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Citation: *The Journal of Chemical Physics* **98**, 8341 (1993); doi: 10.1063/1.464540

View online: <http://dx.doi.org/10.1063/1.464540>

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# Crossed beam studies of four-atom reactions: The dynamics of OH+CO

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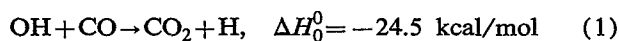
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(Received 9 February 1993; accepted 11 March 1993)

The angular and velocity distribution of CO<sub>2</sub> product from the reaction OH+CO at 14.1 kcal/mole collision energy has been obtained in a crossed molecular beam study. The reaction is found to proceed through an osculating HOCO complex living about one rotational period. About 65% of the available energy goes into product translation.

## INTRODUCTION

The reaction



is of major practical importance, since it represents the main OH removal pathway in the atmosphere<sup>1</sup> and is the second most important elementary reaction in combustion, acting as the last step in the oxidation of hydrocarbons.<sup>2</sup> Because of this, it has been one of the reactions most thoroughly studied in the gas phase kinetics of free radicals. The energetics are outlined in Fig. 1. The rate constant has been determined over a wide range of temperatures and shows an interesting non-Arrhenius behavior with a very pronounced upward curvature above 500 K.<sup>3-5</sup> Kinetic studies at some state selected level have also been carried out.<sup>3(c),6</sup>

Very limited experimental information is available on the dynamics of reaction (1). Early flash photolysis studies,<sup>6(a),6(b)</sup> coupled to time-resolved infrared detection, did not observe any infrared emission from CO<sub>2</sub> formed in reaction (1), and concluded that CO<sub>2</sub> is formed mainly in its ground vibrational state. In a very recent flash photolysis study, Smith and co-workers<sup>3(d),7</sup> using tunable diode laser absorption found that only 6% of the total energy available to the CO<sub>2</sub> product is channeled into vibrational energy at room temperature. A partially state-selected integral cross section of  $19 \pm 10 \text{ \AA}^2$  for reaction (1) was measured by Wolfrum at a translational energy of 1.32 eV by detecting H atoms.<sup>8</sup> New measurements<sup>9</sup> at the same energy give a value of about  $2.4 \text{ \AA}^2$ . Inelastic excitation of OH by CO has recently been investigated in pulsed crossed beams.<sup>10</sup>

More information is available on the reverse endothermic reaction  $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$ , mostly derived from state- and time-resolved experiments with sophisticated laser techniques. Using photolitically produced "hot" H atoms, absolute reactive cross sections and OH internal state distributions were measured in the energy range from 30 to 60 kcal/mol both in gas-phase<sup>11</sup> and in van der Waals complexes formed in supersonic expansions,<sup>12</sup> by using pump-probe laser techniques. In some cases the CO product was monitored.<sup>13</sup> Inelastic excitation of CO<sub>2</sub> by H atoms has also been investigated.<sup>14</sup> Recently, picosecond and femtosecond probing techniques have been used to monitor in real time the birth of OH following the breakup of the HICO<sub>2</sub> van der Waals molecule by UV photolysis; life-

times of the HOCO intermediate complex were also measured.<sup>15,16</sup> Elegant as these dynamics experiments are, they do not provide, however, a sensitive probe of the details of the PES along the minimum energy path. Spectroscopic observation in the gas phase of the HOCO species has recently been reported.<sup>17</sup>

A large amount of theoretical work has been performed on reaction (1) and its reverse. Extensive *ab initio* calculations on the potential energy surface (PES) have recently been carried out.<sup>18,19</sup> An empirical PES based on a fit to the *ab initio* points was used for detailed quasiclassical trajectory studies.<sup>18(b)</sup> For the direct OH+CO reaction this surface exhibits no barrier in the entrance channel and a barrier of about 3 kcal/mol in the exit channel. Cross sections for HOCO complex formation, product energy partitioning, HOCO lifetime distributions, and thermal rate constants were calculated. In spite of all the work done, many questions about the dynamics of reaction (1) are still open, such as (a) is the reaction direct or is it going through a long-lived collision complex?, (b) if it is going through a long-lived complex, what is its lifetime and what is the dynamics of its decomposition?, (c) what is the energy partitioning?, and (d) what is the effect of the relative translational motion of the reagents on the reaction dynamics?

