

New Evidence for Surface Nonspecific Catalysis: The Reaction between Organized Organic Thin Films and O(³P)

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Surfaces play an important role in many aspects of chemistry varying from industrial heterogeneous catalysis to atmospheric chemistry.¹ When they serve the purpose of intentionally enhancing the chemistry, their effect is referred to as "catalysis". However, surfaces also have a destructive effect due to what one refers to in general as the "wall effect". A fundamental question as to what extent surfaces, as such, enhance reaction rates in a surface nonspecific manner. Here we present a systematic investigation of a surface catalytic effect. The process studied, oxidation of hydrocarbons, is of biological and atmospheric importance. Evidence is presented for surface enhancement of the reaction by several orders of magnitude, and a mechanism is suggested to rationalize the effect.

Very few controlled experiments have been performed in order to reveal surface nonspecific catalytic effects and their mechanisms.^{2,3} In order to investigate this subject it was important to choose a system where the gas phase analog has been well studied and the surface-adsorbate interaction is well characterized. The reactions of oxygen atoms with alkanes fit these requirements. These reactions have been thoroughly investigated both in the gas and in the condensed phases, and their analogs can be studied when the saturated hydrocarbon chains are in the form of organized monolayers.

The two lowest lying electronic states of the oxygen are separated by only ≈ 190 kJ/mol, and therefore external perturbation may mix them. In the gas, it was verified that the reaction between O(³P) and saturated hydrocarbons proceeds through an abstraction mechanism generating an alkyl radical and OH.⁴ The exothermicity of the reaction (in kJ/mol) is 9.6 for primary (RCH₃) carbons, 29.3 for secondary (R₂CH₂) carbons, and 43.1 for tertiary (R₃CH) carbons, while the energy barriers are 28.9, 18.8, and 13.8 kJ/mol, respectively. Since the activation energies and the pre-exponential factors were found to be almost independent of the exact nature of the saturated hydrocarbon, rates for large complex hydrocarbons can be estimated as the sum of the rates for individual C–H bonds.⁵ In contrast to the inert nature of O(³P), electronically excited oxygen, in its singlet state [O(¹D₂)], has no barrier for reaction with alkanes and therefore reacts much faster, mainly through an insertion mechanism.⁶ For example, the rate constant for the reaction of singlet oxygen with methane was found⁷ to be 3.1×10^{-10} cm³ molecule⁻¹ s⁻¹ compared with 1×10^{-17} cm³ molecule⁻¹ s⁻¹ for the triplet.⁸ Oxidation of liquid phase hydrocarbons by O(³P) produces mainly alcohols together with keto and epoxy derivatives.⁹ Gas phase studies have demonstrated the possibility for

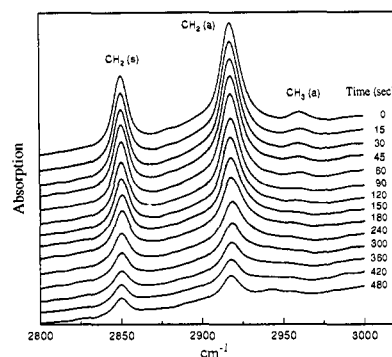


Figure 1. The IR direct absorption spectra of cadmium behenate monolayer adsorbed on silicon as a function of exposure time.

crossing from a singlet potential energy surface (PES) into that of the triplet, in the case where the C–H–O collision complex is in a bent configuration.⁶

In the present experiments, physisorbed monolayers of cadmium behenate [Cdb, (CH₃(CH₂)₂₀COO⁻)₂Cd²⁺] were prepared by the Langmuir–Blodgett method. Chemisorbed monolayers of octadecyltrichlorosilane [OTS, CH₃(CH₂)₁₇SiCl₃] were prepared by self-assembly.¹⁰ Here, the chemisorption process involves the hydrolyzation of the molecules, such that the molecules are attached to the surface through siloxyl groups and cross-linked by Si–O–Si bonds. The substrates were either glass or silicon.

