spite the large values typical for quenching processes.

Also noteworthy is the apparent dependence of quenching rate constants upon the type of substituents in the quenching molecules. The relationships described should be useful for predicting rate constants for quenching of $OH(A^2\Sigma^+)$ by alkanes and haloalkanes where measurements are not available.

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Registry No. OH, 3352-57-6; CCl₄, 56-23-5; CFCl₃, 75-69-4; CF₂Cl₂, 75-71-8; CF₄, 75-73-0; CHF₃, 75-46-7; CHF₂Cl, 75-45-6; CHFCl₂, 75-43-4; CH₂F₂, 75-10-5; CH₃CCl₃, 71-55-6; CH₃CF₂Cl, 75-68-3; CH₃C-F2H, 75-37-6; CF3CHCl2, 306-83-2; CF3CH2Cl, 75-88-7; CF3CH3, 420-46-2; CF3CF2H, 354-33-6; CF3CFH2, 811-97-2; CF2HCF2H, 359-35-3; CF₂HCFH₂, 430-66-0; isobutane, 75-28-5; 2,2-dimethylpropane, 463-82-1; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8.

Production of OH on Polycrystalline Nickel Studied by Thermal **Desorption/Laser-Induced Fluorescence**

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The production of hydroxyl radical following either the reaction of H_2/O_2 mixtures or the dissociation of H_2O on polycrystalline nickel has been studied in a flow system. The hydroxyl radicals were detected in the gas phase by laser-induced fluorescence (LIF) following desorption from the catalyst surface at temperatures above 850 K. The apparent activation energy for OH desorption from nickel varied from 26 to 40 kcal/mol depending upon the O/H ratio. The effect of the partial pressure of O_2 and H_2 on the OH production rate was measured and a mechanism to explain these results is proposed. The reaction of $CO + H_2$ over polycrystalline nickel was also studied. However, no OH radicals were detected desorbing from the surface at temperatures up to 1350 K.

Introduction

There is considerable interest in the interactions of O_2 , H_2 , and H_2O with nickel surfaces and particularly with regard to the presence of a Ni-OH species.¹⁻¹¹ It is known that water will absorb on nickel at room temperature only in the presence of oxygen.^{6,10} Most researchers have attributed this to the formation of some type of OH surface species. However, two oxygen 1s peaks are often observed in the XPS spectra when O₂ and H₂O are coadsorbed on nickel, implying two types of oxygen are present. This has been explained by assuming either the presence of a "defect" nickel oxide² or partial bonding of water to an absorbed oxygen.⁹ Recently, Benndorf et al. have reported observing only a single oxygen 1s peak by XPS and suggested that earlier measurements of an oxygen doublet were caused by a mixture of O, OH, and H₂O surface species.¹⁰

Several groups have detected $Ni_n(OH)^+$ and OH^- fragments from $O_2/H_2/Ni$ systems by SIMS.^{5,8,11} Benninghoven et al. have studied the reactions of O_2 and H_2 with polycrystalline nickel by SIMS and thermal desorption/mass spectrometry.¹¹ OH was detected by SIMS following the reaction of H_2 with oxygen covered polycrystalline nickel. Upon heating, the desorption of water and a loss of the SIMS OH- signal was observed. Interestingly, the temperature at which this process occurred depended upon the degree of oxidation of the surface. This was presumed to be due to variations in the Ni-OH bond strength.

The reactions of CO and H₂ over nickel are very important since this reaction is of industrial importance in the production of methane.11-21 Of the several mechanisms which have been proposed for the methane synthesis reaction, none involve an Ni-OH intermediate.¹² Low-temperature studies of coadsorbed CO and H₂ on nickel to date have revealed no OH bonds by EELS or HREELS.^{17,18} However, at reaction temperatures both CO and H₂ are known to be dissociated on nickel surfaces and both O and H are present on the surface. It is therefore possible that the Ni-OH species is present in this system and may be an in-

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termediate in a competing reaction, i.e., the production of water.²⁰

In the present work we have utilized thermal desorption/laser-induced fluorescence (TD/LIF) to investigate the production of OH from polycrystalline nickel. Previously we have used this method to observe the desorption of OH from polycrystalline platinum and to study its production rate, apparent activation energy of desorption, and energy accommodation.²³⁻²⁶ This

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Figure 1. Production of OH from nickel; dependence on O_2 partial pressure.

technique has the advantage that it offers extreme sensitivity and selectivity for OH radicals. In addition, laser-induced fluorescence can be used at pressures up to several torr, much higher than are possible with most surface science diagnostics. Thus a flow reactor can be utilized which is analogous to actual catalytic systems.

