Substantially different activation energies are quite conceivable for the other molecular rearrangement processes to occur.

Obviously, a more detailed analysis of the observed experimental data on irreversible line broadening needs further detailed thermal cycling experiments. Experiments of this kind have not yet been performed in molecular crystals but would be important to compare with existing data in glasses. Due to the restricted molecular configurations in molecular crystals as compared to glasses, these experiments promise more insight into the principles and mechanism of spectral diffusion processes in organic solid-state materials.

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Stoichiometric Combustion of Methane over $YBa_2Cu_3O_7$ under Anaerobic Conditions

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The reactivity of the $YBa_2Cu_3O_{7-x}$ high T_c superconductor with methane under static atmosphere and in the absence of free molecular oxygen has been studied. At 400 °C methane is stoichiometrically oxidized with oxygen from the superconductor lattice (O_2), according to the reaction $CH_4 + 2(O_2)_L \rightarrow CO_2 + 2H_2O$. The generated CO_2 mainly interacts with the oxide, giving rise to CO_3^{2-} ions, probably as $BaCO_3$. Taking into account that four molecules of superconductor are needed to oxidize a CH_4 molecule, it can be inferred that only one oxygen atom per oxide molecule participates in the oxidation reaction. This result is consistent with the existence of (O^-) and/or (O_2^{2-}) lattice ions, highly mobile and very active in the abstraction of H atoms from the CH_4 molecule to generate $CH_3^\bullet$ radicals. Implications for the selective catalytic oxidation of CH_4 to C_2 hydrocarbons over the YBaCuO superconductor in the presence of dioxygen are considered.

Oxide-supported noble metals as well as single and mixed oxides of transition metals show excellent catalytic properties in hydrocarbons combustion.[1] However, very little is known about the nature of the catalytically active species and on the mechanisms by which C–H bonds become activated. It is generally assumed that oxygen ionic species, generated during the dissociative chemisorption of dioxygen, are involved in the reaction. This is the case of the $O^-(s)$ ion which represents a surface transient generated in the sequence

$$O_2(g) \rightarrow O_2(s) \rightarrow O^-(s) \rightarrow O^{2-}(s)$$

during the oxidation of different metals, as supported by photoelectron spectroscopy experiments.[3] On the other hand, O^- species are known to be very active in both partial and deep oxidative dehydrogenation of alkanes.[4,5] Here we report on the peculiar properties for stoichiometric total oxidation of methane in the absence of free molecular oxygen, over the recently discovered superconducting compound $YBa_2Cu_3O_{7-x}$.[6] The existence of holes delocalized in oxygen $p\pi$ orbitals of CuO sheets or chains,[7] associated with O^- lattice species ($Y^{3+}Ba_2^{2+}Cu_3^{2+}O_6^{2-}O^-$) highly mobile and very active in the abstraction of H from CH_4, may explain the observed behavior. $YBa_2Cu_3O_{7-x}$ ($1 \geq x \geq 0$) was prepared from stoichiometric amounts of analytical grade Y_2O_3, BaO_2, and CuO powders, as described elsewhere.[8] Samples with $x \simeq 0$ ($YBa_2Cu_3O_7$) were obtained after a final heat treatment at 400 °C in flowing O_2 during 24 h, and slow cooling down to room temperature under the same atmosphere. The material so obtained, which was confirmed to show superconductivity at 90 K, was used after being gently ground to an average grain size of about 10 μm. Accordingly, the specific surface area was estimated to be of the order of 1.0 $m^2\ g^{-1}$. The lattice oxygen content of both freshly prepared and used samples was obtained from the measurements of their unit-cell constants. According to Manthiran et al.,[9] the length of c axis at room temperature expands from 11.67 to 11.85 Å when the oxygen content per molecular unit decreases from seven to six atoms (orthorhombic $YBa_2Cu_3O_7$ to tetragonal $YBa_2Cu_3O_6$ phase transition). The X-ray diffractograms were recorded with a Philips diffractometer fitted with a quartz crystal monochromator; NaCl(200) reflection (d = 2.8195) was used as standard to determine unit-cell constants, which were refined by least-squares for Cu $K\alpha_1$ radiation (λ = 1.540 56 Å).