In this Communication, we report preliminary results of the first direct experimental investigation of reaction (1) under single-collision conditions, which give answer to some of the above questions. Angular and velocity distribution measurements of the CO<sub>2</sub> product were obtained from crossed molecular beam experiments at a relative collision energy,  $E_{\text{cm}}$  of 14.1 kcal/mol. These studies were made possible by the development of a continuous supersonic beam of OH radicals, which has permitted us, very recently, to also study in crossed beams the dynamics of another important reaction of OH, namely that with H<sub>2</sub>.<sup>20</sup>

Very recently, Kudla and Schatz,<sup>21</sup> and Clary,<sup>22</sup> using the same *ab initio* potential surface, have carried out quasiclassical and quantum-mechanical, respectively, scattering calculations of the differential cross section for CO<sub>2</sub> formation at several energies, including our experimental collision energy. Hence, direct detailed comparisons between experiment and theory are becoming feasible.

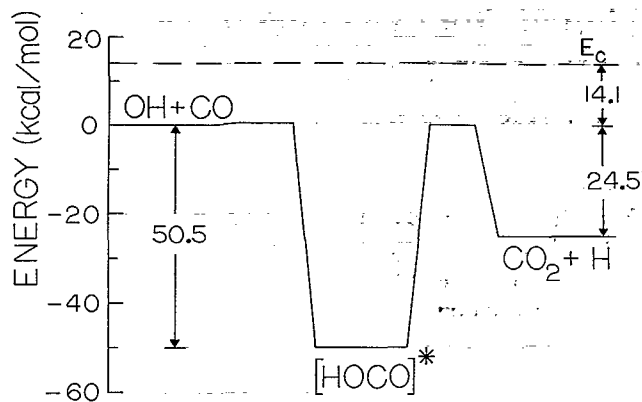


FIG. 1. The generalized reaction coordinate diagram for  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ . The dashed line represents the collision energy  $E_c$ .

## EXPERIMENT

Molecular beams of hydroxyl radicals and carbon monoxide were crossed under single collision conditions in a scattering apparatus which has been described previously.<sup>23,24</sup> In order to produce a continuous supersonic beam of OH radicals, a high-pressure, high power radio-frequency (rf) discharge beam source, similar to that used for producing continuous beams of  $\text{O}(^3P, ^1D)$ , was employed.<sup>24</sup> The rf discharge is maintained in a water cooled quartz nozzle, of 240  $\mu\text{m}$  diam, in 300 mbar of a 2.5%  $\text{H}_2\text{O}$  in helium gas mixture. Operating at 260 W of rf power, an intense beam of OH radicals with peak velocity of about 3100 m/s and velocity spread of about 20% was attained. The OH beam is found to contain also other species, such as atomic oxygen and hydrogen, as well as undissociated water, but they do not interfere because the detected  $\text{CO}_2$  in a single-collision experiment can only originate from the reaction of CO with OH. The OH are expected to be in the ground electronic state,  $^2\Pi$ , and, following supersonic expansion, essentially in  $v=0$  and in the lowest few rotational levels. In fact, possible electronically excited states of OH are short lived ( $< 1 \mu\text{s}$ ),<sup>25</sup> and vibrational and rotational relaxation of OH by water is known to be very fast.<sup>26</sup> Although we have indication from the study of the  $\text{OH} + \text{D}_2$  reaction<sup>20</sup> that OH in the beam is predominantly in the  $v=0$  level, a detailed characterization of its internal quantum states is desirable, and is being pursued using spectroscopic techniques.

The CO beam was produced by a supersonic expansion of pure CO at 4.5 bar through a 75  $\mu\text{m}$  stainless-steel nozzle kept at 600 K. The peak velocity was 1048 m/s with a full width at half maximum (FWHM) spread of about 16%. The CO molecules are expected to be essentially in the lowest ( $j=0,1,2$ ) rotational levels.

