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Dynamics of the reactions of O(1D) with HCl, DCl, and Cl₂

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The reactions O(1D) + HCl → OH + Cl (1a) and OCl + H (1b), O(1D) + DCl → OD + Cl (2a) and OCl + D (2b), and O(1D) + Cl₂ → OCl + Cl (3) are studied at an average collision energy of 7.6, 7.7, and 8.8 kcal/mol for (1), (2), and (3), respectively. H, D, and Cl atoms are detected by the resonance-enhanced multiphoton ionization technique. The average kinetic energies released to the products are estimated from Doppler profile measurements of the product atoms. The relative yields [OCI+H]/[OH+Cl] and [OCl+D]/[OD+Cl] are directly measured, and a strong isotope effect (H/D) on the relative yields is found. The fine-structure branching ratios [Cl(2P₃/2)/Cl(2P₁/₂)] of the reaction products are also measured. The results suggest that nonadiabatic couplings take place at the exit channels of the reactions (1a) and (2a), while the reaction (3) is totally adiabatic.

INTRODUCTION

The dynamics of the reactions of O(1D) with diatomic molecules has been studied experimentally and theoretically. Figure 1 shows the energy diagram for the O(1D) + HCl system. The energy levels of the excited states of the HOCl and HClO are taken from the SCF-CI calculations of Bruna et al.1 Performing a classical trajectory study for O(1D) + HCl on an ab initio surface, Shinke2 concluded that the reaction proceeds via a long-lived HOCl+h complex in the X' A' state before breaking up into the products OH + Cl. Luntz3 measured rotational and vibrational distributions of OH products in the reaction of O(1D) + HCl when O(1D) was produced by the photodissociation of O₃ at 266 nm. Park and Wiesenfeld4 measured rotational and vibrational distributions of OH products up to v' = 4, and reported the characteristic propensity for production of the II(A') diabatic sublevel of OH from the complex. Based on the observation of high rotational excitation in the OH product, they concluded that the formation of OH must proceed via insertion of O(1D) into HCl to form highly vibrationally excited HOCl+h. The other products, OCl, H, and O(3P) are also generated in the reaction of O(1D) with HCl.

ΔH(kcal/mol)

O(1D) + HCl → OH(X' 2Π) + Cl(3P) (1a), -44.4

OCl(X' 2Π) + H(3S) (1b), -63.3

HCl(ν) + O(3P) (1c), -45.4

Balucani et al.6 measured the angular and translational distributions of OCl products in a crossed-beam experiment with a mass spectrometer. Because they could not detect OH products for reaction (1a), they estimated a lower limit for the branching ratio, φ(1b)/φ(1a) > 0.34 ± 0.10.

Kruus et al.8 observed the infrared emission from HCl due to the E-V energy transfer process, estimating the branching ratio φ(1b)/φ(1a) = 0.06 ± 0.02. In this paper, direct detection of Cl and H atoms yields the branching ratio φ(1b)/φ(1a) and measurement of translational energies reveals the reaction dynamics.

We have also investigated the reaction of the isotopic substituted compounds in the reaction (2a) and (2b):

O(1D) + DCl → OD(2Π) + Cl(2P), (2a)

OCl(2Π) + D(3S). (2b)

The product Cl(2P) atom has an open-shell electronic structure characterized by fine-structure splittings due to spin–orbit coupling. The fine-structure branching ratios of Cl(2P) are interpreted in terms of nonadiabatic coupling of potential energy surfaces during the reaction process. In this paper, we measured the ratios of [Cl₈(2P₁/₂)]/[Cl(2P₃/2)] in the reactions (1a) and (2a) in order to study adiabaticity of the potential surfaces involved in this reaction. In connection with this, the following reaction was studied to observe the spin–orbit effect of the Cl atoms:

ΔH(kcal/mol)

H(1S) + Cl₂ → OCl(2Π) + Cl(3P), -51.6. (3)

Figure 2 shows the energy diagram for the O(1D) + Cl₂ system.

