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### Competitive Reaction Rates of Hydrogen Atoms with HCl and Cl<sub>2</sub>. Entropy Considerations of the HCl<sub>2</sub> Transition State\* †

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The relative rates of the reactions

 $k_3$ H+HCl $\rightarrow$ H<sub>2</sub>+Cl

and

$$H+Cl_2 \xrightarrow{\kappa_6} HCl+Cl_2$$

were determined in the temperature range of  $0^{\circ}$  to  $62^{\circ}$ C and found to be given by

 $k_3/k_6 = (0.143 \pm 0.033) \exp(-(1540 \pm 130/RT))$ .

The temperature-independent factor in the above expression is interpreted in terms of the structure and the vibrational frequencies of the HCl<sub>2</sub> transition state. The doubly degenerate bending frequency of this transition state is found to have a value of about 105 cm<sup>-1</sup>.

#### INTRODUCTION

'N connection with recent measurements<sup>1,2</sup> of the L reaction of Cl atoms with isotopically substituted hydrogen molecules, there arose the problem of the relative rates of the fast reaction step H+Cl<sub>2</sub> compared to the back reaction H+HCl. It was shown in a preliminary experiment,<sup>1</sup> that this ratio is sufficiently large so that the back reaction does not affect the measured H<sub>2</sub>/HD isotope effect to any appreciable extent. The present work was undertaken to obtain a more precise value for this ratio of competitive rates.

Pre-exponential factors in the Arrhenius-type expression for rate constants may be used to yield information about the structure and the vibrational frequencies of the transition state.<sup>3,4</sup> Since considerable information exists now 1-3 about the H2Cl transition state, the present study can be used as a starting point for the exploration of the HCl<sub>2</sub> transition state.

#### **EXPERIMENTAL PRINCIPLE**

The rate of appearance of isotopically substituted hydrogen in the photochemically induced reaction of protium with chlorine in the presence of isotopically labeled hydrogen chloride constitutes a measure for

the reaction type  $H+HCl\rightarrow H_2+Cl$ . The total decrease in hydrogen may be used to measure the fast  $H+Cl_2 \rightarrow$ HCl+Cl reaction step. The above statement embodies the basic principle of the present experiment. Further elaborations will now be given.

Tank hydrogen was made to react with a mixture of dry chlorine and tritium-labeled hydrogen chloride. The following reaction steps are to be considered:

$$H_2 + Cl \rightarrow HCl + H \tag{1}$$

$$HT+Cl\rightarrow TCl+H$$
(2a)

$$HT+Cl\rightarrow HCl+T$$
 (2b)

$$HCl+H\rightarrow H_2+Cl \qquad (3)$$

$$TCl+H\rightarrow HT+Cl$$
 (4)

$$HCl+T \rightarrow HT+Cl$$
 (5)

$$Cl_2+H\rightarrow HCl+Cl$$
 (6)

$$Cl_2 + T \rightarrow TCl + Cl$$
 (7)

$$HT + H \rightarrow H_2 + T \tag{8}$$

 $H_2+T\rightarrow HT+H$  $(9)_{-}$ 

$$TCl+H\rightarrow HCl+T$$
 (10)

$$HCl+T \rightarrow TCl+H.$$
 (11)

The chain-initiating step and the chain-terminating steps have been omitted, as well as wall reactions in

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<sup>\*</sup> The experimental aspects of this paper are the work of F.S.K., the theoretical aspects the joint endeavors of both authors.

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 ‡ Most of this work was carried out while M.W. was a visitor

at the Weizmann Institute. He is very grateful to the Institute

<sup>&</sup>lt;sup>1</sup> J. Bigeleisen, F. Klein, R. E. Weston, and M. Wolfsberg, J. Chem. Phys. **30**, 1340 (1959).
<sup>2</sup> W. M. Jones, J. Chem. Phys. **19**, 78 (1951).
<sup>3</sup> K. S. Pitzer, J. Am. Chem. Soc. **79**, 1804 (1957).
<sup>4</sup> D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, J. Chem. Phys. **25**, 736 (1956).

general.<sup>5</sup> Also neglected are molecule-molecule reactions, under the given experimental temperature conditions<sup>6</sup> and reactions which involve two tritiums at the trace tritium concentrations of the present experiment.

