

A Comparative Study of OH Radical Desorption in the $H_2 + O_2$ Reaction on Pt, Pd, Rh, Ir, and Ni

S. LJUNGSTRÖM, J. HALL, B. KASEMO, A. ROSÉN, AND T. WAHNSTRÖM

Department of Physics, Chalmers University of Technology, and University of Göteborg, S-412 96 Göteborg, Sweden

Received November 3, 1986; revised April 22, 1987

OH radicals emitted from Pt, Pd, Rh, Ir, and Ni during the reaction between H_2 and O_2 have been studied by laser-induced fluorescence. The OH emission yields from the different catalysts were determined as a function of total pressure (5×10^{-3} –0.2 Torr), temperature of the catalyst (950–1300 K), and H_2/O_2 partial pressure ratio. When varying the total pressure at a constant mixing ratio of the reactants, a maximum intensity of OH yield is obtained at 0.7 ± 0.1 Torr for all catalysts. The OH production is very sensitive to the mixing ratio of H_2 and O_2 , and shows a maximum at a specific ratio, which varies for the different catalysts. The maximum in the OH production does not coincide with the maximum in the H_2O production. The absolute intensity of desorbed OH radicals varies strongly with the different catalysts in the order Pt > Pd > Rh > Ir > Ni. When the H_2 gas supply is closed, OH radicals are still detected, indicating that the reaction $H_2O_{ads} + O_{ads} \rightarrow 2OH_{ads}$ contributes to the observed OH intensity. The apparent desorption energy of OH shows a weak dependence on total pressure but a strong dependence on the mixing ratio. © 1987 Academic Press, Inc.

1. INTRODUCTION

Heterogeneous catalytic reactions generally consist of a number of consecutive steps on the surface of the catalyst, starting with the adsorption of reactant molecules and ending with the desorption of product molecules. The intermediate steps involve so-called intermediate reaction species. They are usually very short lived; i.e., quickly after formation they react to new species. Identification of intermediate reaction species and their properties (number density, lifetimes, quantum state, etc.) is a key to the mapping and understanding of all chemical reactions, including catalytic reactions, but is difficult to achieve because of low concentrations and short lifetimes (see, e.g., Refs. (1–3)).

In the case of surface catalytic reactions there are at least two types of possible approach to this problem. The first is to apply surface-sensitive spectroscopies to detect intermediate species on the surface. This can be done either under dynamic

conditions or in a “frozen” situation, where the reaction does not proceed once an intermediate species is formed. For example, OH species have been identified on both Pt (4–7), and Pd (8) after low temperature coadsorption of H_2O and O_2 . Coadsorptions of H_2 and O_2 have not produced measurable concentrations of OH on Pt (4–8), but they have been found recently on Rh (9).

The second approach, pioneered by Lin and co-workers (10, 11), is to use laser spectroscopic methods to detect intermediate species, which are desorbed from the surface during dynamic reaction conditions, before they react to a new species. This method offers unique possibilities to simultaneously identify the type of intermediate species, its internal quantum state, and its (apparent) desorption energetics.

We have previously applied laser-induced fluorescence (LIF) to study the emission of OH radicals in the water reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ on platinum (12), and reported (i) the pressure dependence of the

measured OH intensity, (ii) the estimated apparent desorption energies for OH, and (iii) the internal population distributions between rotational levels of desorbed OH. In the present study we have extended the measurements to several other catalysts, namely Pd, Rh, Ir, and Ni. The results show that OH emission is a general phenomenon for the noble metal catalysts, but with expected significant differences in the details of the radical emission, such as dependence on H₂/O₂ ratio and desorption energies. A more detailed analysis of the OH emission from Pt will be given in a forthcoming publication (13).

The motivation for undertaking this study is twofold. The first reason is the unique possibility discussed above to map out surface reaction kinetics and dynamics via studies of desorbed, intermediate reaction species. The second motivation is the potential technological importance of radical emission from surfaces, e.g., in combustion engines. OH radicals are the key ingredients in many combustion processes. The possibility to create OH or other radicals in a controlled way in a combustion environment opens new possibilities to optimize the combustion process. Studies of the presence of radicals, such as OH, in catalytic reactions are therefore of great interest both in basic research, to understand reaction paths, and in applied research for potential improvement of combustion processes.