EXPERIMENT

The spectra of H, D, and Cl(2P) were measured by the (2+1) REMPI technique. The experimental setup was used almost the same as our previous studies.3 O₃ (2 Torr)/HCl(2 Torr), O₃ (2 Torr)/DCl (2 Torr), or O₃ (2 Torr)/Cl₂ (2 Torr) were mixed just before passing through a pulsed nozzle (0.8 ms duration) into a vacuum chamber. Pressure of the reaction and detection chambers pumped...
separately were $1 \times 10^{-4}$ and $1 \times 10^{-5}$ Torr, respectively. A KrF excimer laser light at 248 nm (≈2 mJ/pulse, 10 Hz) dissociated O$_3$ to produce the translationally hot O($^1D$) atoms. For the probe light the output of a tunable dye laser was frequency doubled by a BBO crystal and focused by a lens ($f$=200 mm). The two laser beams were collinearly counter-propagated at right angles to the molecular beam. 40 ns after the KrF excimer laser pulse, a probe UV laser (~0.2 mJ/pulse) was fired to detect H, D, and Cl atoms produced from the reaction using the REMPI technique. The spectra of H and D atoms were measured by (2+1) REMPI at 243.135 and 243.069 nm, respectively. The resulting ions were detected by an electron multiplier. The log-log plots of the MPI signal intensity versus probe laser intensity was found to have a slope of 2.0±0.1 for both H and D atoms. For a polarization experiment two linearly polarized laser beams were crossed perpendicularly with each other. The output of the photolysis laser was polarized by a pile-of-plates polarizer. O($^1D$) produced in the photodissociation of O$_3$ at 248 nm is expected to have a strong anisotropy for the angular distribution. Fairchild et al.\textsuperscript{8} reported an anisotropy parameter for the angular distribution of O($^1D$) to be $\beta=1.2\pm0.2$ from O$_3$ at 274–300 nm. This would be held in photodissociation of O$_3$ at 248 nm in the same Hartley band of O$_3$. Doppler profiles of H and D atoms were taken with the two polarization configurations $E_d||k_p$ and $E_d\perp k_p$, where $E_d$ is the electric vector of the dissociation laser and $k_p$ is the propagation direction of the probe laser.

Relative REMPI sensitivity for H and Cl atoms was checked by the measurement of the ratio of signals from H and Cl atoms in the 193 nm photodissociation of HCl, which was 4.2±0.7. Detection of H is more sensitive than Cl in our REMPI experiment. The Cl($4p^2P_{3/2}$)$\rightarrow$3p$^2P_{3/2}$ REMPI transition is observed at 235.336 nm, and the CI*($4p^2P_{3/2}$)$\rightarrow$3p$^2P_{3/2}$ transition at 237.808 nm.\textsuperscript{9} The relative REMPI sensitivity of Cl and CI* was checked by the measurement of vacuum UV laser induced fluorescence signal intensity ratios of photofragment CI and CI* atoms in the 193 nm photodissociation of HCl, DCl, and chloromethanes. The detection of Cl is more sensitive than CI* in our REMPI experiment by a factor of 2.5±0.1.\textsuperscript{10}

Experiments with a crossed molecular beam configuration were also performed. O$_3$ and HCl (DCI or Cl$_2$) gases passed separately through two pulsed nozzles into the chamber to avoid formation of O$_3$–HCl complexes in the pulsed molecular beam and to make sure that we observe the products from the reaction (1)–(3). The crossed molecular beam experiment gave the same results as the single beam experiment with the mixture of the gases.

**RESULTS**

O($^1D$)+HCl and O($^1D$)+DCI

Typical REMPI spectra of the H, D, and Cl atoms produced from the reactions are shown in Figs. 3 and 4(a). The shapes of the measured Doppler spectra of H and D are almost the Gaussian functions. Measuring the angular distribution of the H atom velocity, the linearly polarized photolysis and probe laser beams were perpendicularly crossed with each other. We found no discernible difference between the Doppler profiles taken with the two polarization configurations $E_d||k_p$ and $E_d\perp k_p$, where $E_d$ is the electric vector of the dissociation laser and $k_p$ is the propagation direction of the probe laser. This indicates that the velocity distributions in the laboratory frame are almost isotropic for the H atoms although O($^1D$) generated in the photodissociation of O$_3$ at 248 nm is expected to have a strong anisotropy for the angular distribution.\textsuperscript{3}

The averaged kinetic energies of the H, D, and Cl atoms in the laboratory frame were calculated from the second moment $\langle \beta^2 \rangle$ of the observed Doppler profiles, and then converted to the total kinetic energy released to the products in the center-of-mass (c.m.) frame, $\langle E' \rangle$. Details of the calculation was reported by Kim et al.\textsuperscript{11} and by Matsumi et al.\textsuperscript{7} The values obtained for $\langle E' \rangle$ are 7.6±0.9 kcal/mol for H formation and 16.7±2.5 kcal/mol for Cl formation, which are listed in Table I with fractions $\langle f_i \rangle$. 

