Reaction pathways in surface femtochemistry: routes to desorption and reaction in $CO/O_2/Pt(111)$

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Abstract

We present new data that address the chemical pathway to desorption of O_2 and formation of CO_2 in $CO/O_2/Pt(111)$ induced by subpicosecond laser pulses. The data show conclusively that the O_2 desorbs molecularly. We also find that if the CO oxidizes by an atomic pathway then the capture of oxygen atoms by the CO is highly efficient; if the CO oxidizes by a molecular pathway then the oxygen atoms in the CO_3^* transition state are inequivalent. © 1997 Elsevier Science B.V.

1. Introduction

The oxidation of CO on $CO/O_2/Pt(111)$ has been studied using cw light [1–4] and both nanosecond [5,6] and subpicosecond [7–11] laser pulses. In the cw regime, the oxidation of CO has been attributed to oxygen atoms released from dissociation [3] of O_2 and to excited oxygen molecules [6]. Recent work by Yates et al. indicates that the rate of CO_2 production by cw light is consistent with dissociation of O_2 prior to the oxidation of CO [1]. Further evidence of O_2 photodissociation by cw light is provided by electron energy-loss spectroscopy of $O_2/Pt(111)$ [2].

With subpicosecond laser pulses the reaction mechanism is very different from that with longer pulses [5]. For example CO_2 production is readily observed at 800 nm [8], well beyond the 550 nm threshold [3] for CO_2 production with light of nanosecond or longer duration. In these femtochemistry experiments, reaction between adsorbates on the surface is attributed to excitation of the adsorbates by the laser-induced transient electron distribution in

the substrate [5,8,9,12]. In this letter we examine the reaction pathway for O_2 desorption and CO_2 production with high-intensity subpicosecond pulses. The data show that the O_2 desorbs as an intact molecule, and the data place constraints on the nature of the transition states in production of CO_2.

2. Experiment

The experiments are conducted on a 12 mm diameter Pt(111) crystal in an ultrahigh-vacuum chamber with a base pressure of 5×10^{-11} Torr. The crystal surface is cleaned using Ne ion sputtering at an ion energy of 0.5 kV, annealing in vacuum at 1100 K, and annealing in 10^{-8} Torr oxygen at 500–1000 K [13]. Surface order is verified with low-energy electron diffraction (LEED); surface cleanliness is verified with Auger spectroscopy [1].

After cleaning, molecular oxygen, atomic oxygen or carbon monoxide are adsorbed to saturation onto the platinum surface. Molecular oxygen is deposited

directly after a cleaning cycle, as soon as the platinum temperature has fallen to 94 K. At this temperature there is no thermal dissociation of the oxygen. To coadsorb CO and O_2, carbon monoxide is deposited after the oxygen. A coverage of atomic oxygen is obtained by exposing the platinum surface to molecular oxygen at a surface temperature of 250 K [14]. The surface is then further cooled before depositing any coadsorbates. Isotopic mixtures of $^{16}O_2$ and $^{18}O_2$ are prepared by mixing the isotopes outside the chamber and then depositing the isotopic mixture as in a regular O_2/Pt(111) preparation. To reduce background pressure while still obtaining saturation coverage, all adsorbates are deposited using a tube of 12 mm diameter that is brought to within 3 mm of the platinum surface. We verified the coverages using temperature programmed reaction spectroscopy and LEED. All laser experiments are performed at a base temperature of 84 K.

We studied the photochemistry of CO/O_2/Pt(111) using the frequency-tripled pulses of a regeneratively amplified Ti:Sapphire laser at 267 nm. The frequency-tripled output of the laser consists of a 1 kHz train of 0.26 ps pulses of up to 25 μJ per pulse. The pulse duration was determined by difference-frequency mixing the pulse with the 800 nm fundamental in a thin BBO crystal [15]. The energy of each laser pulse is measured with a calibrated photodiode. This energy reading is converted into absorbed fluence taking into account spatial profile (determined using a CCD camera), angle of incidence, platinum reflectivity, and absorption and reflection losses of the vacuum chamber window. The fluence varies over the profile of the laser spot; values quoted below refer to the local absorbed fluence at the peak of the spatial profile.