2. EXPERIMENTAL

The experimental setup used for the laser-induced fluorescence studies of thermally desorbed OH radicals has been described in the earlier work on Pt (12). The catalyst, in the shape of a high purity (MRC, 99.995%) rectangular foil (13 × 2 × 0.1 mm), is mounted horizontally on a manipulator in the center of a vacuum chamber. The chamber, where the base pressure is typically 10⁻⁶ Torr, is evacuated by a turbo pump. The gas mixture enters the vacuum chamber under continuous flow

through a vertical tube, perpendicular to the long direction of the Pt foil. A few millimeters below the foil a laser beam passes horizontally through the system. When the foil is heated to sufficiently high temperatures in the reactant gas mixture, OH molecules are thermally desorbed and detected by LIF.

The laser wavelengths, produced in an excimer pumped dye laser (Lambda Physik EMG 102E and FL 2002E), are selected suitably for the $X^2\Pi (v = 0) \rightarrow A^2\Sigma (v = 0)$ OH absorption band. The fluorescence light is collected by a quartz lens system and imaged onto a photomultiplier tube after passing a transmission filter centered at 308 nm with a bandwidth of 20 nm. The output signal is then integrated with a boxcar averager. On a chart recorder a scan is achieved, where each peak represents a transition from a specific rotational level in the OH molecule. The population of the different rotational levels could then be calculated from the measured peak intensities by normalizing with respect to the transition probabilities.

Before an experiment is run, the catalyst surface is cleaned ("activated") with the H₂ + O₂ gas mixture flowing over the actual foil at a total pressure of 0.5 Torr and a temperature of 1200 K for a few minutes. This activation procedure has been shown, by Auger electron spectroscopy, to produce a clean surface of Pt free of contaminants (19). The procedure did not work for the Ni foil, however, because Ni is immediately oxidized. In this case we therefore started with pure hydrogen and successively increased the oxygen partial pressure. Influence of surface oxide on the Ni results is likely.

The total pressure in the system during the experiments is measured with a capacitance manometer with an accuracy of 1%. The composition of the gas mixture is monitored with flow meters before mixing. In general the true partial pressures in the reaction zone are influenced both by the gas flows and by the individual pumping speeds

for the gases. However, test runs indicated that the effective pumping for the combined turbo and rotary pumping unit at 0.1 Torr is still predominantly viscous in nature. Furthermore, the experimental geometry is such that the gas composition at the sample is predominantly determined by the incoming gas flow and that gradients in the gas composition, if any, occur at the outlet. The main uncertainty in the gas composition at the sample actually derives from the surface reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$, which may cause an overestimate of the H_2 partial pressure at maximum water production. The error in the position of the OH maximum, which is the main issue here, will be much less influenced since the production rate of H_2O is much smaller there.

The temperature of the catalyst is determined with a four-point probe arrangement (14), which allows simultaneous heating and resistance measurements. The temper-

ature is then determined from the measured room temperature resistance and the temperature coefficients of resistivity obtained from standard tables (15). This arrangement can also be used to obtain a measure of the water production rate, since the chemical power dissipation in the reaction causes a measurable temperature increase (14).

An extension, in comparison with the earlier experiments (12) where premixed gases were used, is that the system has been equipped with a gas-mixing facility, in which the flow of gas, and thus the partial pressures of the reactants, can be varied.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical fluorescence scan, obtained with the laser beam passing parallel with and 4 mm below a Rh foil catalyst. The foil was kept at 1200 K in an atmosphere of $\text{H}_2 + \text{O}_2$ at 0.1 Torr (partial pressure ratio $\text{H}_2/\text{O}_2 = 0.15$). The peaks in

