_3)(\Delta\alpha_1 + \Delta\alpha_2)] \\
 & + 2F_{d\alpha'}[(\Delta d_1)(\Delta\alpha_1) + (\Delta d_2)(\Delta\alpha_2) + (\Delta d_3)(\Delta\alpha_3)].
 \end{aligned}$$

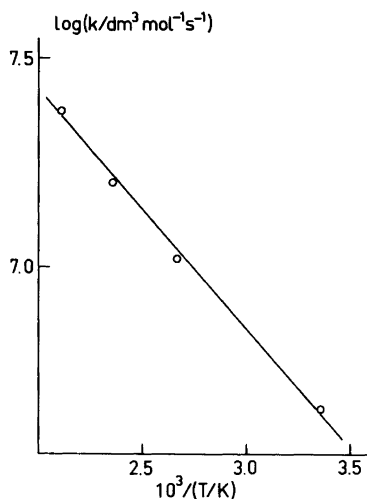


Fig. 1. Arrhenius plot for the reaction  $\text{CH}_3 + \text{DCI} \rightarrow \text{CH}_3\text{D} + \text{Cl}$ .

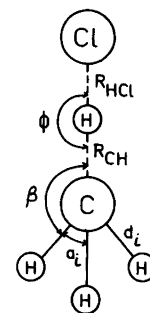


Fig. 2. Assumed geometry and internal coordinates of the activated complex  $\text{CH}_3\text{-H-Cl}$ .

Vibrational force constants for the methyl group in the activated complex were assumed to be the same as those in  $\text{CH}_4$  (Table 2). A tetrahedral configuration for the methyl group was assumed.

Force constants for the bonds Cl–H–CH<sub>3</sub> of the activated complex were determined from potential energies of the linear three-atom system, applying the BEBO method as described below.<sup>9</sup> The force constant  $F_{\beta}$  does not fit either of the preceding groups and therefore different values were tried, as discussed below. The equations needed for the calculation of the vibrational frequencies for a three-atom model can be set up by the methods of Wilson *et al.*<sup>10</sup> For the six-atom model, modifications of the Schachtschneider programs<sup>11</sup> were used to evaluate the necessary G matrices and solve the vibrational secular equations.

### CALCULATION OF ISOTOPE EFFECTS

Ratios of rate constants  $k_{\text{HCl}}/k_{\text{DCI}}$  were calculated in the conventional way<sup>12</sup> from the expression

$$k_1/k_2 = (v_1^*/v_2^*)(f_m/f) (\tau_1/\tau_2)$$

Table 2. Force constants for the methyl group in Cl–H–CH<sub>3</sub>.<sup>a</sup>

| Force constant        | Value |
|-----------------------|-------|
| $F_d$ (mdyn/Å)        | 5.00  |
| $F_{dd}$ (mdyn/Å)     | 0.124 |
| $F_{\alpha}$ (mdyn Å) | 0.520 |
| $F_{d\alpha}$ (mdyn)  | 0.165 |

<sup>a</sup> All other force constants of different interactions are assumed to be zero. In force constants non-SI units are used:  $1 \text{ Å} = 10^{-10} \text{ m}$ ,  $1 \text{ dyn} = 10^{-5} \text{ N}$ .

Table 3. Properties of isotopic hydrogen chloride molecules.

|                  | $\nu/\text{cm}^{-1}$ | $uT$ | $\sigma T$ | $S$ | $A/\text{cm}^{-1}$ | $(E/R)/\text{K}$ |
|------------------|----------------------|------|------------|-----|--------------------|------------------|
| HCl <sup>a</sup> | 2989                 | 4302 | 15.3       | 1   | 2989               | 2146             |
| DCl <sup>a</sup> | 2090                 | 3009 | 7.8        | 1   | 2090               | 1502             |

<sup>a</sup> Values for <sup>1</sup>H<sup>35</sup>Cl and <sup>2</sup>H<sup>35</sup>Cl.

