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A tunable diode laser has been used to observe transient absorptions on transitions in the v_3 infrared bands of CO_2 when it is formed as a product of the flash-initiated reaction between OH and CO. The absence of any population in excited states with $v_3 > 0$ and the limited extent of excitation in the Fermi-linked v_1 and v_2 modes indicate that energy is released largely as repulsion following passage through a transition state in which the OCO atoms are close to their final structure in isolated CO_2 .

The reaction between OH radicals and CO has been studied extensively, partly in response to its importance both in combustion of hydrocarbons and in atmospheric chemistry. At low total pressure, the reaction produces H atoms and CO_2 :

$$OH + CO \rightarrow H + CO_2; \Delta H_{298}^{\circ} = -104.3 \text{ kJ mol}^{-1}$$

It is now about 15 years since it was first proposed¹ that the values of the rate constant and its temperature dependence could be explained if the reaction proceeds *via* initial addition of OH to CO, followed by competition between the redissociation of the HOCO radical complex to OH + CO and its dissociation to H + CO₂. Confirmation of this mechanism has since been provided by: (a) the observation that the overall rate constant for reaction between OH and CO (and OD and CO) depends on total pressure;² (b) the facile relaxation of OH(v = 1), OD(v = 1) by CO at rates 7 and 17 times greater, respectively, than those for reaction between the ground-state radicals and CO;³ and (c) the unusual isotope effect.^{2,3}

The unusual features in the potential-energy surface of the HOCO system, as well as other factors, have also encouraged a variety of state-of-the-art dynamical experiments. Most of these have focused on the results of high-energy collisions between H atoms and CO₂. Using photodissociation of hydrides such as HBr and H₂S to generate hot H atoms, the results of inelastic and reactive collisions have been examined using tunable IR diode lasers to observe CO₂ excited into specific states⁴ and UV laser-induced fluorescence to examine the states of OH.⁵ In addition, the H + CO₂ reaction has been photo-initiated in HBr \cdot CO₂ and HI \cdot CO₂ van der Waals' complexes; state-⁶ or time-resolved⁷ measurements being made on the OH which is produced.

Elegant as these dynamics experiments are, they do not provide a sensitive probe of the details of the potential-energy surface; for example, the energies and structures of the two transition states: TS1 separating OH + CO from HOCO and TS2 between HOCO and H + CO₂. Early qualitative pictures of the minimum-energy path⁸ have now been replaced by the results of *ab initio* calculations.⁹ These support the early suggestion that TS1 and TS2 have similar energies. This likelihood has been further supported by fairly detailed transition state and RRKM calculations which were able to match the kinetic data available at that time.³

TS2 has an energy ca. 104 kJ mol⁻¹ above that associated with the final reaction products $H + CO_2$, *i.e.* essentially the whole exothermicity of the reaction is released after passage through TS2. Because the departing H atom is light, repulsive forces between it and the CO₂ can deposit little energy in the internal modes of CO_2 . Consequently, the nascent vibrational-state distribution of the CO_2 should be the result of any attractive energy release as the CO_2 relaxes from its structure in TS2. In other words, the CO_2 vibrational-state distribution should provide a window into the OCO geometry of TS2. It is this reasoning which provided the motivation for the experiments that we report here.

In order to determine the CO₂ state distribution we have made measurements of transient IR absorptions on a number of rovibrational transitions in the region of 4.3 µm using tunable laser diodes to provide appropriate narrowbandwidth radiation. Many measurements of this kind, but not on this particular reaction, have been made by Flynn and Weston and their co-workers.⁴ They are assisted by the fact that all transitions of the general type $(mn^l p, J) \rightarrow (mn^l p + 1, J \pm 1)$ are unusually strong on account of the large dipole moment for the v_3 fundamental transition in CO₂.

In our experiments, reaction is initiated by flash photolysis of HNO_3 (5–40 mTorr) in *ca.* 1 Torr of CO. The gas mixture flows through a cylindrical quartz tube to allow for repetitive flashing at 1 Hz. The concentric flashlamp, through which 50 J was dissipated, illuminated the central 80 cm of the reaction cell.

The source for probing CO₂ vibrational states is a c.w. tunable IR diode laser (Mütek GmbH, MDS 1500). The power is low (ca. 100 μ W) and the linewidth very narrow (ca. 3×10^{-4} cm⁻¹). After passing the laser output through the reaction cell, it is passed through a 0.3 m focal length monochromator. This separates out the mode of interest from the other laser modes. The transmitted radiation is then directed onto a liquid N₂ cooled InSb photovoltaic detector.