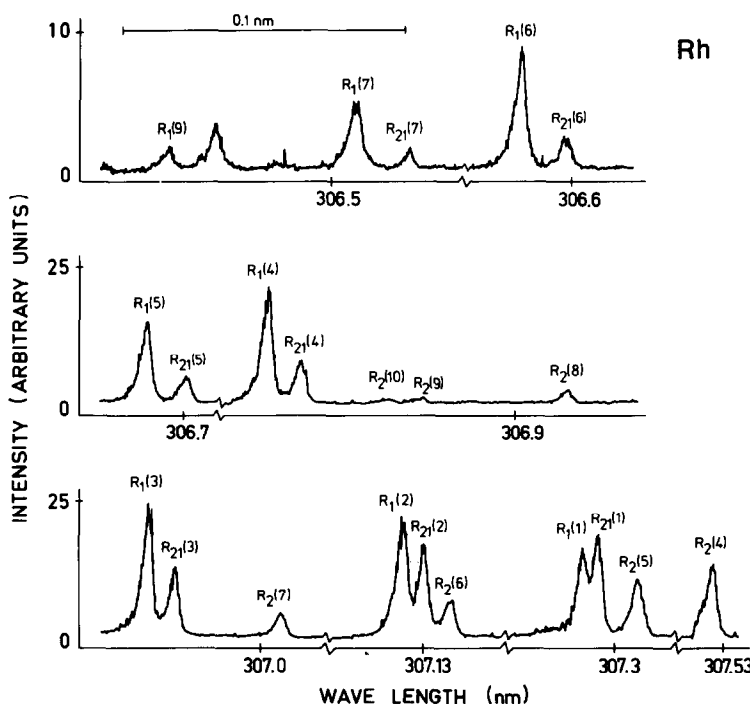


FIG. 1. A scan of the fluorescence intensity vs laser wavelength from a Rh catalyst at 1200 K in 0.1 Torr of $\text{H}_2 + \text{O}_2$ ($\text{H}_2/\text{O}_2 = 0.15$). All peaks with identified transitions are used for a rotational temperature determination. Note the different scales on the intensity axes.

the spectrum reveal, by comparison with known spectroscopic constants for OH (16), the presence of OH molecules. Since the peaks disappear when the foil temperature is decreased below 950 K, and since the intensity at a given temperature and pressure is strongly dependent on the catalyst material, it is ascertained that the OH in the gas phase originates from the surface-catalyzed reaction.

From the heights of the peaks in this type of scan, information can be extracted about the relative OH production efficiency of different catalysts, about "apparent" desorption energies, and about the pressure and temperature dependence of the OH production. The word "apparent" is used because several factors may prevent extraction of the true desorption energy (see Refs. (12, 13) and the discussion below).

Normalization of the peak heights with respect to the transition probabilities makes it possible to determine the population distribution between rotational levels of the desorbed OH molecules (13). Generally, for a complete knowledge and comparison between the different catalysts, spectra should be taken for various reaction conditions. In this work we are particularly interested in analyzing the conditions for maximum yield of OH from different catalysts. The experiments have thus been focused on the dependence of the yield on pressure and mixing ratios of the reactants at a constant temperature of the foil. In addition desorption energies were measured in order to search for a possible correlation between the OH yield and desorption energies. Complementary results for Pt will be presented in a future paper (13).

3.1. Maximum Yield of OH

3.1.1. Dependence on total pressure. Varying the total pressure, with a constant mixing ratio of the reactants, influences the fluorescence signal strongly. For all catalysts a maximum intensity of the OH emission is obtained at a pressure of 0.7 ± 0.1 Torr as visualized in Fig. 2. This curve

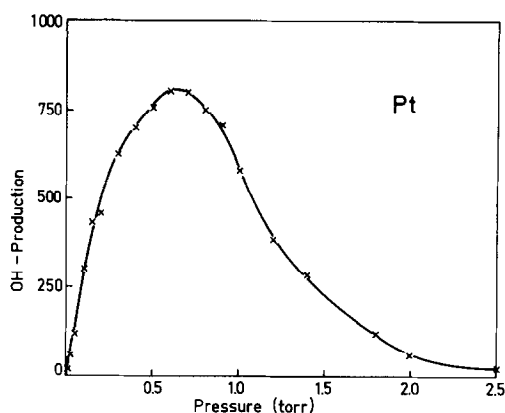


FIG. 2. The OH fluorescence intensity measured for one transition ($R_{21}(2)$) as a function of the total pressure using a Pt catalyst at 1050 K and a premixed gas (20% O₂ + 3.5% H₂ in Ar).

shows the same pressure dependence for different H₂/O₂ ratios although the absolute yield of OH is changed significantly as a function of the ratio (see below).

