

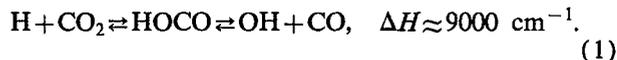
Subpicosecond OH production from photoexcited CO₂-HI complexes

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INTRODUCTION

Equation (1) depicts one of the most thoroughly examined gas phase reactions:



As such, it serves as a good prototype for studies of electronic structure,^{1,2(a)} quantum and classical reaction dynamics,² kinetics,³ statistical rate theories,^{3,4} nascent state distributions,⁵ steric effects,⁶⁻⁹ time resolved reaction rates,¹⁰ etc. In the past decade it has been the focus of a large number of studies involving photolytically produced fast H atoms in environments ranging from gas phase, single collision, arrested relaxation conditions (hereafter referred to as single collision conditions) to weakly bonded complexes formed in supersonic expansions. Under single collision conditions, detailed nascent OH level distributions have been reported for energies in excess of reaction threshold: $2000 \leq E^\ddagger \leq 11\,500 \text{ cm}^{-1}$, with a modest trend noted toward less statistical product level distributions at the higher energies.^{11,12} Thermally averaged rate constants, $k(T)$, have been measured for reaction (1) in the exoergic direction over the range $300 < T < 2000 \text{ K}$, and RRKM theory fits these data satisfactorily.^{3,4} For $E^\ddagger > 4000 \text{ cm}^{-1}$, RRKM theory predicts that HOCO[†] lifetimes will be subpicosecond, dropping to $\sim 120 \text{ fs}$ near $11\,500 \text{ cm}^{-1}$.¹³ It is interesting to see how well RRKM predictions hold up in this short lifetime regime.

Extensive *ab initio* calculations for CO₂-HBr van der Waals complexes have suggested that the main chemical effect of photoinitiating the reaction within the complex is steric, i.e., no significant propensity for carbon-bromine bonding, which would lead to the OC(Br)OH "supramolecule,"¹⁴ was found for either the A' or A'' orientation of the unpaired halogen orbital.^{8,9} These observations imply that the reaction proceeds through the HOCO[†] intermediate, similar to the $\text{CO}_2 + \text{H} \rightleftharpoons \text{HOCO}^\ddagger \rightleftharpoons \text{CO} + \text{OH}$ gas phase reaction.

Earlier reports by Scherer *et al.*,¹⁰ who used pump and probe pulses of several picoseconds duration, confirmed that OH deriving from photoexcited CO₂-HI complexes was produced via an indirect route, presumably involving the HOCO[†] intermediate, even for the high energies and unique entrance channel conditions characteristic of photoexcited complexes. In fact, lifetimes reported in their work were even longer than those estimated by using RRKM theory for the corresponding single collision conditions. This was a landmark study because it demonstrated that bimolecular processes could be clocked in real time.

In this Communication, we report subpicosecond rates for OH production from photoexcited complexes formed by expanding CO₂/HI/He mixtures into vacuum. Though the overall photoinduced reaction involves five atoms, the measured rates agree with a mechanism in which HOCO is formed with nearly the energy of its single collision counterpart and then decomposes as per RRKM theory, with no influence on the rate due to the nearby iodine. The RRKM parameters were obtained by fitting $k(T)$ over the range 300–2000 K.¹³ We suggest that both sets of measurements (ours and those of Scherer *et al.*) may be correct and that reconciling the observed differences can lead to a deeper understanding of such photoinitiated reactions in complexes, as well as in the gas phase.