The two reactant beams, after two stages of differential pumping for OH and one for CO, were crossed at  $90^\circ$  in a large scattering chamber kept in the  $10^{-7}$  mbar pressure range. The  $\text{CO}_2$  product was detected with a rotatable ultra-high-vacuum electron-impact quadrupole mass spectrometer kept in the  $10^{-11}$  mbar range. In order to improve the signal-to-background ratio, experiments were performed using  $\text{H}_2^{18}\text{O}$ . This allowed us to detect  $\text{CO}_2$  at  $m/e=46$ , which has about 2 orders of magnitude lower

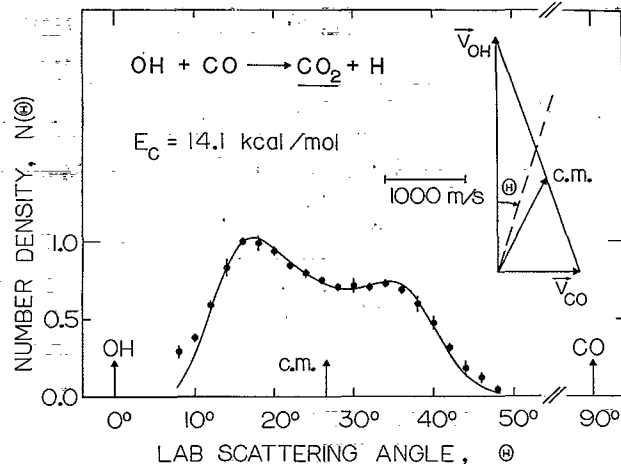


FIG. 2.  $\text{CO}_2$  product laboratory angular distribution from the  $\text{OH} + \text{CO}$  reaction at a collision energy,  $E_c$ , of 14.1 kcal/mol. The kinematic ("Newton") diagram is also shown. The solid line represents the calculated angular distribution with best-fit c.m. angular and translational energy distributions.

inherent background in the detector than  $m/e=44$ . Angular distributions were measured by modulating the CO beam at 160 Hz for background subtraction. Product velocity distributions were obtained at ten angles by the cross-correlation time-of-flight (TOF) technique operating at 5  $\mu\text{s}/\text{channel}$ .

## RESULTS AND DISCUSSION

The angular distribution of  $\text{CO}_2$  product at  $E_c=14.1$  kcal/mol is shown in Fig. 2, together with the most probable Newton diagram. As can be seen, the angular distribution exhibits a backward-forward structure with more intensity in the forward direction (with respect to the OH beam), and it is quite broad for such a heavy product left by a light H atom. This suggests that the reaction is proceeding through the formation of an intermediate complex whose lifetime is comparable to its rotational period, and that a large fraction of the available energy is released into translation. However, for a quantitative correct physical interpretation of the dynamics, the angular and translational energy distributions in the center-of-mass (c.m.) coordinate system were derived from the angular and TOF distributions recorded in the lab system, using a forward convolution trial and error best-fit procedure.<sup>27</sup> The continuous line in Fig. 2 is the lab angular distribution calculated with the c.m. angular distribution depicted in Fig. 3 and with a translational energy distribution witnessing about 64% of the available energy released into translation. From Fig. 3 one immediately sees that the c.m. angular distribution,  $T(\vartheta)$ , is weakly polarized and not symmetric along the relative velocity vector. The absence of any sharp peaking in  $T(\vartheta)$  suggests that there is a weak correlation between the initial and final angular momenta,  $L$  and  $L'$  (see below). Within the "osculating model" for chemical reactions,<sup>28</sup> the asymmetry in  $T(\vartheta)$  is related to the ratio of the mean complex lifetime,  $\tau$ , to its rotational

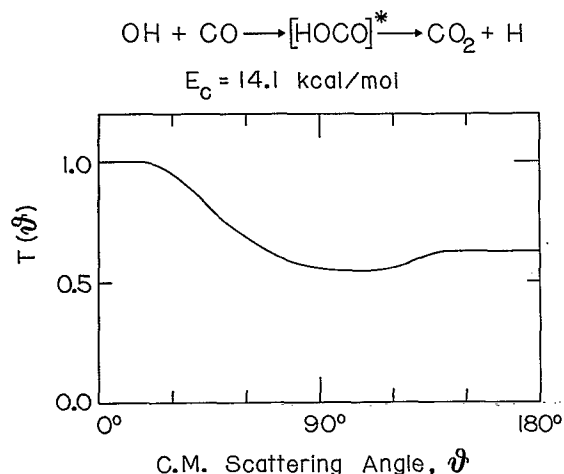


FIG. 3. Center-of-mass frame  $\text{CO}_2$  angular distribution from the  $\text{OH} + \text{CO}$  reaction at  $E_c = 14.1$  kcal/mol.