The form of the intensity vs pressure curve can be qualitatively understood as follows (see also Ref. (12)). At low pressures the number of elementary reactions per unit time producing water molecules (and intermediate OH radicals) from H₂ and O₂ is determined by the impingement rates of H₂ and O₂ on the surface. As the pressure is increased the coverages of H and O atoms increase until they reach a saturation value, and the overall water production rate becomes less pressure dependent. The OH desorption flux from the surface is thus expected to increase linearly with pressure at low pressures and then to reach a saturation value. The position of the transition from linear increase in OH production to saturation depends on the detailed kinetics. The number of detected (i.e., excited and fluorescing) OH molecules, however, is influenced also by gas-phase processes, when the pressure is increased sufficiently. Several mechanisms may contribute to a negative pressure dependence: (i) OH molecules may react in the gas phase, (ii) collisional quenching may change the rotational state of desorbed OH molecules, and (iii) laser-

excited molecules may undergo collisional quenching; i.e., the molecule may return to the electronic ground state via a collision-induced radiationless transition. Factors (i) and (iii) tend to decrease the number of detected OH molecules with increasing pressure, while (ii) may increase or decrease the number. The increase in OH desorption rate with increasing pressure combined with the quenching phenomena will then produce a maximum in the measured fluorescence intensity vs pressure curves. (Note that the number of OH molecules *leaving* the surface probably continues to increase beyond the fluorescence maximum).

The deviation from a linear intensity increase with pressure occurs in the expected pressure range, i.e., when the mean free path of emitted molecules becomes smaller than the sample to laser beam distance. A quantitative description of the intensity vs pressure curve will require model calculations taking into account the processes described above. (In this discussion we did not consider the possibility that a gas-phase reaction contributes to the OH production. So far no evidence has been found for a gas-phase reaction.)

3.1.2. OH production efficiencies and dependence of OH yields on the H_2/O_2 partial pressure ratio. Figure 3 shows the fluorescence intensity from an Ir foil as a function of H_2/O_2 ratio at constant pressure for three peaks in the wavelength scan. The shape of the curves has the same characteristic form for all studied catalysts, but the absolute intensity level varies strongly with different catalysts, and the position of the maximum occurs at different H_2/O_2 ratios.

Since the curves of the type shown in Fig. 3 are taken at constant pressure, they are a measure of the desorption flux from the surface as a function of H_2/O_2 ratio (the variation in gas composition is expected to have a relatively weak influence on the quenching processes discussed in Section 3.1.1.).

In order to make possible a comparison between the OH production yields for the different catalysts, the following procedure was adopted. All measurements were performed at 1200 K and 0.1 Torr. The foil size and the geometry were kept constant. For each material the H_2/O_2 ratio producing maximum OH signal intensity was then determined. These intensities could then be