The YBaCuO reactivity with pure CH_4 (absence of free O_2) was studied in a closed static system at variable temperature. One gram of $YBa_2Cu_3O_7$ (1.5×10^{-3} mol) was introduced into a Pyrex reactor of ~9 cm^3 volume. After evacuation under a residual pressure of 10^{-2} Torr for 4 h, the reactor was filled with pure CH_4 at 760 torr (3.7×10^{-4} mol) and heated overnight at different temperatures ranging between 200 and 400 °C. In each experiment (temperature) a new sample was used. After cooling down to room temperature, the gases produced in the reaction were extracted with a gas-tight 1-cm^3 precision sampling syringe and introduced into a AEI-MS-30 mass spectrometer to be analyzed. According to the mass analysis, the only gas detected up to 300 °C was CH_4. At about 350 °C a small amount of H_2O could be seen, while at 400 °C only H_2O was detected together with traces of CO_2 and CH_4. Therefore, it can be assumed that near 400 °C methane is totally oxidized with oxygen from the oxide lattice, according to the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

The very small amount of CO_2 detected among the reaction products seems to indicate that CO_2 is mainly absorbed by the catalyst.[10] At least partially, the absorbed CO_2 react with the YBaCuO lattice. In fact, a small diffraction peak at $2\Theta = 24°$ (d = 3.7 Å), which can be attributed to the most intense reflections

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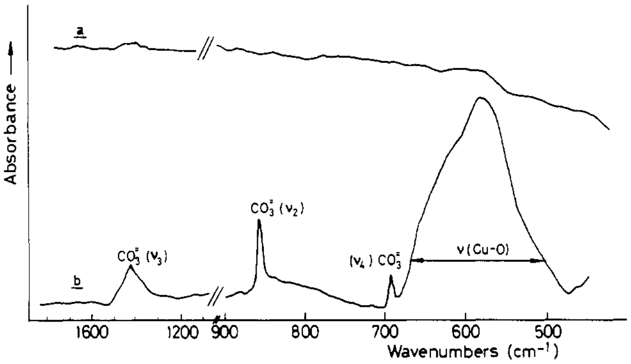

Figure 1. IR spectra of the YBaCuO superconductor obtained at room temperature with a Fourier-transform Nicolet 7199 C spectrometer (KBr pellet method), before (a) and after (b) treatment with CH_4 at 400 °C. Typical bands of the CO_3^{2-} anion are present in the spectrum of the used catalyst. Notice the extremely low intensity of the bands assigned to the Cu-O vibration modes in the fresh $YBa_2Cu_3O_7$ catalyst because of its metallic behavior (existence of free electrons) at room temperature.[16]

(111) and (021) of orthorhombic $BaCO_3$ (ASTM file 5-0378), appears in the diffractogram of the used catalyst. The presence of CO_3^{2-} ions is confirmed by the presence of bands at 1420, 860, and 700 cm^{-1} in the IR spectrum of YBaCuO after treatment, as shown in Figure 1.

Taking into account that the initial $YBa_2Cu_3O_7$ to CH_4 molecular ratio was about 4, it can be inferred that four molecules of catalyst are needed to oxidize a CH_4 molecule. This means that only one oxygen atom per oxide molecule participates in reaction 1. Therefore, the following global reaction might be written

$$4YBa_2Cu_3O_7 + CH_4 \rightarrow 4YBa_{2-x/4}Cu_3O_{6-x/4} + xBaCO_3 + (1-x)CO_2 + 2H_2O \quad (2)$$

where $x < 1$ represents the fraction of CO_2 that reacts with the catalyst generating $BaCO_3$. A significant part of CO_2 (or even CO) could remain absorbed by the catalyst without reacting.[10]

In order to test this hypothesis the unit-cell parameters before and after the reaction were measured. Figure 2 shows the most significant changes of the X-ray diffractogram produced during the reaction, in the 2Θ range corresponding to the main reflections (013), (103), and (110) of YBaCuO. A phase transition from orthorhombic to tetragonal is evident from Figure 2. In fact, while in the fresh catalyst ($YBa_2Cu_3O_7$) the intensity of the first reflection (013) is smaller than that due to overlapped (103) and (110) peaks, as corresponds to the orthorhombic phase,[11] in the used catalyst (103) and (013) reflections merge giving a higher intensity peak than the (110) reflection, as in the tetragonal phase *a* and *b* unit-cell axes become identical. Besides, the (013) reflection appears shifted toward low 2Θ angles with respect to the orthorhombic phase because of the increase of the *c* axis.[9] The calculated lattice parameters were $a = 3.82_5$ Å, $b = 3.88_2$ Å, and $c = 11.67_1$ Å for the orthorhombic fresh sample ($YBaCuO_7$) and $a = 3.86_1$ Å and $c = 11.84_8$ Å for the tetragonal used sample. The tetragonal parameters are very close to those corresponding to the oxide of composition $YBa_2Cu_3O_6$,[9] as assumed in eq 2. No changes other than the orthorhombic to tetragonal phase transformation and the formation of $BaCO_3$ could be observed by X-ray diffraction.