Experimental Section

A complete description of the experimental apparatus appears elsewhere.²⁹ Briefly, a nickel wire (0.5 mm diameter, 25 cm long, 99.9% pure) was coiled into a flat spiral and positioned inside a 3-cm-diameter glass flow reactor in a plane perpendicular to the gas flow. The wire was attached to copper feedthroughs which enabled it to be resistively heated to 1400 K. H₂O was obtained by bubbling argon through deionized distilled water. O₂, H₂, and CO (all 99.9% purity) were used as received without further purification. For a given run, the gases were all mixed upstream of the catatlyst with argon and the argon partial pressure was adjusted until the total pressure was 2 torr. Under these conditions the flow rate was 500 cm/s.

The region 2-cm downstream of the catalyst was probed for OH desorption by LIF techniques. Either a flashlamp pumped or an excimer pumped dye laser was frequency doubled and used to excite the $A^2\Pi \rightarrow X^2\Sigma$ transition of OH near 307.8 nm. The OH fluorescence was focused through a band-pass interference filter centered at 309 nm with a 10-nm bandwidth and imaged onto a RCA 31034 photomultiplier tube. The output of the photomultiplier tube was amplified and averaged by either a signal averager or a gated integrator interfaced to a computer. In both cases the averaged signal was ratioed against the excitation energy of the laser pulse to obtain a measurement of the relative OH radical concentration.

Results and Discussion

Reactions of H_2 , O_2 , and H_2O over Ni. OH radicals produced by the reaction of O_2/H_2 mixtures with polycrystalline nickel and desorbed from the surface were observed downstream of the catalyst at surface temperatures greater than 850 K. Under all the conditions used in this paper the majority of the adsorbed OH react on the surface to form water which subsequently desorbs.¹¹ The desorption of intact OH is a relatively minor channel (we



Figure 2. Production of OH from nickel; dependence on O_2 partial pressure.

estimate the H_2O/OH desorption yield ratio to be >10⁴). This is a distinct advantage of TD/LIF in probing reaction intermediates in that the reaction of interest is essentially unaffected by the "probe".

The OH production rate was dependent upon the partial pressures of both oxygen and hydrogen as shown in Figures 1 and 2. At constant hydrogen pressure, the steady-state concentration of OH increased almost linearly with increasing O_2 partial pressure until the O_2 pressure reached about 60 mtorr. The leveling off of the OH signal at greater oxygen concentrations is believed to be due to saturation of the surface with oxygen atoms. In contrast, increasing the hydrogen partial pressure at constant oxygen pressure caused an initial increase in the OH production rate followed by a decrease with the maximum production of OH occurring at an O_2/H_2 ratio of 2:1 (Figure 2). The decrease in OH concentrations at higher concentrations of H_2 has been observed previously in the reaction of O_2/H_2 with polycrystalline platinum²⁷ and is consistent with the following mechanism:

$$H_2(g) \rightarrow 2H(ads)$$
 (1)

$$O_2(g) \rightarrow 2O(ads)$$
 (2)

$$H(ads) + O(ads) \rightarrow OH(ads)$$
 (3)

$$OH(ads) + H(ads) \rightarrow H_2O(g)$$
 (4)

$$OH(ads) \rightarrow OH(g)$$
 (5)

$$O(ads) + OH(ads) \rightarrow O_2(ads) + H(ads)$$
 (6)

Increasing the hydrogen concentration initially increases the OH(ads) concentration via steps 1 and 3. However, hydrogen is also involved in step 4 which removes OH. At higher hydrogen concentrations the rate of this removal step is increased and the steady-state concentration of OH is reduced. The fact that a similar downturn in the OH production rate is not observed when the O_2 partial pressure is increased implies that the analogous removal process, step 6, is unimportant under these conditions.

The rate of OH production was observed to be strongly dependent on the catalyst temperature. If the concentration of the desorbed gas-phase OH is assumed to be proportional to the concentration of adsorbed OH then an Arrhenius plot of the OH signal vs. 1/T can be used to determine the apparant activation energy of the OH production process. Such a plot showing the activation energies determined from three different O_2/H_2 ratios is given in Figure 3. If the desorption step is assumed to be the slow step in the OH production process, which is likely, then these apparent activation energies are indicative of the Ni–OH bond strength.²⁸ This assumption is supported by the fact that OH was observed from the decomposition of H₂O over polycrystalline nickel