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**FIG. 1.** The energy diagram for O($^1D$)+HCl system. The energies of the HOCI and HClO states are based on the calculation by Bruna et al. (Ref. 1). The energies of the HOCI and HClO are the values for the equilibrium geometries of the ground electronic state.

**FIG. 2.** The energy diagram for O($^1D$)+Cl$_2$ system. 

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of the total available energies $E_{\text{av}}$ released into translation $\langle E'_{t}\rangle$. In this table, the average collision energy $E_{\text{coll}}$ for the $\text{O}^{(1)}D + \text{HCl}$ reaction is calculated with the following equation:\textsuperscript{12}

$$
\langle E_{\text{coll}} \rangle \approx \frac{1}{2} \left( \frac{m(\text{HCl})}{m(\text{O})} \right) \left( \frac{2m(\text{O})}{m(\text{HCl})} \right) \langle E_{\text{LAB}}^{(1)}(\text{O}) \rangle 
+ \frac{2}{m(\text{HCl})} \left( \frac{3}{2} kT \right),
$$

\textbf{TABLE I. Kinetic energy release following reaction with O(1)D.}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\langle E_{\text{coll}} \rangle$</th>
<th>$E_{\text{av}}$</th>
<th>$\langle E'_{t} \rangle$</th>
<th>$\langle E'<em>{t} \rangle / E</em>{\text{av}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}^{(1)}D + \text{HCl} \rightarrow \text{OCl} + \text{H}$</td>
<td>7.6</td>
<td>13.9</td>
<td>7.6±0.9\textsuperscript{a}</td>
<td>0.55±0.06</td>
<td>5</td>
</tr>
<tr>
<td>$\text{O}^{(1)}D + \text{Cl} \rightarrow \text{Cl} + \text{D}$</td>
<td>7.7</td>
<td>12.8</td>
<td>5.0±1.3\textsuperscript{a}</td>
<td>0.39±0.10</td>
<td>5</td>
</tr>
<tr>
<td>$\text{O}^{(1)}D + \text{HCl} \rightarrow \text{OH} + \text{Cl}$</td>
<td>7.6</td>
<td>52.0</td>
<td>16.7±2.5\textsuperscript{a}</td>
<td>0.32±0.05</td>
<td>4</td>
</tr>
<tr>
<td>$\text{O}^{(1)}D + \text{Cl} \rightarrow \text{OD} + \text{H}$</td>
<td>7.7</td>
<td>52.3</td>
<td>17.8±1.8\textsuperscript{a}</td>
<td>0.34±0.03</td>
<td>3</td>
</tr>
<tr>
<td>$\text{O}^{(1)}D + \text{Cl}_2 \rightarrow \text{Cl}_2 + \text{OCl}$</td>
<td>8.8</td>
<td>60.4</td>
<td>22.4±3.7\textsuperscript{a}</td>
<td>0.37±0.04</td>
<td>4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Average collision energy in the c.m. frame.
\textsuperscript{b}Available energy: $(E_{\text{coll}}) - \Delta H_f$.
\textsuperscript{c}Kinetic energy released to the products in the c.m. frame. Errors are 1 sigma values.
\textsuperscript{d}Derived from the Doppler profiles of chlorine atoms in the REMPI spectra.

where $m(i)$ refers to a mass of the $i$ reactant and $T$ is room temperature. $\langle E_{\text{LAB}}^{(1)}(O) \rangle$ is the average translational energy in the laboratory frame (LAB) for the $\text{O}^{(1)}D$ atoms which are produced in the photolysis of $\text{O}_3$ at 248 nm. The vibrational distribution of $\text{O}_3^{(1)A^\prime}$ from the photodissociation of $\text{O}_3$ at 266 nm was reported by Sparks et al.\textsuperscript{13} Based on their results, the fraction of the available energy that is released into translation is estimated to be 0.68. Assuming that the same fraction holds at 248 nm, the collision energies were calculated as shown in Table I.