Attention should be paid to the fact that the orthorhombic to tetragonal phase transformation can be reversed by simply heating the used superconductor in flowing O_2 at 400 °C. This reversible behavior is a proof that the YBaCuO crystalline structure does not undergo any irreversible damage during CH_4 oxidation. On the other hand, these results are consistent with the well-established fact that the variations of oxygen content (x) taking place during $YBa_2Cu_3O_{7-x}$ annealing in an inert atmosphere are responsible for the orthorhombic to tetragonal phase transformation[9,11] of YBaCuO. The orthorhombic phase is stable for $0 < x < 0.5$ while the tetragonal phase becomes stable for $x > 0.5$. The phase transition is, therefore, controlled by the diffusion of oxygen lattice species (0(1) sites in the CuO chains seem to be exclusively involved in this mechanism[12]). Oxygen diffusivity strongly depends on the number of oxygen vacancies (x).[13] Activation energies of 0.5 and 1.3 eV have been recently determined for $x = 0.38$ and $x = 0$, respectively. So, for $x = 0.38$ the diffusion coefficient has been determined to be[13]

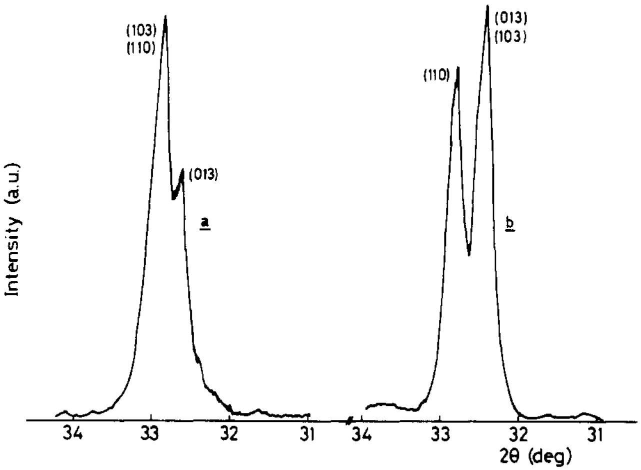

Figure 2. Detail of the X-ray diffraction patterns corresponding to the YBaCuO superconductor before (a) and after (b) treatment with CH_4 at 400 °C. The changes in position and relative intensity of the (013), (103), and (110) reflections clearly indicate a phase transformation from $YBa_2Cu_3O_7$ orthorhombic (a) to $YBa_2Cu_3O_6$ tetragonal (b).

$$D = 0.035 \exp(-0.5 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1} \quad (3)$$

According to eq 3, at 400 °C $D \simeq 10^{-5}$ cm^2 s^{-1}, which is a high diffusion coefficient for ionic species in a solid. The reactivity of YBaCuO in methane oxidation must be attributed not only to the high diffusivity of some oxygen species through the lattice but to the chemical nature of these species. A peculiarity of the electronic structure of the YBaCuO superconductor is the existence of holes delocalized in the energy levels of O 2p parentage. Chemically speaking, this involves the presence of O^- and/or O_2^{2-} lattice ions, which explains the high reactivity of the oxide with H_2O. Both O^- and O_2^{2-} ions are able to abstract protons from water to generate thermodynamically more stable H_2O_2 species which further decompose into O_2 and H_2O. This explains the spontaneous oxygen release from the oxide in contact with water.[8,14] On the other hand, not only O^- species in MgO[4] but also peroxide dianions in $BaPbO_3$[15] are known to be able to catalyze the oxidation of methane to C_2 hydrocarbons because of their efficiency for abstracting H from CH_4 to generate $CH_3^{\bullet}$ radicals.[4] These radicals can further react with lattice O^- species to form methoxide ions that ultimately result in the production of CO and CO_2.[5] This is the case for MgO, which contains about 8 μmol of O^-/mol. The situation should be similar with YBaCuO, although in this case the concentration of O^- species is about 10^4 times greater than for MgO.