EXPERIMENTAL METHOD AND RESULTS

The experimental approach is easy in concept but challenging in execution. The schematic drawing presented in Fig. 1 lists salient features; details will be published later. Briefly, the subpicosecond resolution pump-probe technique is used to detect OH following HI photodissociation within weakly bonded complexes that are formed by expanding mixtures of CO₂, HI, and He into a vacuum chamber through a pulsed nozzle (0.25 mm × 1.0 mm). Typical expansion conditions are 2% HI, 3% CO₂ and 95% He at a total pressure of 2.3 atmospheres. The laser source is a synchronously pumped, modelocked dye laser whose output is amplified to the mJ level with a 3-stage dye amplifier that is pumped with the 532 nm output from a regenerative amplifier system. About 80% of this radiation is doubled in KDP to $\sim 309.1 \text{ nm}$, providing $\sim 50 \mu\text{J}$ of probe radiation, covering a bandwidth of $\sim 100 \text{ cm}^{-1}$. This excites OH with a broad range of rotational quantum numbers, the average being $\langle N \rangle \sim 5.5$. The remaining 618 nm radiation is focused into a D₂O cell to generate a supercontinuum. A portion of this is selected with a dispersion compensated monochromator and amplified with a 2-stage dye amplifier pumped by the 355 nm output from the regenerative amplifier system. This radiation is then doubled into the region 235–255 nm, providing 20–40 μJ of pump radiation. LIF signals are obtained by using gated photon counting; a respectable signal level is one photon per pulse. The amplitude of the signal is found to increase linearly with the CO₂-HI concentration in the beam as measured *in situ* with a quadrupole mass spectrometer. Ion signals from (CO₂)₂HI⁺ and CO₂(HI)₂⁺ are less than 15% of that from CO₂HI⁺. Cross correlations between the pump and probe pulses, $R(t)$, are typically 0.5 to 1.2 ps FWHM, and are recorded simultaneously with the signal by difference

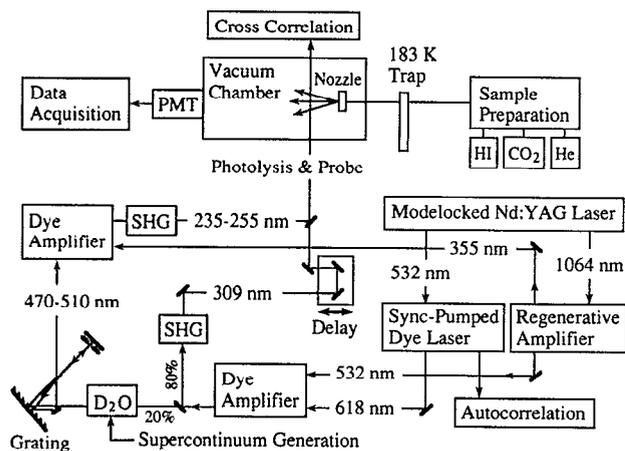


FIG. 1. Schematic drawing of the experimental arrangement.

frequency generation in a 0.1 mm thick BBO crystal right after the vacuum system.

Experimental traces of signal vs pump-probe delay time are presented in Fig. 2. The data are fit by a nonlinear least-squares-fitting routine assuming that coherent effects are not important for our experimental conditions:

$$S(t) \propto \int_{-\infty}^t R(s) \{1 - \exp[-(t-s)/\tau]\} ds, \quad (2)$$

where

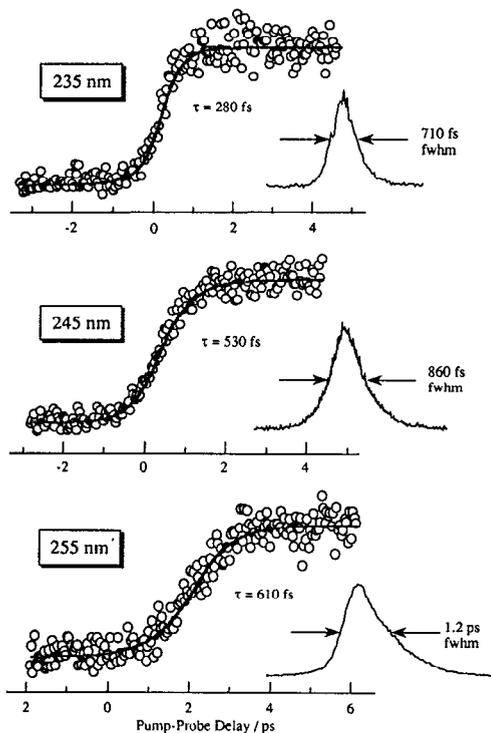


FIG. 2. Traces of OH LIF signal versus pump-probe delay at the indicated photolysis wavelengths. The solid lines are fits to the data using Eqs. (2) and (3). The cross correlations were recorded simultaneously with the LIF signals; those at 235 and 245 nm are typical, while 255 nm shows a "worst case" cross correlation.

$$R(s) = \int_{-\infty}^{\infty} I_{\text{pump}}(t) I_{\text{probe}}(t-s) dt. \quad (3)$$

$S(t)$ is the signal as a function of pump-probe delay time, and $1 - \exp(-t/\tau)$ is the assumed form of the molecular response function.