The fraction $\langle f'_{t} \rangle$ for $\text{O}^{(1)}D + \text{HCl} \rightarrow \text{OCl} + \text{H}$ is 0.55±0.06, which is close to the value of 0.43 obtained from the crossed-beam measurements of translational energy distribution of OCl products.\textsuperscript{5} The $\langle f'_{t} \rangle$ value for $\text{O}^{(1)}D + \text{Cl} \rightarrow \text{Cl} + \text{D}$ is 0.39±0.10. Isotope effect is observed in these $\langle f'_{t} \rangle$ values. However, no discernible isotope effect was observed for $\langle f'_{t} \rangle$ in the $\text{O}^{(1)}D + \text{HCl(DCl)} \rightarrow \text{Cl} + \text{OD} + \text{OH}$ reactions. The fractions $\langle f'_{t} \rangle$ for these reactions are 0.32–0.34, which are slightly higher than the estimation (0.24) from the LIF measurements of ro-vibrational distribution of OH products.\textsuperscript{4} Table I summarizes these results and the reported values.

Table II lists the measured channel branching ratios

\textbf{TABLE II. Channel branching ratios, $\phi_{(1a)}/\phi_{(1b)}$ and $\phi_{(2b)}/\phi_{(2a)}$.}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\phi_{(1a)}$</th>
<th>$\phi_{(1b)}$ or $\phi_{(2b)}$</th>
<th>$\phi_{(2a)}$</th>
<th>$\phi_{(2a)}$</th>
<th>PST\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}^{(1)}D + \text{HCl} \rightarrow \text{OCl} + \text{H}$</td>
<td>0.24±0.06</td>
<td>0.041</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O}^{(1)}D + \text{Cl} \rightarrow \text{Cl} + \text{D}$</td>
<td>0.09±0.02</td>
<td>0.043</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental results.

\textsuperscript{b}Prior state density calculation, based on Eq. (A1).

\textsuperscript{c}Phase space calculation based on Eq. (A4).
$\phi_{(1b)}/\phi_{(1a)}$ and $\phi_{(2b)}/\phi_{(2a)}$. A strong isotope effect was observed on the channel branching ratio, that is, the branching ratio for O($^1D$)+HCl is three times larger than for O($^1D$)+DCl. However, the fine structure branching ratios $[Cl^*(2^3P_{1/2})]/[Cl^*(2^3P_{3/2})]$ for the reaction (1a), and (2a) listed in Table III show little isotope dependence.

$O(^1D)+Cl_2-OCl+Cl(2^3P)$

Figure 4(b) shows the Doppler profile of Cl($^2P_{3/2}$) generated in the reaction, O($^1D$)+Cl$_2$→OCl+Cl($^2P_{3/2}$) at the collision energy of 8.8 kcal/mol. The translational energy $\langle E_t \rangle$ is 22.4±3.7 kcal/mol calculated from the second moment of the Doppler profile, which corresponds to $\langle f_1^2 \rangle = 0.37±0.04$. Cl$^*$ atom concentration was below our REMPI detection limit. Therefore, the fine structure branching ratio $[Cl^*(2^3P_{1/2})]/[Cl^*(2^3P_{3/2})]$ is less than 0.03.

**Statistical (phase space) calculation**

According to statistical considerations, the channel branching ratios $\phi_{(1b)}/\phi_{(1a)}$ and $\phi_{(2b)}/\phi_{(2a)}$ resulting from a long-lived complex are determined by the density of quantum states of the product channels. First, the prior distribution functions were calculated. Details of the calculation are given by Eq. (A1) in the Appendix. Table II shows the calculated ratio $\phi_{(1b)}/\phi_{(1a)}=0.041$, which is too small when compared with our experimental value of 0.24±0.06 for O($^1D$)+HCl. The observed isotope effect is not reproduced by this simple prior calculation. Since this prior calculation does not include the angular momentum restriction, a calculation using phase space theory was subsequently performed. Phase space theory (PST) has been a common tool for calculating branching ratios in unimolecular decay. The theory has been presented by Pechucas et al. and is briefly mentioned in the Appendix. Table II summarizes the results of these calculations based on Eq. (A4). The PST theory predicts better values for $\phi_{(1b)}/\phi_{(1a)}$ than the prior calculation. However, this theory also has difficulty in reproducing the observed isotope effect.