where  $\nu^*$  is the imaginary frequency of the activated complex, and  $\tau$  is a tunneling correction. The quantity  $f$  is the reduced partition function ratio for the activated complex:

$$f = \prod_{i=1}^{d-1} \frac{u_{2i} \sinh(u_{1i}/2)}{u_{1i} \sinh(u_{2i}/2)}$$

where  $u_i = h\nu_i/kT$  and  $d - 1$  is 3 in the case of a three-atom model and 11 for the six-atom model. The quantity  $f_m$  for HCl/DCl is given by<sup>22</sup>

$$f_m = \frac{A_{\text{DCl}}}{A_{\text{HCl}}} \exp\left(\frac{E_{\text{HCl}} - E_{\text{DCl}}}{RT}\right)$$

in which  $A = \nu/S$ ,  $E/RT = (\frac{1}{2}u - \frac{1}{3}\sigma)$ ,  $u = h\nu/kT$  and  $\sigma = hcB/kT$ .  $\nu$  is the stretching frequency ( $\text{cm}^{-1}$ ) of the diatomic hydrogen chloride molecules.  $S$  is the symmetry number, the  $\sigma$  term represents the rotational quantum correction, and  $B$  is the rotational constant. The values for  $A$  and  $E$  can be easily derived from data given by Herzberg.<sup>13</sup> In Table 3 they are presented together with the values which were used for  $\nu$ ,  $uT$ ,  $T$  and  $S$ . The values of  $u$  for isotopic hydrogen chloride do not contain the anharmonicity correction, and in the analogous values of the transition state this correction was likewise omitted.

Tunneling corrections were calculated for unsymmetrical Eckart barriers<sup>14,15</sup> with the curvature fitted to that of the actual potential energy

curve at the maximum. The two barrier heights needed are given by the potential energy of activation less the zero-point energy level of the product C-H or C-D bond. The values for tunneling corrections were estimated from the results of Johnston and Heicklen<sup>23</sup> as a function of  $u^*$ ,  $\alpha'_1$  and  $\alpha'_2$ , where  $u^* = h\nu^*/kT$ ,  $\alpha'_1 = 2\pi\Delta V_1/h\nu^*$  and  $\alpha'_2 = 2\pi\Delta V_2/h\nu^*$ . Here  $\Delta V_1$  and  $\Delta V_2$  are the two barrier heights as described before.

#### DISCUSSION OF THE BEBO MODEL

The BEBO, or Bond-Energy-Bond-Order method developed by Johnston and Parr<sup>9</sup> enables one to calculate the necessary transition state properties of a three-atom system without the introduction of adjustable parameters. The properties of the reactant and product required for its use in the present case are given in Table 4.<sup>9</sup>

Two values of  $D_e(\text{H}_3\text{C}-\text{H})$  and of the stretching force constant of the C-H bond have been used. The force constants for the activated complex change slightly with the different values, as shown in Table 5. The calculated rate constant ratios  $k_{\text{HCl}}/k_{\text{DCl}}$  are quite insensitive to the change of force constant  $F(\text{C}-\text{H})$ , whereas they are decreased slightly by the constants corresponding to a  $D_e$  value of 452.7 kJ mol<sup>-1</sup>. All further calculations were carried out with the parameters designated BEBO4 in Table 5.

Table 4. Properties of reactant and product bonds.

|  | H-Cl  | C-H   | C-Cl  |
|--|-------|-------|-------|
| Interatomic distance $R_e/\text{\AA}$        | 1.27  | 1.09  | 1.76  |
| Dissociation energy $D_e/\text{kJ mol}^{-1}$ | 445.2 | 452.7 | 334.7 |
| Stretching frequency $\nu/\text{cm}^{-1}$    | 2989  | 2917  | 732   |
| Morse parameter $\beta/\text{\AA}^{-1}$      | 1.87  | 1.78  | 1.81  |
| Force constant $F/\text{mdyn \AA}^{-1}$      | 5.16  | 5.00  | 2.82  |
| Empirical constant $p$                       | 0.914 | 1.087 |       |