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Figure 3. Typical Arrhenius plots for the desorption of OH from nickel. For O/H = 300, $O_2 = 300$ mtorr, $H_2 = 1$ mtorr; O/H = 2, $O_2 = 100$ mtorr, $H_2 = 50$ mtorr; and O/H = 0.0025, $O_2 = 1$ mtorr, $H_2 = 400$ mtorr. The total pressure for all runs was fixed at 2 torr by addition of Ar. The solid lines are least-squares fits to the data points yielding apparent activation energies for OH desorption of $28 \pm 2 \text{ kcal/mol}$ for O/H = 300, 39 ± 1 kcal/mol for O/H = 2, and 38 ± 2 kcal/mol for $\dot{O/H} = 0.0025.$

with $E_{des} = 37 \pm 2$ kcal/mol which is essentially the same activation energy observed when OH was produced from $2:1 \text{ H}_2/\text{O}_2$ where $E_{des} = 39 \pm 1$ kcal/mol. This implies that the rate-limiting step is the desorption step and therefore the source of the H and O does not affect the observed activation energies. This has also been observed for the production of OH from polycrystalline platinum surfaces. In that case O2, H2O, and N2O were all used as sources of oxygen for the reaction with H(ads) and no effect on the measured activation energy for the OH desorption process was observed.^{23-25,27}

The similarities between the Ni/OH work presented here and our earlier work on Pt/OH were unexpected. However, there are a number of documented similarities between these two systems. Estimates of the Ni-O and Pt-O bond strengths are similar.³⁰ OH is known to be present and stable on both Ni and Pt surfaces.^{10,31} Absorbed oxygen acts as a promoter for H₂O adsorption on Ni(110) by forming OH(ads). On clean Ni H₂O desorbs at \approx 260 K but on the oxygen predosed Ni this occurs at \sim 300 K.¹⁰ Similarly, H₂O desorbs from clean Pt(111) at \approx 180 K but if the Pt is predosed with oxygen this occurs at ≈ 210 K.³¹

Nonetheless, one possibility for the similarities between the Ni/OH and the Pt/OH experiments could be that the desorption of OH is occurring from a common impurity. We are currently conducting UHV experiments to investigate this possibility. Our initial results confirm that OH does desorb from polycrystalline platinum which has been sputtered clean and shown to have no surface impurities detectable by Auger analysis. This leads us to conclude that similarities between OH desorption from Ni and Pt are real and are not the result of a common impurity.

One significant difference between these two systems is reflected in the dependence of the apparant activation energy for OH desorption on the O_2/H_2 ratio. The activation energy for the desorption of OH from Pt was previously observed to increase steadily from 27 kcal/mol, at a O_2/H_2 ratio of 100 to ≈ 51 kcal/mol, at a O_2/H_2 ratio of 0.037.²⁸ In contrast, the activation energy for the desorption of OH from nickel as a function of the O_2/H_2 ratio approximates a step function as shown in Figure 4.



Figure 4. Dependence of the apparent activation energy for the desorption of OH from Ni as a function of the O/H ratio.

At high oxygen concentrations an activation energy of ≈ 29 kcal/mol was typical whereas at high hydrogen concentrations a value of \approx 39 kcal/mol was observed. This is similar to the work of Benninghoven et al. who observed the formation of OH groups of different binding energies depending on the degree of oxidation of a nickel surface.¹¹ In their experiments, OH⁻ was detected by SIMS following the reaction of H₂ with polycrystalline nickel covered with chemisorbed oxygen. Heating to 325 K resulted in the desorption of water and a loss of the SIMS OH- peak. A similar process occurred at 700 K when H₂ was reacted with polycrystalline nickel covered with a closed oxide (NiO). It was concluded that both observations were due to the reaction 2OH- $(ads) \rightarrow H_2O(ads) + O(ads)$. The higher temperature of desorption for water in the closed nickel oxide case was presumed to be due to a stronger Ni-OH bond.

Under our conditions, both chemisorbed oxygen and NiO should be present in different proportions depending on the O_2/H_2 ratio present in the flow reactor. Auger electron spectroscopic (AES) analysis of the nickel surface performed after running the flow reactor under oxygen-rich conditions indicated the presence of both chemisorbed oxygen and oxygen as NiO in a 2:1 ratio. Desorption of OH under these conditions would occur primarily from the weaker sites, i.e., the chemisorbed O + H(ads) reaction. When $H_2/O_2 >> 1$, however, reaction 4 is expected to dominate the catalytic process, removing OH(ads) predominently from those labile sites on which species move around more rapidly. In this case the desorbed OH would come primarily from the more strongly bound sites, i.e., from the Ni-O + H(ads) reaction. In conclusion, the OH species desorbing with an activation energy of \approx 39 kcal/mol are believed to come from the reaction of Ni–O + H(ads), whereas the reaction of chemisorbed oxygen with H(ads) produces the more weakly bound (≈ 29 kcal/mol) OH species.

Reaction of CO, H_2 over Ni. The CO/H₂/Ni system was also investigated. However, no OH radicals were detected up to 1350 K for reactions of CO/H_2 mixtures ranging from 1:10 to 10:1 on nickel. Apparently little, if any, OH species are formed on the nickel surface and desorbed under these conditions.