**DISCUSSION**

**Potential surfaces**

Figure 1 shows the energy level diagram for the reactions (1). With a collision energy of less than 20 kcal/mol in O($^1D$)+HCl, two singlet states of HOCl are energetically accessible: the ground state, $X^1A'$, and the first singlet excited state, $1^3A''$. Both the $X^1A'$ and $1^3A''$ states of HOCl and HClO correlate directly with the reactants, O($^1D$)+HCl, and the products, OH($X^2II$)+Cl($2^3P$) in linear and bent geometries. Schinke performed classical trajectory calculations, concluding that most of the trajectories leading to OH+Cl products are tangle around the potential minimum of the HOCl complex, that is, the reaction proceeds mostly via an insertion/decomposition mechanism. The high excitation of OH rotation is thought to arise from initial excitation of the HOCl bond during the insertion act. The characteristic propensity for production of the $II(1A')$ $\lambda$ doublet sublevel implies that OH+Cl production results from dissociation of an HOCl$^+$ ($X^1A'$)$^+$ complex, with the nascent $\pi$ orbital remaining in the plane of the dissociating triatomic. The rotational surprisals for OH produced did not display the nonlinear behavior characteristic of that formed in a heavy–light–heavy abstraction. This rotational surprisal analysis for the OH fragment produced also supports the insertion/decomposition mechanism. The formation of rapidly bending HOCl$^+$ is followed by Cl–O bond cleavage to produce OH+Cl.

Concerning the OCl+H channel, in the linear geometry the products OCI($^1II^+$)+H($^3S$) correlate with the excited state $1^1II(1^1A')$ while OCI ($^1II^+$)+H($^2S$) correlate with the ground state $1^1II(1^1A')$ of HOCl and HClO. The crossing can be avoided at bent geometries. Hence, a H atom also could be produced via the bent ground state HOCl and/or HClO. However, we may reject this conclusion because our results of the isotope effect on the branching ratios $\phi_{(1b)}/\phi_{(1a)}$ could not be reproduced by the PST theory. More detailed discussion will be given below.

**Channel branching ratio of primary processes**

Measurements of the absolute rate constants for reaction (1) and product yield at 297 K have been reported by Wine et al. They estimated the branching ratio for reactions (1a) and (1b) to be $k(1b)/k(1a)=0.36±0.10$. Balucani et al. detected OCI products from reaction (1b) in a crossed-beam experiment with a mass spectrometer. Since they could not detect the OH products, they estimated a lower limit of the branching ratio $\phi_{(1b)}/\phi_{(1a)}>0.34±0.10$ at $E_{coll}=12.2$ kcal/mol. Our value of 0.24±0.06 at $E_{coll}=7.6$ kcal/mol is almost consistent with the estimated value, although the average collision energies are different among those estimations and our experiment. Concerning isotope effect, the obtained channel branching ratio $\phi_{(1b)}/\phi_{(1a)}$ is three times larger than that of $\phi_{(2b)}/\phi_{(2a)}$. This large isotope effect should be attributed to the change of the cross section for the OCI+H(D) process and not to that for the OH(OD)+Cl process. Actually, some isotope effect is observed in $\langle f_1^2 \rangle$ for H and D formation while not for Cl formation as shown in Table I.

Figure 1 shows that the exit channel producing OCI+H is 38.1 kcal/mol above that producing OH+Cl. Hence, the dissociation process of the HOCl$^+$ complex to OCI+H is extremely unlikely compared to OH+Cl. Nevertheless, the branching ratio $\phi_{(1b)}/\phi_{(1a)}$ is fairly large. The statistical calculations listed in Table II do not reproduce the observed branching ratios. This suggests that some dynamical constraints affect branching of the reactions. One explanation for the large $\phi_{(1b)}/\phi_{(1a)}$ is that the reaction mechanism for OH+Cl is the insertion/decomposition process, while that for OCI+H is not. The attack of the O($^1D$) atom at the Cl end of HCl could lead to OCI+H products with an abstraction mechanism. The relative velocity between O and Cl atoms is much slower than the motion of the H atom during the reaction of O($^1D$)+HCl. In this abstraction mechanism, the H atom moves out of the vicinity of the Cl atom before the O atom comes near to the Cl atom and the potential surface becomes covalent.
The velocity of a H atom is two times faster than that of a D atom with the kinetic energies listed in Table I, which may result in the large isotope effect observed in the branching ratio, that is, [ClO + H]/[OH + Cl] is larger than [ClO + D]/[OD + Cl]. On the other hand, a sideways attack of O(1D) to HCl forms an HOClI complex, resulting in production of OH + Cl via the insertion/decomposition mechanism. These two different reaction pathways (abstraction and insertion) should be on the same ground state surface (1A′). Since the HClO and the HOCl configuration easily convert between each other due to a small barrier on the ground electronic surface, the two configurations may not be distinguished from each other.