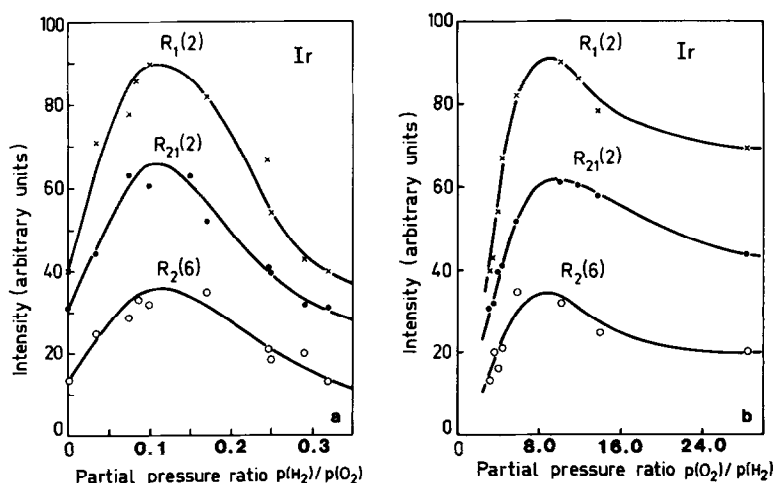


FIG. 3. The dependence of the relative OH intensity for three transitions ($R_1(2)$, $R_{21}(2)$, and $R_2(6)$) as a function of the ratio of the partial pressures of hydrogen and oxygen, for an Ir catalyst at 1200 K and 0.1 Torr. In (a) the OH production is plotted against $p(H_2)/p(O_2)$ and in (b) against $p(O_2)/p(H_2)$. Note the nonzero intercept of the intensity axis at $p(H_2)/p(O_2) = 0$.

TABLE I

Catalyst	$p(\text{H}_2)/p(\text{O}_2)$ ratio producing maximum OH signal at P_{tot} = 0.1 Torr	Relative OH yield	Apparent desorption energy (kcal/mole)
Ni	0.45 ^a	0.2	—
Rh	0.15	16	25
Pd	0.25	80	33
Ir	0.10	1	29
Pt	0.05	360	41

^a Probably influenced by surface oxide formation. Increasing O₂ concentration causes successive increase in oxidation.

compared and used to rank the catalysts with regard to their OH production efficiency. The results are presented in Table I. The intensities from different catalysts are markedly different, which reveals differences in reaction kinetics and energetics on the different materials. Pt is the most efficient OH producer while Ni is the least efficient.

The form of the curves in Figs. 3a and 3b is attributed to the changes in the surface reaction conditions, particularly the coverages of H and O, which occur when the H₂/O₂ ratio is varied [20]. As the ratio is varied from zero (no hydrogen) to infinity (no oxygen) the ratio of hydrogen to oxygen coverages on the surface varies accordingly. At some specific surface H/O ratio the OH desorption rate is maximum, producing a maximum in the fluorescence intensity.

As the gas-phase H₂/O₂ ratio goes to infinity or zero, the OH production should vanish. This is obviously not true in the oxygen-rich end (Fig. 3), since the curve intercepts the intensity axis at a nonzero value. The explanation for this behavior is that, in addition to the H₂ + O₂ reaction, there is also a surface reaction between coadsorbed water molecules and oxygen atoms, which contributes to the OH production via the reaction



A liquid N₂-cooled shield around the catalyst foil reduces the OH yield significantly

at H₂/O₂ = 0, which shows that H₂O adsorption from the background contributes to the OH yield via the reaction above. Several investigations have shown, by use of vibrational spectroscopies and XPS, that this reaction can produce stable OH species on Pd and Pt at low temperatures (5, 8).

The maximum in the OH production does not coincide with the maximum in the water production yield as illustrated in Fig. 5 for Pt. The maximum in the H₂O production vs H₂/O₂ ratio was determined from the maximum in chemical power dissipation from the exothermic, water-producing reaction. At the maximum water production there is a minimum in the electrical power required to keep the temperature of the foil constant. (Actually a correction had to be made for variations in the convection cooling at the foil as the gas composition was varied, since H₂ cools more efficiently than O₂.) The reason for the noncoincidence of the maxima in OH and H₂O production is discussed below in Section 3.3 and in Ref. (20).