For each laser pulse, the reaction yield at one mass-to-charge ratio is measured with a quadrupole mass spectrometer. The mass spectrometer has a tube of inner diameter 4 mm that extends from the ionizer to the sample. Nearly the entire solid angle at the opening of the tube is filled by the Pt(111) crystal. A negative bias of 90 V between the sample and the chamber prevents electrons escaping the ionizer from disturbing the surface preparation. Using a high-speed mechanical shutter, we reduce the laser repetition rate to 2 Hz to allow the gas-phase products to be pumped out of the chamber. The background levels,

measured 50 ms before each laser pulse, do not change over the course of an experiment. The detection limit for each mass-to-charge ratio depends on the background present in the chamber at that mass and on the signal due to cracking of higher mass species in the mass spectrometer ionizer. Counts attributable to the background in the vacuum chamber are subtracted from the data.

3. Results

Fig. 1 shows the yields of O_2 and CO_2 from CO/O_2/Pt(111). Each data point represents the yield from a single laser pulse at a fresh (not previously irradiated) location on the platinum. The data are normalized to the laser spot size to allow comparison between data runs taken with different spot sizes. Note the nonlinear relationship between yield and fluence characteristic of photochemistry initiated with subpicosecond laser pulses at fluences above 10 μJ/mm^2 [12,16]. This Letter focuses on data obtained in this nonlinear regime. We measured reaction yields for several combinations of reactants and isotopes to determine the reaction pathway in the nonlinear regime.

Table 1 summarizes the yields from various surface preparations. The shading indicates which species are deposited on the surface before irradiation. As Fig. 1 shows, the ratio of the CO_2 and O_2 yields is constant between 30 and 80 μJ/mm^2; for all sample preparations, the product ratios vary little over this fluence range. The values in the Table correspond to the laser-induced yields at a fluence of 30 μJ/mm^2 and are normalized to the yield of $C^{18}O_2$ from $C^{18}O$/$^{18}O_2$/Pt(111). Where a maximum yield is given, the yield is below our detection limit for that species and sample preparation.

We first verified that there is no CO_2 production from a surface prepared with just CO. As the data in column 1 of Table 1 show, there is no measurable CO_2 yield within the detection limit. We do, however, observe a small CO yield.

Column 2 shows that, in contrast to experiments with low intensity irradiation [4], some CO_2 is produced from reaction of carbon monoxide coadsorbed with oxygen atoms. We also observe CO desorption for this surface preparation. The oxygen, however,
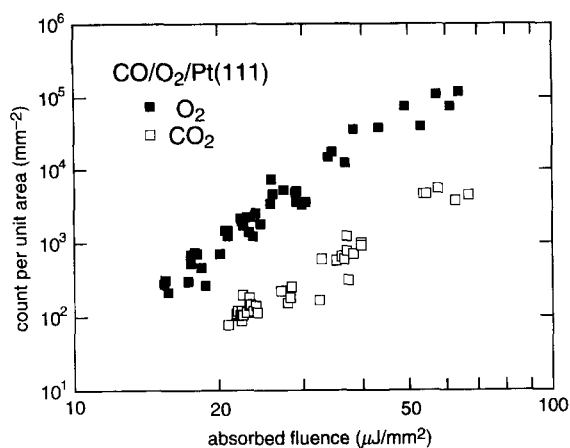
Fig. 1. Laser-induced (267 nm, 0.26 ps) yields of O_2 and CO_2 from CO/O_2 /Pt(111). Each data point represents the yield from a fresh spot on the surface preparation.

does not desorb as either atomic or molecular oxygen.

Columns 3 and 4 summarize yields from a surface preparation of carbon monoxide coadsorbed with oxygen molecules. We used $C^{18}O$ and $C^{16}O$ isotopes to see if the original oxygen atom in the CO gets replaced in the formation of CO_2. The yield of $C^{18}O_2$ reported in column 4 can be attributed to isotopic impurities in the surface preparation and thus we find no evidence for oxygen replacement in the subpicosecond laser-induced CO_2 formation.

The data in column 3 allow us to establish that the CO yield reported in columns 1 and 2 is not due to cracking of CO_2 in the mass spectrometer. In the experiments of column 3, the signal at 30 amu is 0.2 (20% of the CO_2 signal). This gives an upper limit of 20% for the probability of cracking of the laser-produced CO_2 in the ionizer. Thus in column 1, the maximum amount of signal at 30 amu that can be attributed to cracking of CO_2 is 20% of 0.01, which is well below the observed signal.

