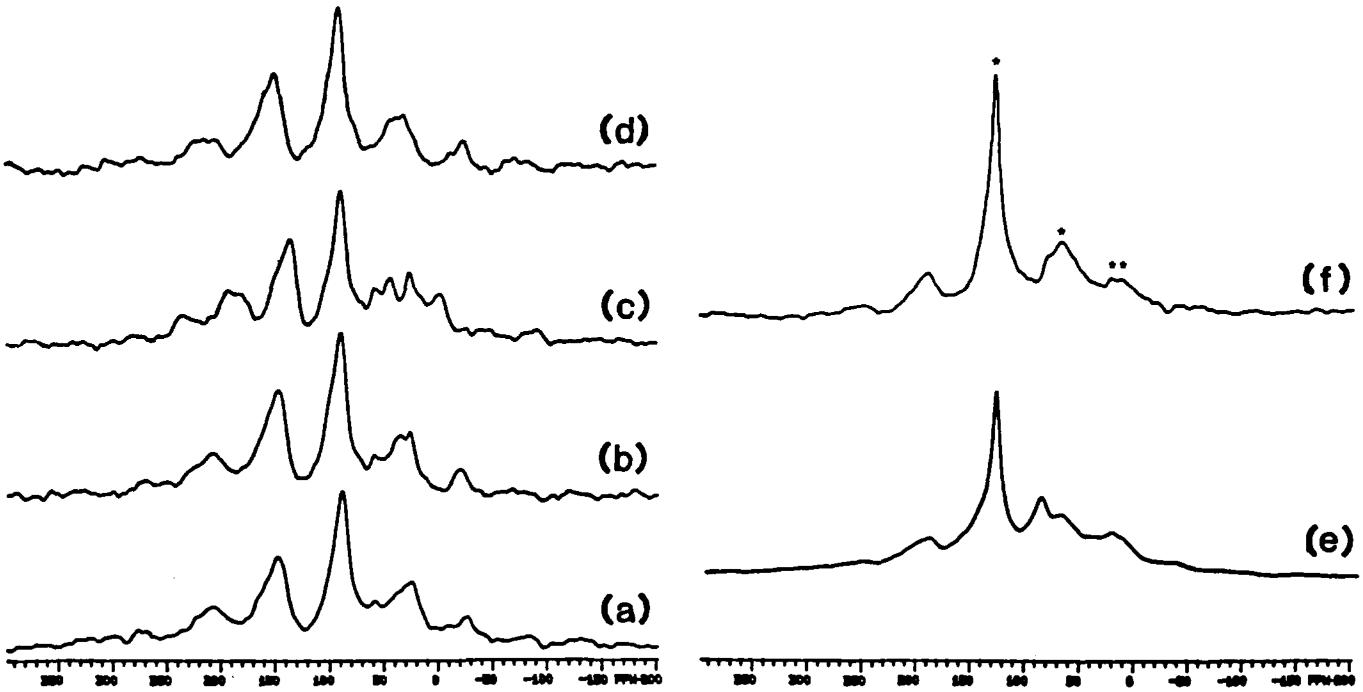


Figure 1. 75.43-MHz ^{13}C solid-state CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed on γ-alumina surface at (a) −54 °C, spinning speed is 4.3 KHz; (b) −25 °C, spinning speed is 4.2 KHz; (c) −0.5 °C, spinning speed is 3.4 KHz; (d) room temperature, spinning speed is 4.4 KHz; (e) adsorbed on 5% Pt/γ-Al_2O_3 at room temperature, spinning speed is 4.5 KHz; and (f) obtained by subtraction of the ^{13}C spectrum of γ-alumina, Figure 1d, from spectrum of 5% Pt/γ-Al_2O_3, Figure 1e. Scaling employed is such that the peaks at 148 and 88 ppm are cancelled (see text for details). Each spectrum results from 20 000 scans. Line broadening of each spectrum is 400 Hz. Scale is in parts per million with respect to TMS. Asterisks (*) in Figure 1f represent isotropic peaks due to the presence of Pt metal.

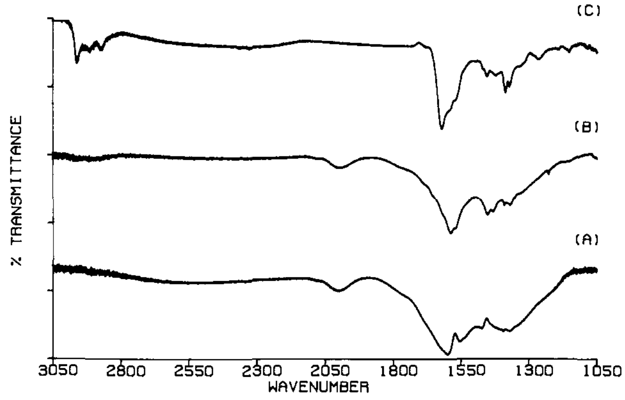
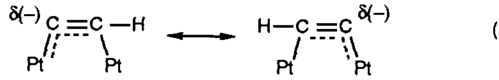