The time rate of change of r, the ratio of the HT concentration to the H<sub>2</sub> concentration, is given by

 $d\mathbf{r}/dt = [1/(\mathrm{H}_2)] \cdot [d(\mathrm{H}_1)/dt] - [\mathbf{r}/(\mathrm{H}_2)] \cdot [d(\mathrm{H}_2)/dt].$ (12a)

$$\frac{d(\text{HT})/dt = k_{5}(\text{HCl})(\text{T}) + k_{9}(\text{H}_{2})(\text{T}) + k_{4}(\text{TCl})(\text{H})}{-(k_{2a} + k_{2b})(\text{HT})(\text{Cl}) - k_{8}(\text{HT})(\text{H}), \quad (12b)}$$

and

$$-(d(\mathbf{H}_{2})/dt = k_{1}(\mathbf{H}_{2})(\mathbf{Cl}) + k_{9}(\mathbf{H}_{2})(\mathbf{T}) -k_{3}(\mathbf{HCl})(\mathbf{H}) - k_{8}(\mathbf{HT})(\mathbf{H}).$$
(12c)

The following expressions are obtained for the steadystate concentrations of H and T,

$$(\mathbf{H}) = \frac{k_{1}(\mathbf{H}_{2})(\mathbf{Cl}) + k_{2a}(\mathbf{HT})(\mathbf{Cl}) + k_{9}(\mathbf{H}_{2})(\mathbf{T}) + k_{11}(\mathbf{HCl})(\mathbf{T})}{k_{3}(\mathbf{HCl}) + k_{4}(\mathbf{TCl}) + k_{6}(\mathbf{Cl}_{2}) + k_{8}(\mathbf{HT}) + k_{10}(\mathbf{TCl})}$$
$$= \frac{k_{1}(\mathbf{H}_{2})(\mathbf{Cl})}{k_{6}(\mathbf{Cl}_{2})}$$
(12d)

$$(T) = \frac{k_{2b}(HT)(Cl) + k_8(HT)(H) + k_{10}(TCl)(H)}{k_5(HCl) + k_7(Cl_2) + k_9(H_2) + k_{11}(HCl)}$$
$$= \frac{k_{2b}(HT)(Cl) + k_{10}k_1(H_2)(TCl)(Cl)/k_6(Cl_2)}{k_7(Cl_2)}.$$
(12e)

In the simplification of Eqs. (12d) and (12e), use has been made of the knowledge of the experimental conditions, especially of the fact that tritium is present only in tracer concentrations and that (HT) $\ll$ (TCl). Use has also been made of a knowledge of some of the rate constants and of isotope effects on these (e.g.,  $k_9$ ,  $k_8 \ll k_1^7$ ). Moreover,  $k_3/k_6$  has been taken to be selfconsistently of the order of 10<sup>-2</sup>. Since (HT) $\ll$ (TCl) and  $k_{10}$ ,  $k_{11} \ll k_7$ ,<sup>8</sup> (T) is so small that the first two terms on the right-hand side of Eq. (12b) make a negligible contribution compared to the third term. The expressions for (H) and (T) are substituted into Eqs. (12b) and (12c) and the resulting expressions for d(HT)/dtand  $d(\text{H}_2)/dt$  are themselves again simplified in the same manner as Eqs. (12d) and (12e). One then ob-

tains

$$d(\text{HT})/dt = k_4 k_1(\text{H}_2) (\text{TCl}) (\text{Cl})/k_6(\text{Cl}_2)$$

$$-(k_{2a}+k_{2b})$$
 (HT) (Cl) (12f)

$$-d(\mathbf{H}_2)/dt = k_1(\mathbf{H}_2) (\mathrm{Cl}).$$
(12g)

The substitution of Eqs. (12f) and (12g) into Eq. (12a) gives<sup>9</sup>

$$dr/k_1(\mathrm{Cl})dl = r(1-R^{-1}) + (k_4/k_6) [(\mathrm{TCl}^0)/(\mathrm{Cl}_2)]$$

or

$$dr/dg = -g^{-1} \{ r(1 - R^{-1}) + (k_4/k_6) [(\mathrm{TCl}^0)/(\mathrm{Cl}_2)] \},$$
(13)

where g is the fraction of hydrogen which finally remains unreacted,  $R = k_1/(k_{2a}+k_{2b})$  and the superscript 0 designates initial concentration. Use has been made of the fact that the TCl concentration changes little during the course of the experiment.