The experiments summarized in column 5 address whether there is exchange of oxygen atoms between $^{18}O_2$ and $^{16}O_2$ during laser-induced desorption from $(^{18}O_2,^{16}O_2)$/Pt(111). The observed yield of $^{16}O^{18}O$ is 240 times smaller than the yield of $^{18}O_2$ or $^{16}O_2$. We find therefore no evidence for exchange of oxygen atoms between oxygen molecules under subpicosecond laser irradiation.

In column 6 we investigate exchange of oxygen atoms between molecular $^{16}O_2$ and coadsorbed atomic ^{18}O. Again we obtain a yield of $^{16}O^{18}O$ that is much smaller than the yield of $^{16}O_2$. This result contrasts sharply with the observation of a reaction between oxygen atoms from the photodissociation of N_2O and coadsorbed oxygen atoms [17].

Column 7 shows that there is no laser-induced recombination of atomic oxygen on the surface. As in the case of coadsorbed CO and O (column 2), there is no detectable desorption of atomic oxygen.

Table 1

Relative nonlinear photochemistry yields for several surface preparations. The asterisk ($*$) indicates the species applied to the surface. The numbers indicate the relative yields of the various molecules and their isotopic variations, normalized to the yield of CO_2 from CO/O_2/Pt(111). Yields are reported for 267 nm, 0.26 ps laser pulses at 30 $\mu J/mm^2$

	CO	CO/O	CO/O$_2$		O$_2$/O$_2$	O$_2$/O	O
	1	2	3	4	5	6	7
^{18}O		($*$) < 0.2 a				($*$)	($*$) < 0.2 a
$^{16}O_2$					($*$) 80 ± 5	($*$) 15 ± 5	
$^{18}O^{16}O$					0.5 ± 0.2	0.05 ± 0.02	
$^{18}O_2$		0 ± 0.001 b	($*$) 25 ± 5	($*$) 25 ± 5	($*$) 40 ± 10		0 ± 0.001 b
$C^{16}O$				($*$)			
$C^{18}O$	($*$) 0.03 ± 0.01	($*$) 0.5 ± 0.2	($*$) < 0.2 c				
$C^{16}O^{18}O$					1 ± 0.2		
$C^{18}O_2$	0 ± 0.001 b	0.01 ± 0.005	1 ± 0.2	0.01 d			

a Signal attributed to water background signal.
b Detection limit.
c Signal attributed to cracking of CO_2.
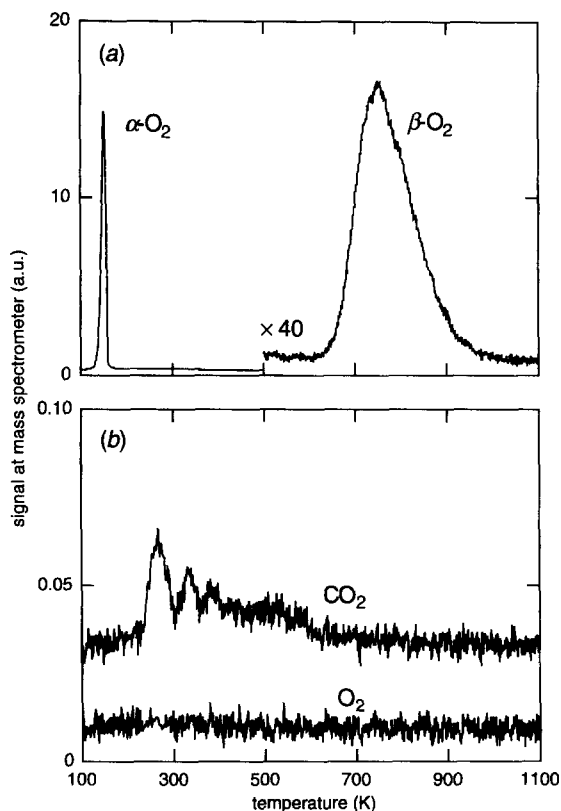d Signal attributed to isotopic impurity in surface preparation.

Fig. 2. Temperature programmed desorption of a saturated 0.44 ML O_2 /Pt(111) surface (a) without irradiation and (b) following irradiation with 800 nm, 55 $\mu J/mm^2$ pulses.