The other explanation for the observed isotope effect on the branching ratio \( \phi_{(1b)}/\phi_{(1a)} \) is the change in the approach of the reactants with the symmetry of 1A″ which leads to ClO + H products (see Fig. 1). Kruus et al. observed infrared chemiluminescence from vibrationally excited HCl(v) molecules which result from the electronic-photodissociation (E-V) energy transfer, that is, O(1D) + HCl → O(3P) + HCl(v). The relative yield of the E-V process for the OH + Cl formation was estimated to be 0.06 ± 0.02. The formation of O(3P) was confirmed by a laser-induced fluorescence experiment at 130.2 nm in the reaction of O(1D) with HCl where O(1D) atoms were produced by N₂O photodissociation at 193 nm. Kruus et al. proposed that the fast E-V process takes place on the 1A″ surface, since 1A″ and 1A′″ surfaces of the HOCl intermediate are nearly energetically degenerate over a large region of the configuration space. The reaction process on the 1A″ surface should have an abstraction mechanism, since there is no potential stabilization between the entrance and the HOCl(1A″) state (see Fig. 1). Therefore, the isotope effect on the branching ratio can be explained by the abstraction through the 1A″ state. In the case of O(1D) + DCI, more trajectories on the 1A″ surface may lead to the E-V transfer or go back to the reactants than those of O(1D) + HCl.

Energy distribution

The average product translational energy in reaction (1a), O(1D) + HCl → OH + Cl is calculated from the Doppler profile of the Cl atoms. \( \langle f'_l \rangle \approx 1/3 \) is smaller than the value (3/7) expected from the prior energy distribution if all vibrational modes are active in energy redistribution. In other words, decomposition of the hot HOCl complex occurs before the excess energy is redistributed in the complex. In reaction (1b), O(1D) + HCl → ClO + H, the average product translational energy is smaller than in the OH + Cl case due to the difference in the available energies, while the average fraction of the available energy partitioned into translation is \( \langle f'_l \rangle \approx 1/2 \). The large \( \langle f'_l \rangle \) for H atom may be explained by the presence of a potential barrier in the exit channel on the 1A″ surface of HOCl or on the ground state collinear H–Cl–O configuration.

Fine structure branching ratios

Table III lists the branching ratios [Cl*]/[Cl] = 0.18–0.20 in reaction (1) and (2). Figure 5 shows a correlation diagram for the OH + Cl (3P) reaction, in which the linear structure of the HOCl intermediate is assumed and the values of the projection \( \Omega \) of the total electronic angular momentum along the internuclear axis are conserved. As described above, with a collision energy of less than 10 kcal/mol the X 4A″ and the 1A″ singlet states of HOCl are accessible. It was proved that reaction (1a) mainly proceeds via the ground state (4A″) since a preferential formation of the OH II (4A′) λ sublevel was observed. These results, however, do not exclude the possibility that a small portion of reaction (1a) takes place via the excited state (1A″) of HOCl. Figure 5 indicates that both the 4A″ (1Σ+) and 1A″ (1Π) state of HOCl correlate to Cl(3P)/OH. The diagram with a bent geometry (C₂ symmetry) also gives the same results. Thus, in the adiabatic limit the branching ratio [Cl*]/[Cl] is expected to be zero.

The fact that both Cl* and Cl atoms were observed in the reactions O(1D) + HCl indicates that the nonadiabatic couplings take place with other electronic states which correlate to Cl(3P)/OH during the course of the reaction. In the diabatic limit, the branching ratio [Cl*]/[Cl] is

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[Cl*]/[Cl(3P)]</th>
<th>Expt.a</th>
<th>Diabaticb</th>
<th>Adiabaticc</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1D) + HCl → OH + Cl</td>
<td>0.20 ± 0.05</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(1D) + DCI → OD + Cl</td>
<td>0.18 ± 0.03</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(1D) + ClI → OCl + Cl</td>
<td>&lt;0.03</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

aExperimental results.
bDiabatic limit case, based on Ref. 21.
cAdiabatic limit case, based on correlation diagram.
expected to be statistical, i.e., 0.5. It is likely that those couplings take place in the exit channel region at large distances between OH and Cl because the adiabatic potential surfaces, correlating to both Cl*(2P1/2) + OH and Cl*(2P3/2) + OH, asymptotically become almost degenerate with the free atom energies that are split only by 2.5 kcal/mol.