Equation (13) is a linear differential equation of the first order which can be easily solved by introducing an

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and

<sup>&</sup>lt;sup>5</sup> In the course of the experiments the inner surface of the reaction vessel became covered by a thin film of mercurous chloride. No difference in results, within experimental error, was found between a fresh Pyrex surface, a surface coated with HgCl and the same after flaming from the outside.

<sup>&</sup>lt;sup>6</sup> M. Steiner and E. K. Rideal, Proc. Roy. Soc. (London) A173, 503 (1939).

<sup>&</sup>lt;sup>7</sup> K. H. Geib and P. Harteck, Z. physik. Chem. Bodenstein Festband, 849 (1931); P. G. Ashmore and J. Chanmugan, Trans. Faraday Soc. 49, 254 (1953).

<sup>\*</sup> M. Steiner and E. K. Rideal, Proc. Roy. Soc. (London) A173, 503 (1939), P. A. Leighton and P. C. Cross, J. Chem. Phys. 6, 345 (1938), and S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 226–229. The high temperature result  $k_s \gg k_{11}$  (with *D* instead of *T*) has been interpreted by Steiner and Rideal in terms of a very low transmission coefficient for reaction type 11 compared to reaction 5 and consequently reaction 7. The activation energies for reactions 10 and 11 are expected to be larger than that for reaction 7.

<sup>&</sup>lt;sup>9</sup> Where possible, calculations were carried out without the various simplifications and it was determined that the error made in the determination of the ratio  $k_3/k_6$  would be less than the order of 1%.

Temper- ature °C	ρ	g	$\mathrm{HCl^0/H_{2^0}}$	$\mathrm{Cl_{2^0}/H_{2^0}}$	$k_{3}/k_{6}  imes 10^{3}$
0.2	7.434	0.7755	1.402	3.229	8.14
	11.59	0.7081	1.358	2.767	7.85
	39.00	0.4261	1.370	2.873	8.51
	16.62	0.6680	1.992	3,906	9.17
25.2	18.24	0.7522	2.846	4.141	9.40
	11.81	0.7989	1.138	2.764	13.13
	36.84	0.5148	2.028	4.530	10.60
	12.21	0.7729	1.658	3.683	10.75
	33.02	0.5261	1.656	3.684	9.74
	58.07	0.4080	1.510	3,400	10.94
62.2	199.0	0.1884	1.192	3.276	14.17
	139.5	0.3144	1.806	3,929	14.59
	146.8	0.2982	1.294	2.830	13.79
25.2	0.5	0.9970	1.226	3.015	

TABLE I. Experimental data. (For all experiments  $\rho_0 = 1.185 \times 10^5$ .)

integrating factor.<sup>10</sup> We find then

$$\frac{g^{[1-(1/R)]}}{\frac{(\mathrm{HCl}^{0})}{(\mathrm{H}_{2}^{0})}} E \int_{g}^{1} dg \left/ \left[ g^{1/R} \left( \frac{(\mathrm{Cl}_{2}^{0})}{(\mathrm{H}_{2}^{0})} - 1 + g \right) \right].$$
(14)

Here, we have immediately written the expression for the ratio of interest by inserting the factor E defined as  $k_4/k_3$ ; s is the initial ratio of TCl concentration to HCl concentration. The hydrogen specific activity  $\rho$  is found directly. The initial hydrogen chloride is converted to hydrogen and the specific activity of this hydrogen is designated as  $\rho_0$ . Then  $r/s = 2\rho/\rho_0$ . The integral in Eq. (14) is evaluated numerically. We can derive E in the following way. We know<sup>2</sup> the ratio of rates of the reactions (1) and (2a) which are the inverse of reactions (3) and (4), respectively. This knowledge of  $k_1/k_{2a}$  involves the previously discussed<sup>1</sup> equality of  $k_{2a}$  and  $k_{2b}$ . One finds then

$$E = k_4/k_3 = f_{\rm HT}/f_{TC1}(2R)^{-1};$$
(15)

f is the deviation of the ratio of the relevant isotopic partition functions from the classical ratio, as defined by Bigeleisen and Mayer.<sup>11</sup>