Figure 2. Infrared spectra of adsorbed C_2H_2 at room temperature on (A) 10% Pt/γ-Al_2O_3, (B) 5% Pt/γ-Al_2O_3, and (C) γ-Al_2O_3. All of infrared spectra were obtained with Nicolet Model 740 spectrometer. The sample used to study the chemisorption of acetylene on alumina and platinum by infrared spectroscopy in the region of 3050–1050 cm^{-1} is cleaned in vacuum by alternating H_2 and O_2 flow at 298 °C. The acetylene is injected to sample cell at room temperature in vacuum. In about 5 min after sample loading the cell is evacuated again to remove any residual of C_2H_2. Spectra of the sample have been ratioed with background after loading.

resonance at 129 ppm is indicative of the formation of platinum π-complexed species in the form of a monoanion of acetylene, i.e.


(3)

The partial triple-bond nature of the species is supported in the IR spectra of the same sample in Figure 2.[10] From a comparison of the room temperature and −54 °C spectra of the 5% Pt/γ-Al_2O_3 sample we observed a loss of intensity and increase of line width of the resonance at 129 ppm. This observation strongly suggests that dynamics are involved. The exact nature of these dynamics will be the topic of further investigations.

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Determination of the Rate Constant of Self-Exchange of the $O_2/O_2^{\bullet -}$ Couple in Water by $^{18}O/^{16}O$ Isotope Marking

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The apparent self-exchange rate of the dioxygen/superoxide couple as estimated from the Marcus cross relationship[1] varies by about 16 orders of magnitude.[2] The present work is the first experimental measurement of this parameter.

The measurements utilize as a probe ^{18}O during the exchange reaction 1

$$^{36}O_2^{\bullet -} + {}^{32}O_2 \rightarrow {}^{36}O_2 + {}^{32}O_2^{\bullet -} \qquad (1)$$

which occurs prior to the second-order dismutation reaction 2.

$$O_2^{\bullet -} + HO_2^{\bullet} \rightarrow O_2 + HO_2^{-} \qquad (2)$$

The rate of reaction 2 is strongly pH dependent[3] and is rather

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slow in our system. Ultimately we measure the amount of ^{18}O incorporated into the product H_2O_2 which in the end is decomposed in reaction 3.

$$H_2O_2 \xrightarrow{\text{catalase}} {}^{1}\!/_{2}O_2 + H_2O \qquad (3)$$

The experiments were carried out as follows.

$^{36}O_2{}^{\bullet-}$ was produced by γ-irradiating 30 mL of an aqueous solution saturated with $^{36}O_2$ and containing 0.3 M 2-propanol, 0.02 M NaOH, and 10^{-3} M diethylenetriaminopentaacetic acid (DTPA) in a 60-mL vessel. This is a standard method for producing superoxide[4] except that we employed 2-propanol as it did not affect the catalase reaction 3. Prior to irradiation the sample was purged with Ar to remove all oxygen. After evacuation the free volume (30 mL) of the vessle was filled with ca. 500 mbar of $^{36}O_2$. Saturation of the aqueous solution was then performed by vigorously shaking the solution. The γ-source had a dose rate of 0.41 Gy/s, and the irradiation time was 5 min. The total production of $^{36}O_2{}^{\bullet-}$ amounted to 7.5×10^{-5} M as was confirmed by UV spectroscopy. After discontinued irradiation the sample was immediately purged with Ar during 1 min to remove the $^{36}O_2$. Subsequently, $^{32}O_2$, pure or mixed with N_2, was bubbled through the solution. After a given time 1 mL of a 1 M NaH_2PO_4 solution was injected to lower the pH to 7 and thus to force the $O_2{}^{\bullet-}$ radicals to dismute into O_2 and H_2O_2 in less than 1 s. The solution was bubbled with Ar and carefully evacuated to remove all O_2. Catalase was then injected to decompose the H_2O_2 into O_2 and H_2O. The oxygen was analyzed by MS in a small quadrupole mass spectrometer by scanning from *m/e* 26 to *m/e* 38 and measuring the peaks at *m/e* 32 and *m/e* 36. The amount of background air in the vacuum system was monitored by measuring the peak at *m/e* 28, and the peak at *m/e* 32 was accordingly reduced. By UV spectroscopy the second-order rate constant for dismutation of $O_2{}^{\bullet-}$ in the irradiated solution (prior to the addition of the phosphate buffer) was found to be 9.5 M^{-1} s^{-1} ($2k_2/\epsilon = 4.7 \times 10^{-3}$ cm s^{-1} at 255 nm[5]). In test experiments utilizing unlabeled O_2 the oxygen formed in reaction 3 was measured with an oxygen electrode and found to be 2.2×10^{-5} M. This shows that catalase decomposes H_2O_2 completely in our system.

$^{36}O_2$ (Merck 97.6% $^{36}O_2$), NaOH (Aldrich semiconductor grade), and DTPA (Aldrich) were used as received. 2-Propanol (Merck p.a.) was distilled over CaH_2, and water was triple distilled in quartz.