Traces of transient absorptions on selected rovibrational transitions in the CO₂ product were obtained by averaging the results of ca. 10 photolysis experiments. Measurements were made on at least two lines within each vibrational band on which absorption could be detected. Fig. 1 shows sample traces. On levels above the ground state, the absorption rises to a maximum and then decays relatively slowly to an equilibrium value. These curves have been fitted assuming pseudo-first-order kinetics for both reaction and relaxation processes. The rate constants for reaction, which determine the rise of absorption at short times are found to be ca. 1.6×10^{-13} cm³ molecule⁻¹ s⁻¹, in agreement with the accepted value of 1.5×10^{-13} cm³ molecule⁻¹ s⁻¹.^{2,3} The signals from vibrationally excited states decay as a result of collisionally induced relaxation, apparently by HNO₃, as the rates scale with the partial pressure of HNO₃ in the mixture. The full details of the analysis will be published elsewhere.



Fig. 1 Transmitted intensity of diode laser radiation tuned to lines in the rovibrational spectrum of CO_2 : (a) the P(32) line of the (01¹¹, 01¹⁰) band, with 1.2 Torr of CO present; (b) the P(34) line of the (10⁰1, 10⁰0) band, with 1.3 Torr of CO present

The strengths of the absorption signals were converted to populations assuming equilibration amongst each set of rotational levels and identical transition dipole moments for all v_3 vibrational transitions. The relative populations in different levels could be estimated by comparing the signals associated with different vibrational transitions. Measurements were made on at least two lines in each vibrational band and the vibrational populations derived from the different measurements were found to be consistent. No absorption could be detected from the (001) level. There is strong mixing by Fermi resonance of the zeroth-order levels 02°0, 10°0 and 03¹0, 11¹⁰. The populations which we found in each element of the Fermi dyads were very similar.

The fractional populations listed in Table 1 can be used to estimate an average vibrational energy yield of $\langle E'_{vib}/hc \rangle =$ 510 cm⁻¹. This yield corresponds to *ca*. 6% of the total energy available to the H + CO₂ products of thermal reaction between OH and CO and suggests that there is very little difference between the OCO structure in transition state TS2 and in the CO₂ molecule. If one assumes that the yield of vibrational energy is entirely associated with the bending vibration and, furthermore, that it results only from impul-

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Table 1Measured populations in vibrational levels of CO_2 formedin the reaction between OH and CO

level	$(E_{\rm vib}/hc)$ /cm ⁻¹	(g_{vib})	$(N_{\rm vib})_{\rm obs}{}^a$	$f_{vib}{}^{b}$
00°0	0	(1)	1.00	0.55
01 ¹ 0	667.4	(2)	1.33×10^{-1}	0.25
$(10^{\circ}0, 02^{\circ}0)$	1285.4	(1)	3.64×10^{-2}	0.034
02²0	1335.1	(2)	2.72×10^{-2}	0.050
$(10^{\circ}0, 02^{\circ}0)$	1388.2	(1)	3.77×10^{-2}	0.035
$(11^{1}0, 03^{1}0)$	1932.5	(2)	1.64×10^{-2}	0.030
03 ³ 0	2003.2	(2)	8.6×10^{-3}	0.016
$(11^{1}0, 03^{1}0)$	2076.9	(2)	1.37×10^{-2}	0.025
04 ² 0	2585.0	(2)	9.5×10^{-3}	0.017

^{*a*} Population is given sub-level relative to the equilibrium population in the (00⁰0) ground state; *i.e.* the population in (00⁰0) at long times. ^{*b*} f_{vib} is the fractional population produced in the specified level by the reaction.

sive release from a bent configuration of OCO in TS2, then one can equate 510hc to the potential energy, $\frac{1}{2}k_{\delta}\delta^2$, in TS2 where k_{δ} is the bending force constant and $(\pi - \delta)$ is the OCO angle. This simplistic calculation suggests that the OCO angle in TS2 is ca. 171°, *i.e.* the structure is only ca. 9° from collinear. This is closer to collinearity than suggested by Schatz's calculation⁹ (OCO = 159°) and it would be difficult to reconcile the degree of bending in TS2 predicted by the *ab initio* calculations with the low yield of CO₂ excitation measured in our experiments.

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