#### EXPERIMENTAL PROCEDURE

The experimental apparatus was essentially the same as described in the work cited in footnote 1 except that an additional storage vessel for tritium-labeled hydrogen chloride was attached to the line next to the chlorine vessel. The experiment was carried out in a similar manner as described previously.<sup>1</sup> Measured quantities of dry chlorine gas followed by hydrogen chloride were frozen into the reaction vessel and a measured volume of pure tank hydrogen was then added. The reaction was run and the residual hydrogen was measured as before. A hydrogen sample was taken for radioassay. The tritium specific activity  $\rho$  was measured in a conventional Geiger gas counter. The initial specific activity  $\rho_0/2$  of hydrogen chloride was measured by the same method after converson of the hydrogen chloride to pure hydrogen gas (specific activity  $\rho_0$ ) on zinc amalgam and suitable dilution with tank hydrogen. The tritium-labeled hydrogen chloride was prepared by the distillation of tritiated water onto phosphorus pentachloride. The resulting hydrogen chloride was carefully dried by passage through an efficient multiple freeze-out trap cooled in a dry iceacetone mixture.

### EXPERIMENTAL RESULTS

The experimental results, calculated according to Eq. (14), are given in Table I. The last experiment in Table I is a dark run to check the efficiency of the separation of the hydrogen from the reaction mixture. Table II gives the relevant values of R taken from Jones<sup>2</sup> and the values of  $E^{-1}$  calculated as described above. By least-squares method we determined the constants of the Arrhenius-type equation for  $k_3/k_6$  and found

$$k_3/k_6 = 0.143 (\pm 0.033) \exp[-(1540 \pm 130)/RT].$$
 (16)

These results again prove the correctness of the assumption made in the work cited in footnote 1, that the back reaction (3), (H+HCl), to reaction (1), (H<sub>2</sub>+Cl), does not significantly affect the isotope effect considerations in that work. The above results may be compared with the value indirectly deduced by Morris and Pease,<sup>12</sup>

$$k_3/k_6 = 0.1 \exp(-|> 1400|/RT).$$

In a preliminary set of experiments by the method outlined in the work cited in footnote 1, a mixture of equal parts of 99.6% deuterium gas and tank hydrogen was reacted with chlorine at room temperature. The remaining unreacted hydrogen was analyzed on a CEC Model 21-401 mass spectrometer for the formation of HD in the sample. The accuracy was impaired by equilibration of  $D_2$  with  $H_2$  in the mass spectrometer.

TABLE I	I. Va	lues of	$E^{-1}$ :	$= k_3/k_4$	and	of	R.
---------	-------	---------	------------	-------------	-----	----	----

Temperature °C	R	<i>E</i> -1		
0.2	3.73	8.19		
25.2	3.43	6.85		
62.2	3.09	5.53		

<sup>12</sup> J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).

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<sup>&</sup>lt;sup>10</sup> See, for instance, A. Cohen, An Elementary Treatise on Differential Equations (D. C. Heath and Company, Boston, Massachusetts, 1933), p. 30. <sup>11</sup> J. Bigeleisen and M. G. Mayer, J. Chem. Phys. 15, 261 (1967)

<sup>(1947).</sup> 

The experiments permitted only the setting of an upper limit of 0.05 to the ratio  $k_3/k_6$ .

#### DISCUSSION

The interpretation of the rate ratio will be undertaken within the framework of the transition state theory. The configurations of both the H<sub>2</sub>Cl and HCl<sub>2</sub> transition states will be assumed to be linear. The ratio  $k_3/k_6$  is then given by<sup>13</sup>