The small $C^{18}O_2$ and $^{16}O^{18}O$ yields in columns 4–6 of Table 1 are due either to laser-induced processes or to isotopic impurities in the surface preparation. We therefore compared the laser-induced yields with thermal yields obtained by temperature programmed reaction spectroscopy (TPRS). Fig. 2a shows a TPRS scan for saturation coverage of O_2 on platinum. As the temperature is raised, some of the oxygen molecules desorb and some dissociate into atoms. The large, narrow peak at 145 K (α-peak) in Fig. 2a is due to desorption of intact oxygen molecules; the broad peak around 750 K (β-peak) is due to atoms that recombine and then desorb as O_2 molecules [14]. To determine the thermal yield of oxygen, we measured the areas under the α-peaks of the various isotopes of O_2 for $(^{18}O_2,^{16}O_2)$/Pt(111) and $^{16}O_2/^{18}O$/Pt(111) surface preparations. Thermal CO_2 yields were obtained by integrating the areas under corresponding CO_2 TPRS scans for a

$C^{16}O/^{18}O_2$/Pt(111) sample preparation. The thermal yields are reported in Table 2, labeled and normalized within each column for easy comparison to Table 1. The $C^{18}O_2$ and $^{16}O^{18}O$ yields in Table 1 are comparable to those in Table 2. It is therefore likely that the small $C^{18}O_2$ and $^{16}O^{18}O$ yields reported in Tables 1 and 2 are due to isotopic impurities.

To determine if high-intensity subpicosecond laser pulses cause photodissociation of oxygen, we irradiated the entire surface of a saturated [14] 0.44 ML $^{18}O_2$/Pt(111) preparation and then determined the remaining surface coverage with a post-irradiation [18] temperature programmed reaction scan. The lower trace in Fig. 2 shows the temperature programmed reaction scan for $^{18}O_2$ following irradiation of the $^{18}O_2$/Pt(111) surface with 55 $\mu J/mm^2$, 800 nm pulses. We used 800 nm pulses because there is no linear photo-dissociation of O_2 at that wavelength [2,3]. Any photo-dissociation at 800 nm must therefore be due to the mechanism responsible for nonlinear chemistry. However, we observe no desorption of α-O_2 or β-O_2 (lower trace in Fig. 2b). This indicates that no detectable amount of oxygen molecules or oxygen atoms is left on the surface after irradiation.

Does this mean that the laser pulses do not dissociate the oxygen molecules? It is possible that the laser dissociates a small fraction of the O_2 molecules, and that the O atoms are scavenged by background gas molecules that adsorb to the surface. For exam-

Table 2
Summary of relative temperature programmed desorption yields. The asterisk indicates which species were dosed to the surface. The numbers indicate the relative yields of the molecules and their isotopic variations. In column 4, the yields are normalized to the $C^{16}O^{18}O$ yield; in columns 5 and 6, the yields are normalized so that the $^{16}O_2$ yields match the corresponding values in Table 1

	CO/O_2 4	O_2/O_2 5	O_2/O 6
^{18}O			(*)
$^{16}O_2$		(*) 80	(*) 15
$^{18}O^{16}O$		0.3	0.07
$^{18}O_2$	(*)	(*) 45	
$C^{16}O$	(*)		
$C^{18}O$			
$C^{16}O^{18}O$	1		
$C^{18}O_2$	0.01		

ple, if $C^{16}O$ adsorbs during the experiment, it could react with atomic ^{18}O created by the laser and prevent this oxygen atom from appearing as $\beta-O_2$ during the temperature programmed reaction scan. Fig. 2b shows a small amount of $C^{16}O^{18}O$. This very low CO_2 signal could be due to a thermally induced reaction on the sample mount. If, however, we attribute all of this signal to reaction on the platinum surface between laser-dissociated oxygen and background contamination, we obtain an upper limit for laser-induced dissociation of 1.8% of the initial O_2 coverage.

4. Discussion

Let us now examine different pathways that can lead to O_2 desorption and CO oxidation. First we consider an atomic pathway — oxidation of CO due to interaction with an oxygen atom:

$$O_2(ad) \rightarrow 2O^*(ad),$$

$$O^*(ad) + CO(ad) \rightarrow CO_2(g).$$
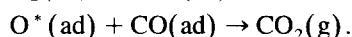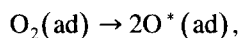
The observed ratio of CO_2 formation to O_2 desorption at 800 nm is 1:70 and so, if each time an oxygen molecule dissociates both atoms react with CO, then the ratio of O_2 dissociation to desorption must be about $1/140 \approx 0.7\%$. This is below the upper limit of 1.8% we established for the probability of O_2 dissociation and so we cannot rule out an atomic pathway even though such a pathway would require an efficiency of at least $0.7/1.8 \approx 40\%$ for the capture of the oxygen atoms by CO.