The reaction was performed in a high-vacuum chamber in which the monolayer can be probed "in situ" while the reaction proceeds. O(³P) was produced by 2450-MHz microwave discharge and was introduced into the chamber through a 30-cm-long quartz tube, which served to quench reactive O(¹D) atoms.^{4a} The absence of singlet oxygen in the beam was further verified by probing the rotational energy distribution in OH radicals formed in the reaction with gas phase saturated hydrocarbons.¹¹ The reaction chamber was implanted into the sample compartment of a Bruker IFS66 Fourier transform IR spectrometer. Complementary XPS measurements (Kratos AXISHS) were performed on an OTS monolayer adsorbed on native aluminum oxide on top of a 500-Å aluminum film evaporated on glass.

Figure 1 presents the direct absorption spectra of a Cdb monolayer, at 298 K, as a function of exposure time to O(³P). Three absorption peaks were monitored corresponding to the CH₂ symmetric, CH₂ asymmetric, and CH₃ asymmetric stretching. In addition, a broad peak in the FTIR spectra corresponding to OH vibrations coupled by hydrogen bonding was observed at 3100–3450 cm⁻¹ (Figure 2). The absorption of the CH₂ and CH₃ groups versus reaction time is shown in Figure 3. Pseudo-first-order reaction kinetics is indicated. The same kinetics was observed also for OTS.

In order to compare with the identical gas phase reactions, we have calculated the reaction probability (R_p) for both phases. The reaction probability represents the ratio between the rate of "productive" collisions (P_c) in the hydrocarbon (either attached to the surface or in the gas) to the total number of collisions per second (Z). In the gas, the "rate of productive collisions per functional group" is the kinetic rate constant, taken from the literature ($K_{CH_2} = 1.2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, $K_{CH_3} = 5.1 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹),⁸ multiplied by the concentration of oxygen atoms. For the monolayer, this number equals the slope in Figure 3:

$$P_c = -\frac{1}{I} \frac{dI}{dt} = -\frac{d(\ln I)}{dt} k[O] = k \frac{f}{AV} \quad (1)$$

where I is the absorption intensity and $[O]$ is the concentration of oxygen atoms at the surface. f is the flow rate of oxygen

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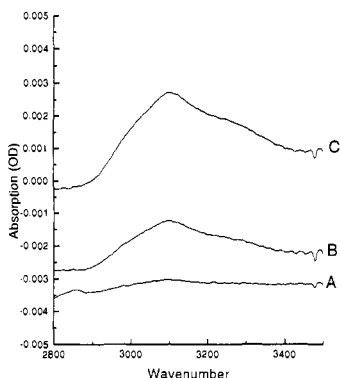


Figure 2. The IR absorption of cadmium behenate monolayer in the region corresponding to the OH absorption: (A) before exposure to O(³P), (B) after exposure for 30 s, and (C) after exposure for 90 s to the O(³P) beam. The spectra were shifted vertically on the absorption scale for clarity of the presentation.

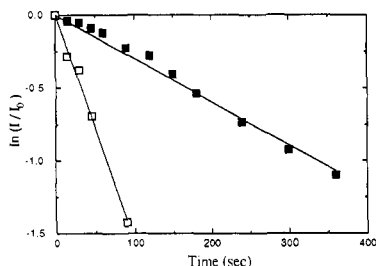


Figure 3. A logarithmic scale plot for the absorption signals of the CH₂ (filled squares) and CH₃ (open squares) asymmetric stretching bands as a function of reaction time for a monolayer of cadmium behenate.