$$k_{3}(\mathrm{H}_{2}\mathrm{Cl})/k_{6}(\mathrm{H}\mathrm{Cl}_{2}) = (\kappa_{3}/\kappa_{6}) (m_{\mathrm{H}_{2}\mathrm{C}} 1/m_{\mathrm{H}}m_{\mathrm{H}\mathrm{C}} 1)^{\frac{3}{2}} \\ \times (m_{\mathrm{H}}m_{\mathrm{C}} 1_{2}/m_{\mathrm{H}\mathrm{C}} 1_{2})^{\frac{3}{2}} (I_{\mathrm{C}} 1_{2}/I_{\mathrm{H}\mathrm{C}} 1) (I_{\mathrm{H}_{2}\mathrm{C}} 1/I_{\mathrm{H}\mathrm{C}} 1_{2}) \\ (s_{\mathrm{H}\mathrm{C}} 1^{s} s_{\mathrm{H}\mathrm{C}} 1_{2}/s_{\mathrm{C}} 1_{2} s_{\mathrm{H}_{2}\mathrm{C}} 1) \alpha \exp(-A/T), \quad (17)$$

where

$$\alpha = \left[1 - \exp(-u_{\rm HCl}) / \prod_{3} (1 - \exp(-u_{\rm H_2Cl}))\right] \\\times \left[\prod_{3} (1 - \exp(-u_{\rm HCl_2}) / (1 - \exp(-u_{\rm Cl_2}))\right].$$

Here A is the difference (in degrees) in the activation energies (zero point of reactants to zero point of transition state) for the two reactions;  $\kappa_3$  and  $\kappa_6$  are transmission coefficients, assumed to be equal; the m, I, and s factors are defined in the usual way with  $s_{\rm HC1}$ =  $s_{\rm HC12}=s_{\rm H_2C1}=1$ ,  $s_{\rm C12}=2$ ; and  $u=h\nu/kT$ . The products run over the three vibrational frequencies of the respective transition states.

It has been possible to express the experimental results for  $k_3/k_6$  in the temperature range in question in the form  $k_3/k_6 = Ce^{-D/T}$  [see Eq. (16)]. Equation (17) is already in the form  $k_3/k_6 = C'\alpha e^{-A/T}$ . If one assumes that the individual factors of  $\alpha$ , namely,  $(1-e^{-u})^{-1}$ , can be expressed as  $ae^{b/T}$  (both *a* and *b* being temperature independent) one finds:  $\ln a = (\partial/\partial T)[T \ln(1-e^{-u})^{-1}]$ . The derivative is evaluated at some average temperature in the region of interest.

An actual attempt at least-squares fitting of  $\ln(1-e^{-u})^{-1}$  by means of a straight line over the temperature range of interest has led to very similar values for  $\ln a$ as those from the derivative expression above. The derivative expression is of course recognized as the vibrational entropy of an harmonic oscillator (except for the gas constant R) and the proper combination of the factors  $\ln a$  becomes just as expected, the difference between the vibrational entropies of activation of the two reactions (again except for the gas constant R). Similarly then C (calculated) is the anti  $\ln$  of  $R^{-1}$  times the difference between the total entropies of activation of the two reactions.

The factor D which does yield information about the total relative energies of the respective transition states will not be pursued further here.

Attention will be focused on the factor C which depends on the structure and on the vibrational fre-

quencies of the transition states and the reactants. The necessary knowledge for the diatomic molecules is readily available in the literature.<sup>14</sup> Considerable information about the  $H_2Cl$  transition state has been obtained both from entropy of activation considerations of the hydrogen-chlorine reaction<sup>3</sup> and from the study of the isotope effects in this reaction.<sup>1</sup>

The unknowns contributing to the factor C, depend then only on the moments of inertia of HCl<sub>2</sub> and upon its doubly degenerate bending frequency  $\nu_{\phi}$ . The stretching frequency of the HCl<sub>2</sub> transition state is assumed sufficiently large so that it makes little contribution to the entropy. Since one can make reasonable assumptions on the moments of inertia, the present experimental data then serve to give information about the doubly degenerate bending frequency of HCl<sub>2</sub>.

In his entropy considerations with respect to the  $H_2+Cl$  reaction, Pitzer<sup>3</sup> had to estimate H–H and H–Cl distances in the H<sub>2</sub>Cl transition state. He used  $d_{H-H}=0.9$  A and  $d_{H-Cl}=1.5$  A. Proceeding similarly for HCl<sub>2</sub> we choose  $d_{H-Cl}=1.5$  A and  $d_{Cl-Cl}=2.2$  A. With these distance values one finds

$$(I_{\rm C1_2}/I_{\rm HC1}) (I_{\rm H_2C1}/I_{\rm HC1_2}) = 3.6.$$

(

If one permits independent or combined increases of 0.2 A for any of the above estimated bond distances of the HCl<sub>2</sub> transition state, this ratio can increase by 35% or decrease by 15%. Using the above value of 3.6 one obtains for C' of Eq. (17): C'=1.85.