Finally, let us make some remarks about oxygen diffusivity in $YBa_2Cu_3O_{7-x}$. According to Krebs and Wördenweber,[11] under vacuum or in Ar atmosphere the onset of orthorhombic to tet-

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ragonal transition at the equilibrium state occurs at about 550 °C. Here we have shown that under CH$_4$ atmosphere the onset temperature is lowered by at least 150 °C. This result is consistent with the assumption that the out-diffusion rate of oxygen in the YBaCuO compound is limited by a surface barrier of 1.7 eV, which is involved in the surface diffusion of O$^-$ species and the further formation and desorption of O$_2$.[13] In the presence of methane this surface barrier is lowered as a result of the strong chemical interaction between O$^-$ surface species and CH$_4$ molecules of the gas phase.

New experiments are being conducted in our laboratory in order to determine the catalytic properties of the YBaCuO superconductor in the selective oxidation of methane to C$_2$ hydrocarbons in the presence of free molecular oxygen.

Registry No. CH$_4$, 74-82-8; YBa$_2$Cu$_3$O$_7$, 109064-29-1.

FEATURE ARTICLE

Excited States, Electron-Transfer Reactions, and Intermediates in Bacterial Photosynthetic Reaction Centers

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The three-dimensional structure of a photosynthetic reaction center has recently been obtained at atomic resolution using X-ray crystallography by Deisenhofer, Epp, Miki, Huber, and Michel [*J. Mol. Biol.* **1984**, *180*, 385–398; *Nature* **1985**, *318*, 618–624]. This breakthrough provides the fundamental structural information needed to understand the mechanisms of the initial energy- and electron-transfer steps in photosynthesis. The structure reveals the distances among the reactive bacteriochlorophylls and quinones as well as the location of all nearby solvent molecules, the amino acids of the reaction center protein. Thus, the reaction center provides a complex but well-defined solid-state reactive system for the study of fundamental physical and chemical processes with implications and applications well beyond this specific system. We review recent studies of the reaction intermediates and mechanism of electron transfer in which the energetics and reaction dynamics have been perturbed with external electric and magnetic fields. These approaches complement picosecond transient absorption spectroscopy and theoretical treatments of the problem. Electron-transfer mechanisms which have been proposed are reviewed critically in light of the available data, and electron transfer in the reaction center is compared with electron transfer in other biological and nonbiological systems.

Introduction

The initial charge separation and energy storage steps in photosynthesis take place in a membrane bound, chlorophyll–protein complex called the photosynthetic reaction center (RC). In this article, we will focus on the initial photophysical and photochemical processes that take place in RCs from photosynthetic bacteria. The three-dimensional structure of the RC from two species of purple non-sulfur bacteria has been determined to atomic resolution during the past several years[1-6] as shown in Figure 1. The breakthrough was the crystallization of the protein complex by Michel,[7] followed by solution of the X-ray crystal structure by Deisenhofer et al.[1] Although a great deal of spectroscopic and kinetic data[8] had been obtained before the crystal structure was solved, the availability of the atomic coordinates of all the reactive components and their solvent (the RC protein) prior to charge separation has stimulated great interest in understanding the underlying physics of the RC function.

At the outset, it is worth noting a few of the features of these initial events that have stimulated the interest of so many physical chemists. It is probably safe to say that no other system undergoing long-distance electron transfer has been studied in so much detail both experimentally and theoretically. In addition, this system has provided the inspiration for many ingenious model systems. The primary electron donor, a strongly interacting but not covalently connected pair of bacteriochlorophylls called P, is electronically excited either directly or by highly efficient energy transfer from other pigments within the RC or the adjacent antenna complex. The lowest energy singlet electronic excited state of P, ^{1}P, decays within a few picoseconds by electron transfer to produce the charge-separated intermediate, P$^{\bullet+}$H$^{\bullet-}$, where H is a monomeric bacteriopheophytin (Figure 1).[9-14] Not only is the reaction very fast, but it is also only weakly dependent on temperature, actually speeding up as the temperature is decreased.[9,12] Since the donor and acceptor are separated by about 10 Å (edge-to-edge), this is a remarkably rapid long-distance elec-

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