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Communications to the Editor

A New View of the Norrish Type II Elimination: Product Rotational State Distributions

Yuping Niu, Elizabeth Christophy, and
Jeanne M. Hossenlopp*

Department of Chemistry, Marquette University
P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

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Investigation of the patterns of reaction product internal energy release is an important tool in developing a fundamental understanding of the molecular-level mechanisms of reactions and, in particular, revealing insight into the details of the relevent potential energy surfaces (PES). Photochemical reactions which produce simple products have been the focus of a great deal of attention.[1] Our goal is to investigate the dynamics of reactions which produce polyatomic species, such as the well-known Norrish Type II elimination.[2] Reported here is the first study of Norrish Type II photodissociation dynamics. Relative populations were determined for selected rotational states of HCOOH produced in the 222-nm photolysis of isobutyl formate as shown in reaction 1.

$$(CH_3)_2CHCH_2OCHO + h\nu\ (222\ \text{nm}) \rightarrow (CH_3)_2C{=}CH_2 + HCOOH \quad (1)$$

Formic acid can be treated as a planar, nearly-prolate rotor.[3] Rotational states can be identified where the total angular momentum is projected on either the *a*-axis or the *c*-axis. Projection on the a-axis corresponds approximately to rotation about the C=O bond axis and is designated with the rotational quantum state $J_{J,0}$. The *c*-axis projection, $J_{0,J}$, corresponds to rotation in the plane of the molecule.[4] The experimental method involves monitoring the populations of rotational states, as shown below, which correspond to the two limiting cases for angular momentum projections described above.

$$HCOOH(\nu_3 = 0, J''_{Ka'',Kc''}) + h\nu\ (\sim 1770\ \text{cm}^{-1}) \rightarrow HCOOH(\nu_3 = 1, J'_{ka',Kc'}) \quad (2)$$

The general approach is similar to recently reported experiments on the Norrish Type I dissociation of acetaldehyde where no *K*-level dependence was observed for the HCO fragment.[5] Here, we demonstrate that a nonstatistical rotational state distribution with an apparent propensity for rotation about the *a*-axis can be observed even in room temperature bulb gas experiments.

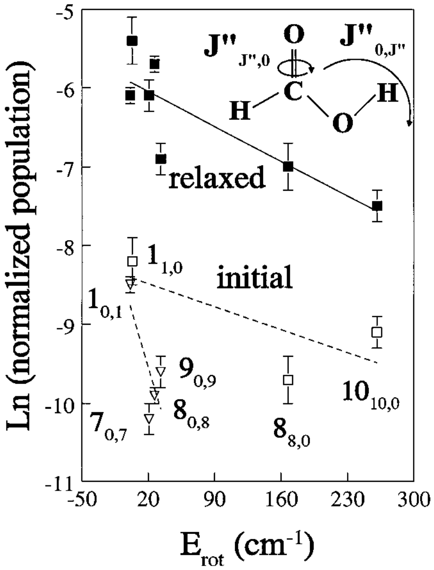

Figure 1. Rotational state Boltzmann distribution plots. The lower set of points, which are labeled with respect to the rotational level of the lower state used in each IR transition, correspond to signals acquired on an approximately 3 collision time scale. Dashed lines are drawn solely to guide the eye. The upper set of points is the limit of the exponential fit where $T_{rot} = 240 \pm 80$ K.

The experimental apparatus is described in a paper on quantum yield measurements.[6] All of the dynamics experiments were performed with 222-nm photolysis of 100-mTorr samples of isobutyl formate. Transient IR signals were obtained for seven rotational states with $J \leq 10$ using R-branch transitions of the carbonyl stretching vibrational band. In order to normalize for infrared transition intensities, formic acid (Lancaster, 97%) was carefully degassed via multiple freeze−pump−thaw cycles in liquid nitrogen. Under the experimental conditions used here, the vapor was significantly enhanced in HCOOH[7] and no correction was made for the presence of water vapor. Pressures were corrected for the HCOOH monomer−dimer equilibrium.[8] IR absorption coefficient measurements were made using diode laser current modulation settings which were identical to those used in the transient IR measurements. Line strengths were normalized with respect to the fraction of HCOOH molecules in a given rotational state at room temperature. The standard asymmetric rotor expansions were used to calculate rotational energies.[9]