Dissociation of O_2 could also lead to other reactions. However, we observe no recombination of oxygen atoms back to O_2 (column 5, Table 1) and no reaction of the dissociation fragments with coadsorbed oxygen atoms (column 6, Table 1). So, if dissociation occurs, we must conclude that the fragments of oxygen dissociated with subpicosecond laser pulses do not react with other oxygen atoms or molecules, in sharp contrast to the oxygen atom formed in the photodissociation of N_2O [17]. The required high capture efficiency of oxygen atoms, and the absence of other reactions between these oxygen atoms and other coadsorbates, suggest that the atomic pathway is not likely to account for the CO_2 yield.

Next we consider a molecular pathway — CO oxidation by direct interaction with an oxygen molecule:

$$O_2(ad) \rightarrow O_2^*(ad),$$

$$O_2^*(ad) + CO(ad) \rightarrow CO_3^*(ad)$$

$$\rightarrow O(ad) + CO_2(g).$$
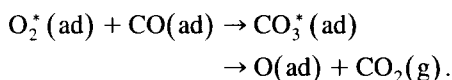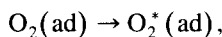
In this scheme, the carbon dioxide is produced not via dissociation of oxygen but through a CO_3 intermediate. A stable CO_3 species has been observed on Ag(110) [19], but has not been reported on Pt(111). In fact, we observe no exchange of the oxygen atom originating on the CO molecule to better than 1 part in 100 (column 4, Table 1). Therefore, if CO is oxidized by the molecular pathway, the oxygen atoms of the CO_3^* intermediate must be highly inequivalent and the intermediate is constrained to dissociate into CO_2 and O without eliminating the oxygen initially present on the CO.

It is also possible that the reaction between oxygen and carbon monoxide occurs in a concerted process without involving an equilibrated CO_3 intermediate; instead the O_2 and CO may interact so that the O–O bond is stretched as a new O–CO bond is formed.

Let us next turn to the desorption of oxygen. Suppose the oxygen molecules dissociate and atomic oxygen then recombine to give O_2:

$$O_2(ad) \rightarrow 2O^*(ad),$$

$$2O^*(ad) \rightarrow O_2(g).$$
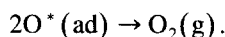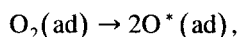
Such a pathway should lead to mixing of oxygen isotopes in $(^{16}O_2, \, ^{18}O_2)/Pt(111)$, but we do not observe this experimentally (column 5, Table 1). Furthermore, if they fail to recombine, the oxygen atoms should equilibrate with the surface. However, we observe very few oxygen atoms in the post-irradiation temperature programmed desorption experiments. This observation also excludes the possibility [20] that oxygen desorption is caused by displacement due to nearby chemisorption of atomic oxygen. Our observations therefore show that the observed O_2 products are due to desorption of intact molecules.

Columns 1 and 2 of Table 1 show that there is yield of CO from CO/Pt(111) and of CO and CO_2 from CO/O/Pt(111) when stimulated with 0.26 ps, 267 nm laser pulses. These yields could be due to thermal desorption induced by laser heating of the

phonon modes, or they could be due to laser-excited electrons.

5. Conclusions

Our results show that the oxygen molecules desorb from O_2/Pt(111) without exchange of atoms between molecules, like the $\alpha-O_2$ product in thermal chemistry. We observe no yield of O_2 from O/Pt(111) nor from a reaction between a fragment of O_2 and a coadsorbed, equilibrated oxygen atom in O_2/O/Pt(111).

Our results show that if the CO oxidizes by the atomic pathway, then the capture of oxygen atoms by the CO must be highly efficient. In view of the required high efficiency ($\approx 40\%$) and the absence of other reactions with coadsorbates, however, the atomic pathway is not likely to account for the observed CO_2 yield. If the CO oxidizes by the molecular pathway, then our isotope exchange experiments show that the CO_3^* intermediate has very inequivalent oxygen atoms.

Acknowledgements

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