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COMMUNICATIONS

Rovibronic state to rovibronic state reaction dynamics: $O(^3P)+HCl(v=2,J)\rightarrow OH(v',N')+Cl(^2P)$

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An ultimate aim in the study of reaction dynamics of elementary processes is to specify at will the relative translational and internal energies of the reagents and to determine the resulting relative translational and internal energies of the products. We report here what we believe may be a major advance toward obtaining this goal, namely, rovibronic state to rovibronic state reaction dynamics. The system chosen for study is

$$O(^3P) + HCl(v=2,J) \rightarrow OH(v'=0 \text{ and } 1, N') + Cl(^2P), \tag{1}$$

where HCl is prepared in a single rovibronic level using a tunable optical parametric oscillator (OPO) and the rovibronic levels of the OH reaction product are monitored using laser-induced fluorescence (LIF).

For the nearly thermoneutral reaction of $O(^3P)$ with ground state HCl ($\Delta H_0^0 = 0.9$ kcal/mol) numerous experimental[1–5] and theoretical[6,7] studies have concerned the reaction rate enhancement by vibrational excitation of the HCl reagent. The reaction rate constant for $HCl(v=1)$ and $HCl(v=2)$ is roughly a factor of 10^2 and 10^4 larger, respectively, than the room temperature (293 K) rate constant of $1.3 \pm 0.2 \times 10^{-16}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ (Ref. 8). Quasiclassical trajectory (QCT) calculations for this reaction system have been performed by both Brown and Smith[6] and Persky and Broida.[7] The latter constructed two LEPS surfaces, denoted I and II, which reproduce the available kinetic data, but which show very different dynamical behavior with respect to rotational excitation of $HCl(v=0)$. Surface I exhibits a modest increase in reactivity for $J > 6$ and predicts substantial rotational excitation of the OH product. For surface II the reaction cross section decreases strongly with J of $HCl(v=0)$ and yields much less rotational excitation of the product.

Our experiment is carried out in a (1:1) flowing mixture of HCl and NO_2 maintained at 0.100 Torr. Photolysis of NO_2 with 355 nm light produces $O(^3P)$ exclusively,[9] with a velocity spread corresponding to a distribution over the internal product states of $NO(X\,^2\Pi)$.[10,11] Simultaneously the pulsed output of an OPO, propagating collinearly to the photolysis laser, selectively prepares $H^{35}Cl(v=2,J)$ by pumping at $\approx 1.75\,\mu$m. Following a short delay a third counterpropagating laser beam, probes the OH product via LIF using the $A\,^2\Sigma^+$-$X\,^2\Pi$ electronic transition in the region of 280–350 nm. The OH rotational distributions were invariant for delays of 200 ns or less. The fluorescence is collected perpendicular to the laser beam axis through appropriate interference filters. Both the photolysis and the probe lasers operate at a repetition rate of 20 Hz while the OPO runs at 10 Hz, thereby allowing subtraction of background signals not resulting from reaction of rovibrationally excited reagents.

Figure 1 presents the rotational distribution of $OH(v'=1)$ for three different initial rotational states of the reagent $HCl(v=2)$. As reagent rotation increases from $J=1$ to 6 to 9 ($E_{\text{rot}} = 21, 445, 953\ \text{cm}^{-1}$), the $OH(v'=1)$ rotational distribution is shifted to higher N' and becomes slightly more peaked. We also observe highly rotationally excited OH in its ground vibrational state. For reaction of $O(^3P)$ with $HCl(v=2,J=6)$ we find that the $OH(v'=0)$ distribution peaks at $N' \approx 15$–16 and extends to $N' = 20$. Initial estimates indicate that the rates of formation of $OH(v'=0)$ and $OH(v'=1)$ are comparable.