The reaction of CO plus H₂ over nickel used to produce methane is generally reported to proceed by the following mechanism:^{12,15}

$$CO(g) \rightarrow C(ads) + O(ads)$$
 (7)

$$H_2(g) \rightarrow 2H(ads)$$
 (8)

(10)

$$C(ads) + H(ads) \rightarrow CH(ads)$$
 (9)

$$CH(ads) + H(ads) \rightarrow CH_2(ads)$$
(10)
$$CH_2(ads) + H(ads) \rightarrow CH_3(ads)$$
(11)

$$CH_3(ads) + H(ads) \rightarrow CH_4(g)$$
 (12)

In this mechanism CO is dissociated on the nickel surface (reaction

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7). Since it has already been shown that adsorbed oxygen and hydrogen can react to produce OH which can desorb, it seems plausible that OH should be observed for this system. The fact that OH was not observed leads us to conclude that the steady-state concentration of either H(ads) or O(ads) is very low under the conditions examined. It is known that O(abs) reacts with CO to form CO₂ which subsequently desorbs.^{12,14,15} AES analysis performed by other investigators on an active catalyst surface following reaction with H_2/CO indicated the absence of oxygen.^{32,33} We have observed that the addition of O₂ to the H_2/CO stream results in an observable OH signal. Therefore it is likely that the steady-state concentration of O(ads) is very low when

only \dot{H}_2 and CO are present which results in a low steady-state concentration of OH(ads).

Conclusions

The desorption of OH has been clearly observed following either the oxidation of H_2 or the decomposition of H_2O on a polycrystalline nickel surface. The apparant activation energies for this process range from approximately 27 to 41 kcal/mol and are believed to be a measure of the Ni–OH bond strength. In the CO + H_2/Ni system no OH was observed up to a temperature of 1350 K. This is believed to be due to an extremely low concentration of adsorbed oxygen atoms and hence, adsorbed OH.

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Electron Spin Resonance Investigation of Intramolecular Hydrogen Transfer and Alkyl Attack in Ester Cation Radicals

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Reactions of the cation radicals of a number of butyl and neopentyl ester cations have been investigated by electron spin resonance spectroscopy. Radicals are formed at cryogenic temperatures by γ -irradiation of dilute CFCl₃ frozen solutions of the esters. Ester cation radicals have been shown to be especially reactive intermediates in previous work. However, in this work a number of neopentyl ester cations have been stabilized at 77 K. The major couplings in these cations arise only from three of the protons on the terminal methyl groups of the neopentyl portion of the cation. Thus the charge is predominantly located in the neopentyl group. In this work it is shown that, on annealing, the cation radicals of certain neopentyl, *tert*-butyl, and butyl esters form alkyl radical intermediates by intramolecular hydrogen transfer, presumably to the carbonyl oxygen. These ester radicals further undergo intramolecular alkyl attack on oxygen to form a rearranged radical via a heretofore unknown mechanism. Neopentyl formate cation radical undergoes a different reaction first by loss of a *tert*-butyl cation structure to form isobutene cation radical. Selective deuteration at various positions on the alkyl side groups is used to verify the assignment of hyperfine couplings to positions on the radical structures as well as to verify the rearrangement and fragmentation reactions. The reactivity of ester cation radicals is discussed and summarized.

Introduction

Ester cation radicals formed by γ -irradiation, at cryogenic temperatures, of haloalkane solutions of the parent ester have been shown to undergo a surprising diversity of chemical reactions, some even occurring at 4.2 K.¹⁻⁷ Since most organic compounds form stable cation radicals under the same conditions, it was unexpected that the ester cation radicals should be as unstable and reactive as they are. At this time, the only ester cation radical which is stable at 77 K that has been properly identified in the literature is that of neopentyl formate.⁶ Since the ester cation radicals are unstable, an obvious question evolves regarding what reactions they undergo.

There are two types of reactions which have been described for ester cation radicals in solid-state Freon matrices. One is intramolecular hydrogen or proton transfer, frequently from the alcohol β -carbon, to another site on the molecule.^{2,3,5-7} Ethyl formate typifies this reaction.^{6,7}

$$\begin{array}{cccc} O & CH_3 & OH & CH_2 \\ H & C & - CH_2 & - - - + & - + & - + \\ H & - C & - & CH_2 & - - + & - + & - + \\ H & - & C & - & CH_2 & - & - + \\ \end{array}$$
(1)

Propyl acetate undergoes a similar reaction.⁶ At times, hydrogens other than those from the β -carbon reaction, as is the case for *n*-propyl formate^{3,6} in which a hydrogen on a γ -carbon reacts and isopropyl formate⁶ in which it is a hydrogen on an α -carbon. Experimental evidence regarding the actual location of the transferred hydrogen has been reported only for methyl formate.³ By analogy with this result and accepted mass spectroscopic cation radical mechanisms, we have also generally assumed that the hydrogen has been cited as a potential site for transfer.^{8,9} We refer

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