In the reaction O(1D) + Cl2, when O(1D) is far from Cl2, it has five degenerated singlet states and hence there are five potential surfaces on which the reaction could take place. The products OCI(2Σ) + CI*(2P1/2) are in 16 possible states. One of them is correlated with the ground state Cl2O. The experimentally obtained value of [Cl*]/[Cl] < 0.03 indicates that reaction (3) proceeds adiabatically along the reaction pathway.

The degree of adiabaticity is governed by the following parameter:

\[ \xi = \frac{(R/v)}{(\hbar/\Delta E)} \]

where \( R \) is the length of the interaction region, \( v \) is the relative speed of the separating fragments. For a slow separation process, that is, \( v \) is small, the adiabaticity parameter \( \xi \) is large. The value of \( \xi \) is large for a large energy separation of the interacting states \( \Delta E \). The value of \( \Delta E \) may be almost equal to the spin–orbit energy splitting of the CI*(2P) fragments, and hence, \( \hbar/\Delta E \) is considered as a measure of the time for precession of electrons in the molecule. Thus, the branching ratio is a function of both relative velocity of the separating fragments and strength of mixing of potential curves due to the spin–orbit interaction.

The negligible formation of Cl* in reaction (3) can be explained by this adiabaticity parameter. The intermediate state OCI2 has two chlorine atoms in the molecule. Since the spin–orbit interaction in OCI2 is larger than that in HOCI, the dissociation of OCI2 proceeds more adiabatically. This also has been observed in the photodissociation LIF measurements of OCI2.

The correlation diagram shown in Fig. 5 for O(1D) + HCl predicts that 2Π(Ω = 3/2) states of OH radicals will be formed in an adiabatic process, if the OH(2Π) + CI*(2P) process takes place via the X 1A' surface. In the LIF measurements of OH from reaction (1a), it seems that \( \Omega = 3/2 \) states are a little more populated than \( \Omega = 1/2 \) states (see Fig. 2 of Ref. 4). Since the energy splitting between OH(2Π) 2 / 3 and \( \Omega = 1/2 \) states is quite small (0.36 kcal/mol), the adiabaticity parameter \( \xi \) becomes small for branching of the 3/2 and 1/2 states. Therefore, the population ratio of [2Π(Ω = 1/2)]/[2Π(Ω = 3/2)] may become close to the diabatic limit, that is, \( \xi = 0.5 \) due to nonadiabatic coupling of the potential curves at the exit channel.

**SUMMARY**

(1) In the reaction of O(1D) with HCl and DCI, we found a large isotope effect on the reaction branching ratio [OCI + H]/[OH + Cl] > [OCI + D]/[OD + Cl]. This isotope effect cannot be reproduced by the statistical theories which are the prior distribution and the phase space theory. This isotope effect suggests that the H (D) formation arises from abstraction by O(1D) of Cl from HCI (DCI) while the CI formation by insertion/decomposition.

(2) In the reaction of O(1D) with HCl, the average product translational energy for OH + Cl is larger than the values calculated from the statistical theory. These results imply that decomposition of the hot HOCI complex occurs before the excess energy is redistributed in the complex.

(3) The fine-structure branching ratios for the CI*(2Pj) products imply that reaction take place nonadiabatically for O(1D) + HCl while completely adiabatically for O(1D) + Cl2.

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**APPENDIX**

The level density for \( AB(v_f,j_f) + C \) products from a reaction \( A + BC \) at a given total energy \( E_{\text{total}} \) is, \(^{19}\)

\[ \rho(v_f,j_f,E_{\text{total}}) = \frac{\rho_T(E'_{\text{total}})}{(2j_f+1)} \rho_T(E'_{\text{total}}) \]

where \( E'_{\text{total}} \) is the relative energy of translation. Then, the total density of states, \( \rho(E_{\text{total}}) \) is obtained by summing over the various possible final states,

\[ W_f(E_{\text{total}}) = g_f \sum_{v_f} \sum_{j_f} (2j_f+1) \rho_T(E-E'_{\text{total}}) \]

where \( E'_{\text{total}} \) is the internal energy of \( AB(v_f,j_f) \) and \( g_f \) is the degeneracy of the product electronic state. The prior distribution predicts the channel branching ratio \( \phi_{(1b)/1a} \) by \( W_f(E_{\text{total}}) \).