The stretching frequency of  $H_2Cl$  which is about 1340 cm<sup>-1 1</sup> makes no contribution to  $\alpha$  in the temperature range in question. It is also assumed that the stretching frequency of HCl<sub>2</sub> makes no contribution, as mentioned above. A stretching frequency for the HCl<sub>2</sub> transition state larger than the Cl<sub>2</sub> frequency is plausible on the basis of the findings with respect to the H<sub>2</sub>Cl transition state, where the most reasonable model appears to be one with a large H–Cl force constant. This postulate will be tested by the measurement of the isotope effect in this reaction, now in progress. If this frequency were as low as 500 cm<sup>-1</sup>,  $\alpha$  would increase by about 40%. Our later analysis shows that such an increase has little effect on the final value of the bending frequency.

The following values are used in the calculation of the contributions of the  $Cl_2$  and  $H_2Cl$  frequencies to  $\alpha$ ,

$$\nu_{\rm C12} = 565 \text{ cm}^{-1}, \quad \nu_{\phi \rm H_2C1} = 540 \text{ cm}^{-1},$$

where  $\nu_{\phi}$  refers to the doubly degenerate bending frequency of the linear triatomic molecule. An average temperature of 304°K is employed. Using the experimental value of C=0.143, one finds then that

 $\{(\partial/\partial T) T \ln[1 - \exp(-u_{\phi HCl_2})]^{-1}\} = 1.711,$ 

<sup>&</sup>lt;sup>13</sup> S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

<sup>&</sup>lt;sup>14</sup> G. Herzberg, *Molecular Spectra and Molecular Structure I.* Spectra of Diatomic Molecules (D. Van Nostrand Corporation, Inc., Princeton, New Jersey, 1950).

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which means that<sup>15</sup>

#### $\nu_{\phi \text{HC}_{12}} = 105 \text{ cm}^{-1}$ .

The experimental error of  $\pm 0.033$  in C leads to an error of  $\pm 12$  cm<sup>-1</sup> in the bending frequency.<sup>16</sup> On the other hand the uncertainty in the moment of inertia ratio leads to an uncertainty of  $\pm 13$  cm<sup>-1</sup> in the estimated frequency. Thus the bending frequency  $\nu_{\phi HCl_2}$  is not expected to deviate by more than 20 cm<sup>-1</sup> from the value of 105 cm<sup>-1</sup>. It may be men-

tioned that the raising of Pitzer's frequency  $\nu_{\phi H_2C1}$  has a negligible effect on the present result, whereas a considerable lowering of that frequency would only produce a comparatively small lowering of the present value of  $\nu_{\phi H_2C1}$ . The comparison of  $\nu_{\phi H_2C1}$  and  $\nu_{\phi H_C12}$  leads to a value of the relative bending force constants<sup>14</sup>  $k\delta_{H_1C12}/k\delta_{H_2C1}=0.345$ .

The experiment has thus served to give us our first insight into the potential energy surface of the HCl<sub>2</sub> transition state. Isotope effect studies will give us further information. As has been noted before,<sup>1</sup> however, they will not yield further data with regard to  $\nu_{\phi HC l_2}$ .

#### ACKNOWLEDGMENTS

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<sup>&</sup>lt;sup>16</sup> J. B. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Table AIX 4. <sup>16</sup> A least-squares calculation has been carried out to fit by C

<sup>&</sup>lt;sup>16</sup> A least-squares calculation has been carried out to fit by  $C \exp(-D/T)$  the values of  $k_3/k_6$  given by Eq. (17) at the three temperatures of the experiment with the known molecular parameters (including  $\mathbf{v}_{9HC12}=105 \text{ cm}^{-1}$ ) and with a value of A chosen to give the correct magnitude of  $k_3/k_6$ . The result of this calculation was  $C=0.144\pm0.0004$ . This result justifies our procedure and indicates that the error introduced by the temperature variation of a is small compared to the experimental error.