3.2. Apparent Desorption Energies

The intensity of a given rotational transition was measured as a function of temperature in order to obtain a measure of the OH desorption energy for the different cat-

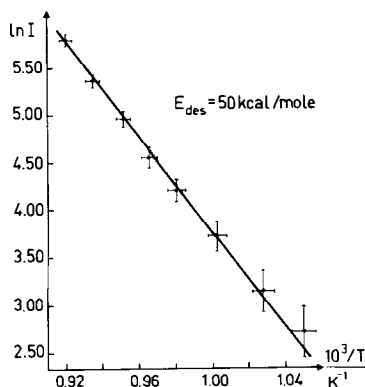


FIG. 4. An Arrhenius plot of the recorded fluorescence intensity for OH vs the reciprocal temperature of a Pt foil. (Total pressure 50 mTorr, H₂/O₂ = 0.2.)

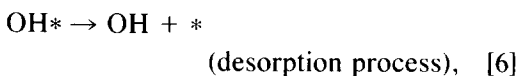
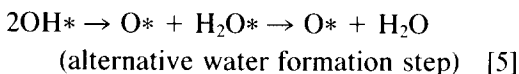
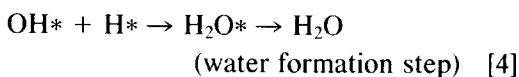
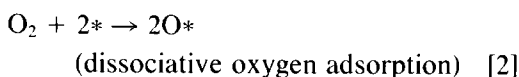
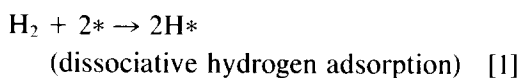
alysts. Somewhat surprisingly (see below) Arrhenius plots of such data (logarithm of intensity vs inverse temperature) produced relatively straight lines (Fig. 4), so that an activation energy could be defined. The extracted activation energy for a particular catalyst shows only weak dependence on total pressure (5%) in the range 0.01–0.2 Torr and on the choice of rotational transition (5% variation for three different transitions), but is strongly dependent on the H_2/O_2 ratio as previously observed by Fujimoto *et al.* (11). For example, as the mixing ratio is varied from 0.025 to 0.1 for Pt at 0.1 Torr, the apparent desorption energy varies from 38 to 48 kcal/mole, while at larger ratios it stays relatively constant at 48 kcal/mole. This probably reflects changes in the surface reaction conditions with the change in H_2/O_2 ratio. Influence from the $H_2O + O \rightarrow 2OH$ reaction is also possible at $H_2/O_2 \leq 1$.

In order to make possible a comparison between apparent desorption energies for the different catalysts, in spite of the complications mentioned above, the temperature dependence for a given rotational transition was measured for all catalysts at the same total pressure and at the H_2/O_2 ratio producing maximum OH yield. The desorption energies obtained from Arrhenius plots of such data are presented in Table 1. The variation in apparent desorption energy for the different catalysts is surprisingly large. We wish to stress again, however, that the activation energies are "apparent" desorption energies rather than "true" activation energies for desorption. The reason is that the results are influenced not only by how strongly the OH molecule is bound to the catalyst surface, but also by the details of the reaction kinetics. For example, in applying a simple Arrhenius type of analysis it is implicitly assumed that the OH concentration on the surface varies slowly with temperature, which may not be the case (see Section 3.3 below). There is actually no reason a priori to expect a straight line in an Arrhenius plot of the data. To obtain

more correct desorption energies and to explain the variation in apparent activation energies with the H_2/O_2 ratio require model calculations of the reaction kinetics. Such work is in progress (18).

3.3. Discussion of Mechanisms

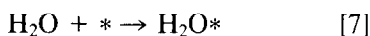
To simplify the discussion we adopt the following commonly accepted reaction scheme for the $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ reaction on the Pt group metals:



where an asterisk denotes a surface adsorption site. Some reaction steps, unimportant for the present discussion (but not for a quantitative modeling), have been omitted, e.g., desorption of H_2 and O_2 (the reverse of steps [1] and [2]) and decomposition of OH (the reverse of step [3]). Two different H_2O -forming steps are included ([4] and [5]), since both are frequently suggested in the literature. For example, step [5] has been shown to be the major mechanism below 300 K on Pd [8]. It is likely that the relative importance of these two steps vary with catalyst, temperature, and H_2/O_2 ratio.