Preliminary measurements reveal a marked increase in reaction cross section with reagent rotation. The increase is approximately a factor of 3 over the range $J = 1$–10 in $HCl(v=2)$, but is not necessarily monotonic for low J. This finding is based on the relative magnitudes of the OH LIF intensity scaled by the relative concentrations of $HCl(v=2,J)$ excited (proportional to the thermal Boltzmann populations of the pumped level, the laser power, and the relative transition probabilities). A more quantitative procedure for measuring the number of $HCl(v=2,J)$ molecules prepared, together with a more detailed measurement of the product state distribution, is currently underway.

This increase in reaction cross section with reagent rota-

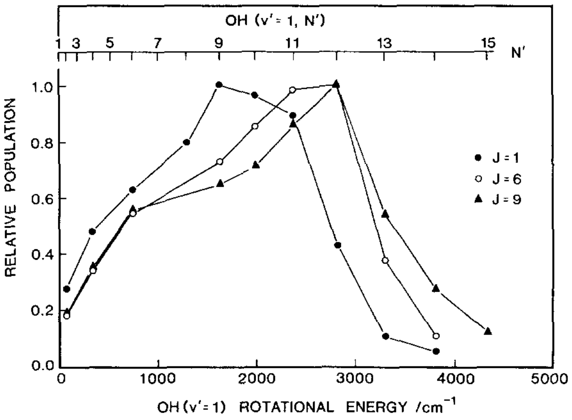

FIG. 1. Relative rotational population distributions of the OH($v' = 1$) product from the reaction of O(^3P) with HCl($v = 2,J$) for $J = 1$, 6, and 9. Each distribution has been normalized to the most populated level.

tion is consistent with surface I of Persky and Broida but clearly contradicts the predictions of surface II. An analogous light atom transfer reaction, Cl + HCl($v = 0,J$) → ClH + Cl, investigated theoretically using the centrifugal sudden distorted wave and QCT calculations, also exhibits a reaction rate enhancement with reagent rotation.[12] The competition between energy and orientational effects is often considered to control the way in which reagent rotation affects reaction cross sections. Both enhancement and suppression of reactivity with increasing rotational excitation of the reactants have previously been observed.[13]

The high degree of OH rotational excitation for O(^3P) + HCl($v = 2,J$) is similar to that which we have observed[9] for the related reaction of O(^3P) with ground vibrational state HBr. The high rotational excitation of the products can be explained as resulting from a repulsive X--H interaction in the exit channel. If the O–H–X geometry is slightly bent, the heavy + light–heavy mass combination readily channels this repulsive interaction into heavy–light product rotation.

The comparable production of OH($v' = 0$) and OH($v' = 1$) in reaction (1) is in contrast to the more extreme vibrational inversion of the analogous reaction of O(^3P) with HBr, where essentially no OH($v' = 0$) was observed.[9,14] The present direct observation of substantial branching into the vibrational ground state of OH from the reaction of O(^3P) with HCl($v = 2$) contradicts the conclusion of Butler *et al.*,[5] arrived at by kinetic modeling in Ref. 5, that the production of OH($v' = 0$) from this reaction is insignificant.

With the ability to exploit laser techniques for the definition and control of the initial conditions of the reactants and for the interrogation of the resultant products, we anticipate that the O(^3P) + HCl(v,J) reaction system can be studied with unprecedented detail.

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Theory of the molecular origins of the entropic portion of the Flory χ parameter for polymer blends

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Flory–Huggins (FH) theory[1-3] of polymeric fluids, including melts, blends, concentrated polymer solutions, micelles, etc.,[4] has been quite successful in explaining the general immiscibility of polymer blends, in part, because of a small entropy of mixing. However, comparisons of FH theory with experiment exhibit glaring discrepancies with the assumptions of the original lattice model from which mean field FH theory is approximately derived.[2] Foremost among these deficiencies is the need for a substantial composition dependent entropic component to what in the model is a purely enthalpic composition independent interaction, called the Flory χ parameter. Huggins' approach[2] produces an entropic χ^{entr} of magnitude too small to explain experimental data. Equation of state theories of polymeric liquids[5]