Table 5. Results of BEBO calculations for the Cl-H-C complex.

|  | BEBO1 <sup>a</sup> | BEBO2 <sup>b</sup> | BEBO3 <sup>c</sup> | BEBO4 <sup>d</sup> |
|--|--------------------|--------------------|--------------------|--------------------|
| $V_a$                                  | 34.39              | 30.87              | 34.39              | 30.87              |
| $n_{\text{HCl}}$                       | 0.65               | 0.70               | 0.65               | 0.70               |
| $n_{\text{CH}}$                        | 0.35               | 0.30               | 0.35               | 0.30               |
| $R_{\text{HCl}}$                       | 1.38               | 1.36               | 1.38               | 1.36               |
| $R_{\text{CH}}$                        | 1.36               | 1.40               | 1.36               | 1.40               |
| $F_{\text{HCl}}$                       | 2.372              | 2.863              | 2.394              | 2.876              |
| $F_{\text{CH}}$                        | 0.388              | 0.186              | 0.394              | 0.186              |
| $F_{\text{int}}$                       | 1.505              | 1.405              | 1.517              | 1.411              |
| $F_{\phi}/R_{\text{HCl}}R_{\text{CH}}$ | 0.0239             | 0.0229             | 0.0239             | 0.0229             |

<sup>a</sup> With input parameters  $F(\text{C-H})=4.65$ ,  $D_e=441.4$ . <sup>b</sup>  $F(\text{C-H})=4.65$ ,  $D_e=452.7$ . <sup>c</sup>  $F(\text{C-H})=5.00$ ,  $D_e=441.4$ . <sup>d</sup>  $F(\text{C-H})=5.00$ ,  $D_e=452.7$ . Energies in  $\text{kJ mol}^{-1}$ , force constants in  $\text{mdyn \AA}^{-1}$  and distances in  $\text{\AA}$ .

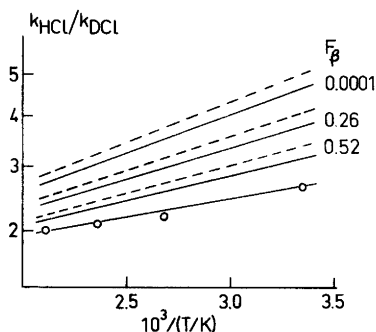


Fig. 3. Solid lines, rate constant ratios calculated with BEBO4 parameters, without tunneling corrections, and with various values of  $F_{\beta}$ . Dashed lines, tunneling correction included with  $F_{\beta}=0.52$ , 0.26 and 0.0001  $\text{mdyn \AA}^{-1}$ . Experimental points: O.

Calculated isotope effects were sensitive to the choice of  $F_{\beta}$ . The lowest value of  $F_{\beta}$  (0.0001) is an approximation to zero. The value of 0.520 is that of the corresponding force constant in methane, and the value 0.26 used by Johnston<sup>16,17</sup> is one half of the corresponding force constant in methane. The force constants  $F_{\beta}$  and calculated vibrational frequencies are shown in Table 6.

The theoretical curves for the kinetic isotope effect are presented in Fig. 3 with the tunneling correction as described above. In addition, in each case a curve is given in which the tunneling factor has been omitted. Since the imaginary stretching frequency  $\nu^*$  is very low, the respective Eckart tunnel correction is low too. With and without correction for tunneling, the best fit to  $k_{\text{HCl}}/k_{\text{DCI}}$  is provided by the calculations when the value of  $F_{\beta}$  is

Table 6. Vibrational frequencies for the activated complex Cl-H-CH<sub>3</sub>. For the six-atom model force constant set BEBO4 was used. Force constants for the methyl group were as in Table 2.