Normalized rotational state populations were obtained by dividing the IR $\Delta I/I_0$ by the $(2J + 1)$ rotational state degeneracy and by the infrared line strength. In addition, the relative populations were normalized with respect to the UV laser energy and ester sample pressure in order to correct for small fluctuations between measurements. The rise in IR absorption at short times was fit to an exponential function. Figure 1 shows the resulting Boltzmann plots for $\Delta I/I_0$ obtained in two ways. The lower set of points, which are labeled with respect to rotational state, are the values for ln(normalized population) at 1 μs after the photolysis pulse. The upper set of points represent the normalized populations in the limit $t = \infty$ of the exponential rise fitting. A rotational temperature of 240 ± 80 K is obtained

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from a least-squares fit to these data. This corresponds to the initial distribution being nearly relaxed to room temperature. There is no clear evidence of any angular momentum projection dependence on populations at the long time limit. Error bars were calculated by propagating the uncertainty obtained in fitting the transient signals along with uncertainty in laser energy and sample pressure. Multiple experiments on a given transition agree to within 10%.

The results shown in Figure 1 demonstrate that the HCOOH rotational state populations are nonstatistical at 1 μs after ester photolysis. The population of HCOOH molecules with rotational excitation corresponding to in-plane rotation drops off faster with respect to rotational energy than does the population of the other limiting-case angular momentum projection. The effect continues to persist during the first 5 μs. Over a period of tens of microseconds, the populations slowly relax toward an equilibrated, room temperature distribution. While the 1 μs populations are partially relaxed for a 100 mTorr bulb gas sample, there is clear evidence of a nonstatistical partitioning of rotational energy.

The Norrish Type II reaction in aliphatic compounds is believed to be initiated via both singlet and triplet state hydrogen abstraction.[2] While esters have not been as well-studied as ketones and aldehydes, Hg($^3P_1$) sensitized experiments suggest that the triplet channel is important for esters.[10] In solution[11] and in the gas phase,[12] lifetimes for aliphatic triplet Norrish Type II diradicals have been reported to range from tens of nanoseconds to microseconds, depending on detection technique. This may contribute to the observation in this work that the nonstatistical rotational distribution is evident for several microseconds.

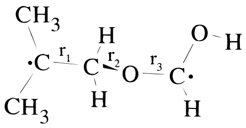

Figure 2. Isobutyl formate diradical elimination transition state. The optimized UHF/STO-3G structure was obtained by mixing the HOMO and LUMO as described for calculations on ethylformate.[6] Normal mode calculations were performed and identification of the diradical minimum and transition state structure was verified by the presence of respectively zero and one negative eigenvalue in the derivative matrix. The optimized values of r_1, r_2, and r_3 are 1.53, 1.45, and 1.40 Å, respectively, for the diradical and 1.44, 1.81, and 1.43 Å for the elimination transition state.

The UHF/STO-3G structure of the transition state for the singlet diradical elimination is shown in Figure 2. At this level of calculation, the OCOC dihedral angle in the transition state is 78°. Application of a simple impulsive model,[13] with the initial force placed along the axis of the breaking bond, leads to the prediction that in-plane rotation would be not be favored. This is consistent with the observed initial rotational state populations. A complete analysis of the source of nonstatistical rotational distributions must include the possibility of other factors such as a strong exit channel effect, dissociation from bending states (ref 1, Chapter 10), and diradical torsional motions.

Further experimental and computational results are necessary to provide a more detailed picture of the source of the observed rotational state propensities. It is clear, however, that even for room temperature bulb gas samples, determining rotational state populations for the limiting-case angular momentum projections on the principal molecular axes is a powerful tool for exploring polyatomic photodissociation dynamics. Work is in progress to develop this view of the Norrish Type II reaction of formate esters.

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