The phase space theory (PST) presented by Pechucas et al.\(^{14}\) conserves total angular momentum as well as total energy. The potential functions of the interaction were assumed to be van der Waals type \( V(r) = -C_6 r^{-6} \) for both entrance and exit channels. The \( C_6 \) constants were estimated from dipole moment and polarizability. The \( C_6 \) values used in calculation are listed in Table IV. The rotational and vibrational constants of the reactants and products are taken from Huber and Herzberg.\(^{20}\) Internal freedoms of the reactant HCI (DCI) were assumed to be in the ground vibrational and rotational states, that is, \( \nu_j = 0 \) and \( j_i = 0 \). Since both the exothermicity of the reaction and
TABLE IV. $C_6$ constants used in the phase space calculations.

<table>
<thead>
<tr>
<th></th>
<th>O–HCl</th>
<th>OH–Cl</th>
<th>OCI–H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6(10^{-6} \text{ erg cm}^6)$</td>
<td>32$^a$</td>
<td>30$^b$</td>
<td>25$^b$</td>
</tr>
</tbody>
</table>

$^a$ Taken from Ref. 22.
$^b$ Calculated by using the approximation given by Ref. 23.

the c.m. velocity of O$(^1D)$ are sufficiently large, this assumption would not alter the results very much.

The PST models determine the maximum orbital angular momentum of the initial state for formation of the complex,

$$L_i(L_i+1)\frac{4}{9}L_f(L_f+1)\frac{4}{9}2L_f$$

The symbols used are $E$ for energy; $n$ for vibrational quantum number; $J$, $L$, and $j$ for total, orbital, and rotational angular momentum quantum numbers; and $\mu$ and $I$ for three-body reduced mass and two-body moment of inertia; suffix $i$ and $f$ refer to initial and the final state, respectively.

The probability of forming a complex is $1/(2L_f+1)$ and the total energy $E_{\text{total}}$ is

$$E_{\text{total}}=E_f+E(v_f)+(J_f(J_f+1)\frac{4}{9}L_f)+Q_f$$

where $Q_f$ is the zero–zero exothermicity of the reaction $i\rightarrow f$ and $v_f$ is the vibrational quantum number. Conservation of angular momentum implies that each manifold $(L_f,j_f)$, such that

$$|L_f-j_f|<L_i<L_f+j_f,$$

contains one state accessible from $(L_i,L_i)$. Further, the requirement that the complex be able to dissociate over the final-state orbital angular momentum barrier restricts by

$$L_f(L_f+1)\frac{4}{9}6\mu_j C_6^{1/3}[E(j_f)/2]^{2/3}$$

For given $v_f$ and $j_f$, Eqs. (A2) and (A3) define a bound region in the $(L_f,j_f)$ plane: The number of states of reaction product accessible from $(E_{\text{total}},L_{\text{total}},L_{i2})$ is the number of integer-pair points $(L_f,j_f)$ within or on the boundary of the region. Denote this number by $N(v_f,E_{\text{total}},L_{\text{total}},L_{i2})$ and let

$$N(E_{\text{total}},L_{\text{total}},L_{i2})=\sum_j \sum_{v_f} g_f N(v_f,E_{\text{total}},L_{\text{total}},L_{i2}),$$

where the summation over $f$ is that over the reaction paths, that is, the OH+Cl and OCI+H paths. The probability of dissociation of the complex to an accessible manifold $(v_f,E_f',L_{f'},j_{f'})$ is

$$P(v_f,E_f',L_{f'},j_{f'};E_{\text{total}},L_{\text{total}},L_{i2})=1/N(E_{\text{total}},L_{\text{total}},L_{i2}),$$

where $E_f'$ is the relative energy of translation in the final state. The cross section for a reaction path is

$$\sigma_f=\frac{g_f \pi \mu_j^2}{2\mu_j E_f'} \sum_{v_f} \sum_{j_f} \sum_{L_f} (2L_f+1)$$

$$\times \sum_{L_f} P(v_f,E_f',L_{f'},j_{f'};E_{\text{total}},L_{\text{total}},L_{i2}),$$

(A4)

where $E_f'$ is the relative energy of translation in the initial state. The branching ratio may be predicted as a ratio of the $\sigma_f$ values.