An absence of coherent effects cannot be assumed *a priori* when reactions are initiated and probed with subpicosecond laser pulses. We did not observe recurrences, oscillations, etc., in $\text{HOOH} + h\nu \rightarrow 2\text{OH}$, which occurs via a repulsive potential surface. Though such a reaction is a prime candidate, coherent effects are lessened by the large bandwidths of our laser pulses, which are much broader than the transform limit. OH production lifetimes < 150 fs were obtained for hydrogen peroxide by using Eqs. (2) and (3). Observing coherence is even less likely in a reaction like $\text{CO}_2\text{-HI} + h\nu \rightarrow \text{CO} + \text{OH} + \text{I}$, because the HOCO^\ddagger intermediate decomposes by a unimolecular decomposition mechanism that scrambles the OH phases as these species are produced.

Data were collected at several photolysis wavelengths in the range 235–255 nm. At each wavelength, many scans were taken, each requiring 1–4 h. Over a period of three months, over 70 scans were accumulated. Some look better than those shown in Fig. 2; many look about the same; most appear not as good. However, all share the common features of (i) distinctly subpicosecond τ values and (ii) being adequately represented by a single exponential rise, albeit within our limited S/N. Estimating experimental uncertainties is subjective. For the present results, we believe that $\pm 50\%$ is conservative; this will improve in the future.

DISCUSSION

The results presented in Fig. 2 show that OH is produced with a characteristic time—the single exponential rise time τ given by Eq. (2)—that is subpicosecond over the photolysis wavelength range 235–255 nm. This would be anticipated on the basis of (i) single collision conditions for photoinitiated reaction within the complex, and (ii) calculations of HOCO unimolecular decomposition rates using RRKM theory, such as those reported previously by our group.¹³ Figure 3 shows the RRKM rate vs E^\ddagger ; we consider this a reasonable estimate of $k(E)$ for the energies appropriate to the present experiments.

In contrast to single collision conditions, where there is a one-to-one correspondence between the energy of the HOCO^\ddagger intermediate and the photolysis wavelength, it is not possible to assign *a priori* either a single E^\ddagger value or a distribution of E^\ddagger values in experiments with complexes. The process of transferring the H atom from I to CO_2 can impart translational recoil between I and HOCO that is not present in the gas phase—the "squeezed atom effect"—and also a distribution of speeds may result. Consequently, at a given photolysis wavelength, HOCO^\ddagger can have somewhat less energy when formed via a complex than in the gas phase. This is borne out in calculations for Ar-HCl complexes,¹⁵ and experiments and calculations for Ar-HBr complexes.¹⁶ It remains to be seen how large the effect will

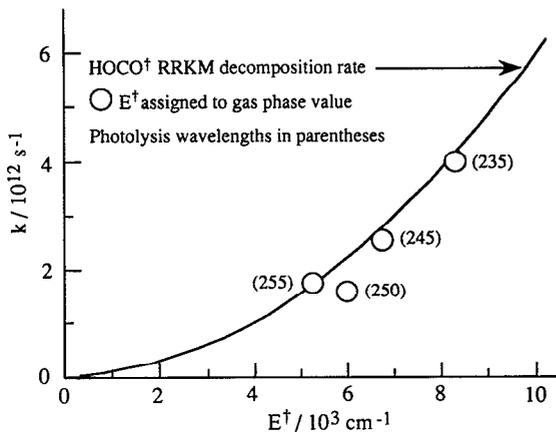


FIG. 3. The solid line is the RRKM HOCO⁺ decomposition rate (Ref. 13). Open circles are measured rates that are assigned to the E^\ddagger values of the corresponding gas-phase reactions; the assigned E^\ddagger values are upper limits. Uncertainties in the measured rates are $\pm 50\%$.

be for a case like CO₂-HI where a reactive window opens and takes in the hydrogen.