Step [6] is the OH desorption step, which is the reaction step responsible for the production of the gas-phase OH molecules detected in the present work. It is probably a minority step not influencing the overall water-producing reaction. OH molecules are produced on the surface by recombina-

tion of hydrogen and oxygen atoms (step [3]). The latter are formed by dissociative adsorption of H₂ (step [1]) and O₂ (step [2]). To make the picture more complete we must also incorporate the following steps:



which actually is the reverse of the reaction sequence [5]. These two consecutive steps followed by step [6] may contribute to the OH yield as well, and are most likely to be responsible for the nonzero intercept of the intensity axis in Fig. 3. The water comes in the present experiments from the background H₂O atmosphere in the vacuum system produced by the forward reaction. The reverse of step [4] (water decomposition) does not seem to be important since no OH is observed in the absence of O₂ in the gas phase, i.e. in the absence of adsorbed O on the surface.

The production yield of OH from the surface for a particular catalyst, at a given H₂/O₂ ratio, total pressure, and temperature, is proportional to the coverage of OH molecules on the surface, and to the rate constant for desorption. In simple rate theory this can be written as

$$I \sim Y \sim \nu_d \exp(-E_d/kT)\theta_{\text{OH}}, \quad [9]$$

where I is the measured fluorescence intensity, Y is the desorption flux of OH, ν_d is the preexponential (or frequency) factor for desorption, E_d is the activation energy for desorption, T is the temperature, and θ_{OH} is the coverage of OH molecules on the surface. By use of the reaction scheme [1]–[8] and expression [9] one can qualitatively analyze several of the experimental observations: Pt seems to produce a comparatively high coverage of OH since Pt has both the highest OH yield and the highest activation energy. By the same arguments Ir produces a low OH coverage, since it has both the lowest yield (excluding Ni) and the lowest activation energy.

The OH coverage depends critically [20] on the relative magnitudes of the rate con-

stants for OH formation and OH consumption, respectively, which may explain the somewhat surprising result that Pt with the highest desorption energy for OH also shows the highest OH yield.

One can also understand, at least qualitatively, why the maxima in OH desorption and H₂O production yields do not coincide. At maximum H₂O production, in steady state, there is also a maximum in the number of *produced* OH per unit time on the surface. However, the coverage of OH is determined by the balance between the rate constants for formation and consumption, i.e., by the lifetime of an OH once it is formed. If the OH lifetime has its maximum value at a different H₂/O₂ ratio than the one producing the maximum number of H₂O per unit time, the OH and H₂O maxima will generally not coincide. Since the OH lifetime is dependent on the surface concentration of H atoms (step [4]) it seems plausible that the OH maximum occurs at a lower H₂/O₂ ratio than the H₂O maximum, which is also observed (Fig. 5).

It is not the purpose of this paper to pursue a detailed discussion along these lines, but we stress that the observed OH yields are intimately coupled to the details of the surface reaction kinetics, such as sticking coefficients for H₂ and O₂ and

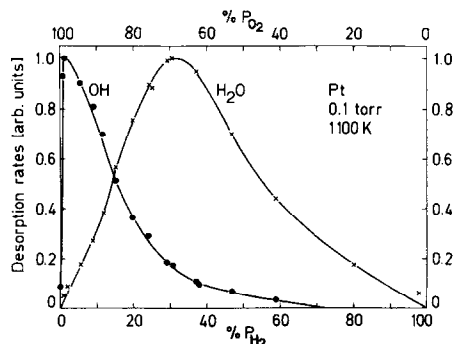


FIG. 5. OH desorption and H₂O production on Pt as functions of percentage H₂ in H₂ + O₂ at 1100 K and 0.1 Torr total pressure. The intensities of the curves are, respectively, normalized to unity. Note that the OH maximum occurs at a different percentage H₂ value from the H₂O maximum.

activation energies for OH formation and decomposition. Measurements of OH yields may therefore be a very rewarding tool in establishing correct reaction kinetic schemes. More detailed data will be required for quantitative analyses in these terms.