The amount of $^{32}O_2$ incorporated into the H_2O_2 product is a measure of the extent of reaction 1. Obviously the ratio of O_2 to N_2 in the purging gas and the time elapsed between the onset of the bubbling and the addition of the quencher solution determine the amount of $^{32}O_2{}^{\bullet-}$ formed in reaction 1.

In a first set of experiments we used 100%, 20%, and 10% $^{32}O_2$ and varied the bubbling time from 10 to 2 min. We could only detect a significant increase in the amount of remaining $^{36}O_2$ when 10% O_2 was used during 2 min. This revealed that the rate constant of reaction 1 is larger than 100 M^{-1} s^{-1}.

In principle, the measurements would improve upon diminishing both the oxygen content and the bubbling time. In working with a gas–liquid interface the time to equilibrate the solution with $^{32}O_2$ cannot be reduced to less than ca. 15 s as was evidenced by the response of an oxygen electrode. Thus we chose to use a time of 1 min which corresponds to an effective reaction time of 45–60 s. The lower the $^{32}O_2$ concentration the more severe is the demand to reduce $^{36}O_2$ in the solution prior to bubbling. 5% O_2 proved a practical compromise. The results of these experiments are presented in Table I. The radiation chemical yield of H_2O_2 in our system (in $10^7 \times$ mol/J units) is 3.7, from which 0.7 derives from H_2O_2 formed[4] from $H_2{}^{16}O$ and the remaining 3.0 is produced in reaction 2. Thus, 19% of the total H_2O_2 yield should always turn up as $H_2{}^{32}O_2$, which is close to the experimental value (see first row in Table I). This amount should be subtracted from the yield of $H_2{}^{32}O_2$ obtained in the presence of $^{32}O_2$. The dismutation of superoxide (reaction 2) proceeding during the time of irradiation and subsequent Ar bubbling will form $H_2{}^{36}O_2$. The value, calculated to be 12% from the experimental $2k_2$ and the dose rate, is in agreement with the percentage of $H_2{}^{36}O_2$ measured subsequent to bubbling with 100% $^{32}O_2$ for 10 min. The good match between expected and found values shows that no unwanted side reactions occur. After allowing for these backgrounds we obtain the corrected values presented in columns 4 and 5. It is seen that out of the total H_2O_2 measured only 71% is affected by reaction 1.

Table I. The Percentage of $^{32}O_2$ and $^{36}O_2$ As Measured by Mass Spectromety After Decomposing the Product H_2O_2 into Oxygen and H_2O by Catalase

O_2 in N_2, %	*t*, s	$^{32}O_2$, %	$^{36}O_2$, %	corr $^{32}O_2$, %	corr $^{36}O_2$, %
0	0	17	83		
100	600	88	12		
5	60	77	23	60	11
5	60	75	25	58	13

The rate constant for reaction 1 is given by

$$\ln \frac{{}^{32}O_2 + {}^{36}O_2}{{}^{36}O_2} = \ln \frac{71}{12} = k_1[O_2]t$$

where the values on the left-hand side are the corrected values in Table I, while $[O_2]$ is the concentration of $^{32}O_2$ in the solution during bubbling (6.5×10^{-5} M). k_1 is found to be 450 ± 160 M^{-1} s^{-1}. The error is estimated from the spread in the tabulated values (10%) and the uncertainty in the product $[O_2]t$ during bubbling (25%).

From the Marcus relationship[1] k_1 yields $\lambda^\circ = \lambda^\circ_{in} + \lambda^\circ_{out} = 45.5 \pm 0.7$ kcal/mol. By using molecular parameters[6] and the harmonic approximation[1] λ°_{in} is estimated to be 15.9 kcal/mol resulting in λ°_{out} = 29.6 kcal/mol. The latter value corresponds to an effective radius of ca. 3 Å.

In the experiments no $H_2{}^{16}O{}^{18}O$ (less than 0.1%) is formed. The complete absence of the isotopically mixed product confirms[7] that reaction 2 is an electron transfer in contrast to the dismutation[8] of two $HOO^\bullet$. Assuming similar effective radii for the $O_2/O_2{}^{\bullet-}$ and the $HO_2{}^\bullet/HO_2{}^-$ couples $k_{ex}(HO_2{}^\bullet/HO_2{}^-) = 17$ M^{-1} s^{-1} is calculated from the Marcus cross-relationship[1] when applying the kinetic[3] and thermodynamic[9] parameters reported for reaction 2.

In outer-sphere autoxidation reactions, where the effective radius of the partner couple is larger than that of the $O_2/O_2{}^{\bullet-}$, the λ°_{out} values are not strictly additive.[10] Consequently, the apparent $k_{ex}(O_2/O_2{}^{\bullet-})$ as calculated from the Marcus cross-relationship may turn out lower than k_1 by up to a few orders of magnitude. Values of 1–1000 M^{-1} s^{-1} as obtained in ref 11 and 12 are therefore consistent with k_1. However, apparent k_{ex} values much lower and in particular significantly *higher* than the experimental k_1 would seem to mitigate against an outer-sphere electron transfer.

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