|   | Three atom | Six-atom BEBO4 |       |       |
|---|------------|----------------|-------|-------|
| Force constant $a_{F_{\beta}}$            |            | 0.0001         | 0.260 | 0.520 |
| Vibration frequencies in $\text{cm}^{-1}$ |            |                |       |       |
| $\nu_1(a_1)$                              | 988        | 841            | 935   | 961   |
| $\nu_2(a_1)$                              |            | 3007           | 3007  | 3007  |
| $\nu_3(a_1)$                              |            | 1076           | 1199  | 1356  |
| $\nu_4(a_1)$                              | 639i       | 652i           | 648i  | 647i  |
| $\nu_5(e)$                                |            | 3012           | 3014  | 3015  |
| $\nu_6(e)$                                | 397        | 398            | 266   | 274   |
| $\nu_7(e)$                                |            | 1408           | 1416  | 1445  |
| $\nu_8(e)$                                |            | 12             | 905   | 1218  |

<sup>a</sup> In units of  $\text{mdyn \AA}$ .

Table 7. Kinetic isotope effects in hydrogen abstraction from hydrides.

|                               | Attacking radical | $A_H/A_D$ | $E_D - E_H$<br>kJ mol <sup>-1</sup> | $k_H/k_D$<br>100 °C | $\Delta E_0^a$<br>kJ mol <sup>-1</sup> | $k_H/k_D^a$<br>pred. | Ref.      |
|-------------------------------|-------------------|-----------|-------------------------------------|---------------------|--|----------------------|-----------|
| H <sub>2</sub>                | CH <sub>3</sub>   | 1.01      | 4.18                                | 3.86                | 7.9                                    | 12.5                 | 18        |
| H <sub>1</sub>                | CF <sub>3</sub>   | 1.35      | 4.2                                 | 5.3                 | 7.9                                    | 12.5                 | 2         |
| HCl                           | CH <sub>3</sub>   | 1.23      | 1.85                                | 2.23                | 5.3                                    | 5.6                  | this work |
| HCl                           | CF <sub>3</sub>   | 0.9       | 2.9                                 | 2.5                 | 5.3                                    | 5.6                  | 3         |
| CH <sub>4</sub>               | CH <sub>3</sub>   | 1.58      | 1.3                                 | 2.36                | 5.0                                    | 5.0                  | 18        |
| CH <sub>4</sub>               | CF <sub>3</sub>   | 1.34      | 7.1                                 | 13.2                | 5.0                                    | 5.0                  | 19        |
| N <sub>2</sub> H <sub>4</sub> | CH <sub>3</sub>   | 1.4       | 5.8                                 | 8.9                 | 5.8                                    | 6.6                  | 5         |

<sup>a</sup>Based on the assumption that, on passing from reactants to the transition state, the zero-point energy associated with the stretching vibration of the bond attacked is lost.

0.520, corresponding to the value for stable molecules.

#### COMPARISON WITH OTHER EXPERIMENTAL WORK

The kinetic isotope effect for reactions involving methyl or trifluoromethyl radicals and hydrogen shows substantial degrees of tunneling. The ratios of rates  $k_H/k_D$  in general lie between the tunneling and nontunneling curves. Kibby and Weston<sup>2</sup> show that if the value corresponding to the stable molecule can be assumed for the force constant of the bending coordinate, then tunneling must take place in the reaction of CF<sub>3</sub> with hydrogen. Likewise in the study of Shapiro and Weston<sup>1</sup> (CH<sub>3</sub> + H<sub>2</sub>/D<sub>2</sub>) a small but nonzero tunneling correction appears necessary. Nevertheless, because of the uncertainty involved in the choice of force constant for the bending coordinate, it is not possible to decide if tunneling through the potential energy barrier is important here.

The isotope effects obtained in this study are compared in Table 7 with those for hydrogen abstraction from some other hydrides. The origin of small isotope effects has been attributed<sup>20</sup> to the motion of the central atom in the symmetrical vibration [Cl...H...CH<sub>3</sub>] 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  $k_{HCl}/k_{DCl}$  values found for HCl since the transition state is asymmetric ( $F_{HCl} \sim 15F_{CH}$ ). Large  $k_H/k_D$  ratios have been explained<sup>21</sup> in terms of tunneling and loss of bending vibrations in the transition state.

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