3.4. Technological Implications

Finally, we draw attention to the second aspect of these results, as mentioned in the Introduction, namely the fact that the significant amounts of OH radicals produced in both the $H_2 + O_2$ and the $H_2O + O^*$ reactions may be of considerable practical importance. Since OH radicals are important in initiating combustion chain reactions, catalysts may be used to influence such reactions via production of radicals. (Note that O_2 , H_2O , and H_2 are always present during combustion of hydrocarbons.)

The observations above may also be of relevance in an analysis of ignition points for various explosive or combustible gas mixtures, which frequently are believed to be influenced by wall effects, e.g., catalytic wall reactions (17).

More generally the present results point toward the possibility of a coupling between surface reactions and homogeneous phase reactions, which may be utilized, for example, in future combustion engines.

4. CONCLUSIONS

Desorption of OH during the $H_2 + O_2$ reaction is a general phenomenon for noble metal catalysts at temperatures above 900 K. Laser-induced fluorescence monitoring of desorbed OH and of their internal quantum states gives new interesting information about reaction kinetics not available from other types of measurement. Such results will be valuable in the theoretical modeling of reaction mechanisms and kinetics. Radical formation and emission by catalysts may find technological applications in combustion systems.

ACKNOWLEDGMENTS

We thank Mr. H. Riedl for chemical and technical collaboration during experiments. Furthermore, we thank Dr. K. E. Keck for many fruitful discussions and continuous help with experimental details. Financial support was obtained from the National Swedish Board for Technical Development (STU) and from the Swedish Natural Science Research Council (NFR). Special thanks are given to the Swedish Council for Planning and Coordination of Research (FRN) and the Erna and Victor Hasselblad Foundation for financial support in the purchase of the laser system.

REFERENCES

- Bernstein, R. B., "Chemical Dynamics via Molecular Beam and Laser Techniques." Oxford Univ. Press, London, 1982.
- Leone, S. R., *Science* **227**, 889 (1985).
- Lawrence, W. D., More, Bradley C., and Petek, H., *Science* **227**, 895 (1985).
- Fisher, G. B., and Sexton, B. A., *Phys. Rev. Lett.* **44**, 683 (1980).
- Fisher, G. B., Gland, J. L., and Schmiege, S. J., *J. Vac. Sci. Technol.* **20**, 518 (1982).
- Gland, J. L., Fisher, G. B., and Kollin, E. B., *J. Catal.* **77**, 263 (1982).
- Fisher, G. B., and Gland, J. L., *Surf. Sci.* **94**, 446 (1980).
- Nyberg, C., and Tengstål, C. G., *J. Chem. Phys.* **80**, 3463 (1984).
- Fisher, G. B., Private communication.
- Talley, L. D., Saunders, W. A., Bogan, D. J., and Lin, M. C., *Chem. Phys. Lett.* **78**, 500 (1981); *J. Chem. Phys.* **75**, 3107 (1981).
- Fujimoto, G. T., Selwyn, G. W., Keiser, J. T., and Lin, M. C., *J. Phys. Chem.* **87**, 1906 (1983).
- Rosén, A., Ljungström, S., Wahnström, T., and Kasemo, B., *J. Electron. Spectrosc. Relat. Phenom.* **39**, 15 (1986).
- Ljungström, S., Wahnström, T., Kasemo, B., and Rosén, A., to be published.
- Kasemo, B., Keck, K-E., and Högberg, T., *J. Catal.* **66**, 441 (1980).
- Landolt-Börnstein, "Zahlenwerte und Funktionen aus Naturwissenschaften und Technik." Band III/15a, Springer-Verlag, Berlin/Heidelberg, 1982.
- Dieke, G. H., and Crosswhite, H. M., *J. Quant. Spectrosc. Radiat. Transfer* **2**, 97 (1962).
- Nicholas, J., "Chemical Kinetics." Harper & Row, London, 1976.
- Hellsing, B., and Kasemo, B., to be published.
- Keck, K. E., and Kasemo, B., *Surf. Sci.* **167**, 313 (1986).
- Hellsing, B., Kasemo, B., Ljungström, S., Rosén, A., and Wahnström, T., *Surf. Sci.*, in press.