period,  $\tau_r$  (used as a "clock") according to the relation  $T(\delta = 180^\circ)/T(\delta = 0^\circ) = e^{-(\tau_r/2\tau)}$ . From the experimental ratio  $T(\delta = 180^\circ)/T(\delta = 0^\circ) = 0.63$ , one gets  $\tau/\tau_r = 1.08$ . If a reasonable estimate of  $\tau_r$  ( $\tau_r = 2\pi I/L_{\max}$ ,  $I$  being the moment of inertia of the rotating complex and  $L_{\max}$  its maximum angular momentum) can be made, the oscillating model can tell us the complex lifetime. The moment of inertia is calculated from the *ab initio* geometry,<sup>18(b)</sup> while a reliable upper bound on the impact parameter  $b_{\max}$  ( $b_{\max} = L_{\max}/\mu v_r$ , where  $\mu$  is the reduced mass and  $v_r$  is the relative velocity) for complex formation is obtained from the opacity function calculated by Kudla and Schatz<sup>21</sup> using quasiclassical trajectories on the *ab initio* surface. They found that the maximum impact parameter for the  $\text{OH} + \text{CO}$  reaction is about 1.6 Å at 14 kcal/mol translational energy, with the opacity function being approximately flat and dying out to zero at 1.6 Å. From  $b_{\max}$  one gets a lower limit of 0.64 ps for the mean complex lifetime (see Ref. 29). This value compares with other experimental and theoretical estimates. From their quasiclassical trajectory studies Kudla *et al.*,<sup>18(b)</sup> obtained an HOCO lifetime of 0.73 ps at a translational energy of 13.84 kcal/mol. Zewail and co-workers<sup>15</sup> recently measured HOCO lifetimes from studies of the reverse of reaction (1), starting from van der Waals impacted reagents and using real-time picosecond probing techniques. At an energy corresponding to about 14 kcal/mol above the  $\text{OH} + \text{CO}$  asymptote, they report a value of 3.9 ps. Very recently, Wittig and co-workers<sup>16</sup> have also carried out similar measurements in slightly different conditions than Zewail's group using femtosecond pulses and obtained, at a comparable energy, a lifetime of 0.6 ps.

The large fraction of available energy released into translation (64%, corresponding to about 25 kcal/mol) indicates the existence of strong repulsive forces between H and  $\text{CO}_2$  after the saddle point is passed. The repulsion in the exit channel disposes essentially all the potential energy associated with the high exit barrier (see Fig. 1) into translational motion of the products. For the specific mass com-

bination of reaction (1), angular momentum partitioning arguments<sup>31</sup> predict a significant correlation between the initial  $L$  and the final rotational angular momentum  $J'$ , from which it is deduced that the initial translational energy ( $E_c$ ) of the reagents is mainly deposited into  $\text{CO}_2$  rotational energy. These considerations are consistent with the bent geometry of the *ab initio* transition state:<sup>18(b)</sup> the strong torque exerted by the departing H atom to the  $\text{CO}_2$  moiety will, in fact, result into significant rotational excitation, which accounts for the weak polarization of the experimental angular distribution (see Fig. 3). This leaves very little room for the excitation of the vibrational degrees of freedom; indeed, very little  $\text{CO}_2$  vibrational excitation has been observed in flash-photolysis studies.<sup>3(d),6(a),6(b),7</sup>

The present experimental results provide a basis for a quantitative test of very recent dynamical calculations. Kudla and Schatz<sup>21</sup> have performed extensive quasiclassical trajectory calculations, on the *ab initio* surface, of the reactive differential cross section for  $\text{OH} + \text{CO}$  at the energy of our experiment, and Clary<sup>22</sup> has carried out similar calculations, on the same potential surface, using an approximate quantum-mechanical method.<sup>32</sup> Preliminary comparisons show reasonable agreement between experiment and theory.

Experiments at other collision energies and on the isotopic OD + CO variant are currently under way and should ultimately serve as a very sensitive test of the potential energy surface for this fundamental chemical reaction.

## ACKNOWLEDGMENTS

This work has been supported by MURST, CNR Bilateral Agreements and "Progetto Finalizzato Chimica Fine," ENEA and EEC Science Program. We thank G. C. Schatz and D. C. Clary for communicating to us their results prior to publication.

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