To get an idea of how large the squeezed atom effect might be, we draw upon earlier estimates of the distributions of HOCO E^\ddagger values that derive from state-to-state measurements for 239 nm photoexcited CO₂-HI complexes. A maximal entropy analysis of the OH rotational populations led to a bimodal distribution of E^\ddagger values: $\sim 30\%$ at $\sim 1000 \text{ cm}^{-1}$ and $\sim 70\%$ at $\sim 6000 \text{ cm}^{-1}$.¹³ Under single collision conditions at the same photolysis wavelength, E^\ddagger is approximately 7900 cm^{-1} . The bimodal distribution was necessary to fit the data, but the fit was not sensitive to the exact locations and/or widths of the two E^\ddagger clumps. We interpreted the 6000 cm^{-1} peak as due to the squeezed atom effect—as if the H + CO₂ collision energy of 16900 cm^{-1} for single collision conditions had been dropped by 1900 cm^{-1} , an 11% decrease. The $\sim 1000 \text{ cm}^{-1}$ peak was thought to be due to another mechanism, most probably higher-than-binary complexes. A similar analysis for 193 nm photoexcited CO₂-HBr complexes resulted in similar conclusions: $\sim 25\%$ at $E^\ddagger \sim 2000 \text{ cm}^{-1}$ and $\sim 75\%$ at $E^\ddagger \sim 9000 \text{ cm}^{-1}$, the latter corresponding to a 12.5% drop from the collision energy of 20500 cm^{-1} for single collision conditions.¹¹

To get the experimental rates into Fig. 3, we assigned them to the E^\ddagger values of the corresponding single collision reactions at the same photolysis wavelengths. These assigned E^\ddagger values are therefore upper limits. The photolysis wavelengths are given in parentheses. This *ad hoc* assignment of E^\ddagger values, with its attendant uncertainty, enables the reader to see, at least roughly, where the experimental rates fall relative to those calculated by using RRKM theory. The data presented in Fig. 3 were obtained by averaging a number of rates such as the ones shown in Fig. 2 at each photolysis wavelength. One sees that despite the experimental uncertainties in the measured rates, and despite the uncertainty in assigning E^\ddagger values, the results are in qualitative accord with the RRKM predictions.

The question remains: Why do the rates reported here differ from those reported by Scherer *et al.* by as much as an order of magnitude? We deem it unlikely that either measurement is incorrect, so does this suggest a coherent effect and/or a dependence on the OH($v=0$) rotational state being probed? With our broad probe bandwidth, an ensemble of OH rotational states is excited having $\langle N \rangle \sim 5.5$. On the other hand, Scherer *et al.* probed mainly $N=1$, though 3 points were obtained for $N=6$. Indeed, they found that lifetimes obtained monitoring $N=6$ were shorter than those obtained with $N=1$. Were a microcanonical ensemble of HOCO⁺ precursors responsible for the OH, this would be a strikingly non-RRKM result. Perhaps some reconciliation can be obtained by consideration of our maximal entropy analysis that discovered a source of cold OH that could be assigned to HOCO⁺ with $E^\ddagger \sim 1000 \text{ cm}^{-1}$. Unimolecular decomposition of HOCO⁺ intermediates having such low E^\ddagger leads to relatively long OH production lifetimes as well as OH rotational distributions peaked at low N . Specifically, E^\ddagger values around 1000 and 6000 cm^{-1} yield quite different OH rotational distributions, with 1000 cm^{-1} favoring low OH rotational excitation. For example, with 30% at 1000 cm^{-1} and 70% at 6000 cm^{-1} , 80% of OH($N=1$) comes from $E^\ddagger \sim 1000 \text{ cm}^{-1}$, the minor constituent. We plan to examine this interpretation in future studies.

In summary, OH production rates obtained with the subpicosecond resolution pump-probe technique, monitoring an ensemble of OH($v=0$) rotational levels having $\langle N \rangle \sim 5.5$, are in qualitative agreement with RRKM predictions. Combinations of state and time resolved measurements may prove useful for isolating contributions from different complexes.

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