atoms, estimated to be $(1.7 \pm 0.2) \times 10^{15}$ molecules s⁻¹ based on mass spectrometry measurements which determined the atomic oxygen concentration (about 10%) in the molecular oxygen beam. A is the cross section of the beam at the surface (measured to be 6.15 cm²), and V is the mean velocity of the oxygen atoms, 6×10^4 cm s⁻¹. The total number of collisions per second per one functional group was calculated, assuming a hard sphere model:

$$Z = \pi r^2 \frac{f}{A} = \pi r^2 [O] V \quad (2)$$

where r is the radius of collision (taken as 2 Å). With the above considerations the reaction probability at 300 K for CH₃ in the gas phase is 5×10^{-6} whereas for the methyl group of the monolayer R_p was found to be more than 3 orders of magnitude larger (4×10^{-2}). As for the methylene, the difference in the reaction probability for the gas and for the monolayer is less pronounced (2×10^{-4} and 9×10^{-3} , respectively). The errors in the calculations for the reaction probabilities are, at most, less than 1 order of magnitude and result from some uncertainty in measuring the beam diameter and in the percentage of atomic oxygen in the beam. The high reaction probability is another indication that no contamination of electronically excited oxygen is responsible for the observation, since it requires few percent contamination of O(¹D). This amount could be easily detected by the methods used by us (as described in ref 11).

Figure 4A shows the carbon (1s) XPS signal from the monolayer prior to exposure, peaking at a binding energy of 285.5 eV. Parts B and C of Figure 4 show the same peak after 90 and 300 s of exposure to O(³P). Note the formation of a shifted peak at ca. 289.0 eV corresponding to formation of C–O bonds. By fitting the peak of the carbon to two Gaussians we were able to estimate the extent of C–O bonding relative to the methylenic carbons. For exposure times of 90 and 300 s, $21 \pm 5\%$ and $35 \pm 5\%$,

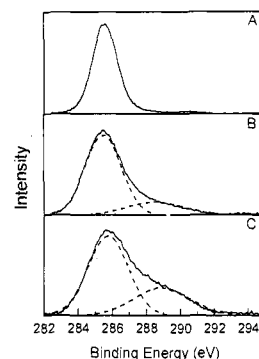


Figure 4. The carbon (1s) signal in an XPS measurement of OTS/Al: (A) prior to reaction, (B) after 90 s of exposure to O(³P), and (C) after 300 s.

respectively, of the total carbon concentration are attributed to carbons attached to an oxygen. These numbers are consistent with the FTIR results which measure the loss of CH₂.

The two new findings in the present experiments are as follows: (1) the large enhancement of the reaction probability of the methyl group, which is 3 orders of magnitude larger than the reaction probability in the gas phase; (2) the larger reaction rate observed for the methyl compared to the methylene group. The enhancement in the reactivity can be rationalized as due to an efficient intersystem crossing which causes the oxygen atom to react as if it is in its singlet state instead of the initial triplet state. It is known⁶ that the two PES cross each other if the collision complex is in a T shape; therefore, triplet atoms may cross to the singlet, and react on the singlet PES to create alcohols. Since the intersystem crossing occurs at the entrance channel, and since the singlet oxygen does not have any barrier for the reaction with saturated hydrocarbons, the activation energy under such a scenario is close to 0 and the reaction rate constant is enhanced. The probability for curve crossing depends on the overall time that the reactant spends in the crossing region.¹² Therefore, formation of a long-lived collision complex increases the probability for such event. An indication for curve crossing from O(³P) to O(¹D) was obtained in the gas phase in the reaction between cyclohexane clusters and O(³P).¹¹ There, the low-frequency van der Waals modes of the cluster provided the density of states required to stabilize the collision complex. The observed effect, in the reaction of organic monolayers, can be attributed to the long residence time of the O(³P) atom on the surface which enables curve crossing and reaction on the singlet PES. As a support for this mechanism, we have found that when a single methyl group is attached to the surface in the form of a monolayer of methyltrichlorosilane (MTS), it reacts more slowly than the methyl group of a "floppy" long-chain amphiphile such as the OTS monolayer.

The enhancement in reactivity probably occurs for both methylene and methyl groups. However, for the former there is a steric hindrance for the oxygen to reach the CH₂ groups which are closer to the surface, due to the barrier for penetration between the chains. Therefore, the enhancement of the reactivity observed is less pronounced, compared to that in the gas phase.

The present work demonstrates clearly how "walls" can effect reactivity with no specificity. It is important to realize that this effect is expected to be significant when curve crossing can occur and where this nonadiabatic interaction can affect significantly the reaction mechanism.

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