# Kinetic Oscillations during the Isothermal Oxidation of Hydrogen on Platinum Wires

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Sustained oscillations of the reaction rate were observed during the oxidation of hydrogen on a platinum wire whose temperature was maintained constant by a constant-temperature anemometer. The oscillations were usually of the relaxation type and often had more than one peak per cycle. The oscillations were sensitive to changes in the surface temperature and to pretreatment of the wire. Interesting steady-state multiplicity patterns were observed, such as the existence of two different oscillatory states at the same operating conditions. When either argon or helium replaced the nitrogen diluent, the oscillations decayed after some time, and a constant, time-invariant rate was attained.

## INTRODUCTION

Several investigators have observed periodic oscillations in the rate of certain catalytic reactions. Oscillations in the rate of hydrogen oxidation were reported by Wicke et al. (*1, 2*), Horak and Jiracek (*3*), Slinko et al. (*4–6*), and Boudart et al. (*7*). Oscillations during the oxidation of carbon monoxide were reported by Hugo and Jakubith (*8*), Wicke et al. (*1, 2*), Dauchot and Cakeberghe (*9, 10*), Carberry et al. (*11*), Sheintuch and Schmitz (*12, 13*), and Cutlip and Kenney (*14*). Krylov et al. (*15*) noted oscillations during the oxidation of cyclohexane on zeolite NaX. A comprehensive review of the literature has been presented recently by Sheintuch and Schmitz (*12*).

Most investigators suggest that the oscillations are due to mutual interactions

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between the catalytic surface and the adsorbed species. Many mechanisms have been suggested as the cause of this intriguing phenomenon, such as a shift between two states of the adsorbed reactants (*2, 8*), a change in reaction mechanism with surface coverage (*9–11*), dependence of the reaction rate constants on surface coverage (*5, 6, 12, 16*), fluctuations in surface temperature (*17*), oscillations in the concentration of an adsorbed inactive species (*18*), and changes in the state of a surface oxide (*7*). Unfortunately, none of the existing models is capable of predicting quantitatively the experimental observations, and the causes of this interesting behavior are not yet clear.

An understanding of the kinetic oscillations should enhance the understanding of rate processes occurring during catalysis and facilitate the finding of new reactions for which oscillations occur. This phenomenon can also be exploited for discrimination among rival kinetic mecha-
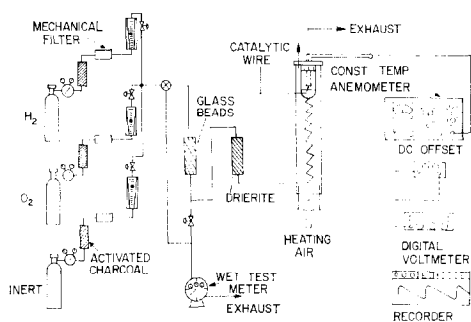
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FIG. 1. Schematic diagram of the experimental apparatus.

nisms since those which cannot predict oscillations are either wrong or over-simplified (13).

We present here some new observations of oscillations in the reaction rate during the oxidation of hydrogen on a platinum wire whose temperature was maintained at a constant value. This information should lead to a better understanding of the influence of various operating conditions on this phenomenon and enable a critical test of any new proposed mechanism.

## METHODS

*Apparatus.* The instantaneous reaction rate was determined by measuring the electric power required to maintain a platinum wire, on which the hydrogen-oxidation reaction occurs, at a constant temperature (electrothermic technique). The measured difference in the energy required to maintain the resistance (temperature) of the wire constant under reacting and nonreacting conditions equals the heat generated by the reaction and yields directly the rate of the exothermic reaction.

The apparatus (Fig. 1) consisted of a gas metering and control section, the reactor, and a measuring and recording section. Extra-dry-grade hydrogen, oxygen, and inert gas from gas cylinders were passed through beds of activated charcoal to remove any traces of oil and hydrocarbons. The metered reactants and dilu-

ents were mixed by being passed through two beds packed with glass beads and Drierite pellets, respectively.

The preheating section of the reactor (Fig. 2) consisted of a Pyrex coil to which heat was supplied by a heating gun (Master Appliance Corp. HG201B) controlled by a variable autotransformer. The catalyst was a high purity platinum wire (United Mineral and Chemical Corp.,) 51 mm long and 0.051 mm in diameter, with an external surface area of 0.082 cm². It was supported by two brass rods insulated by a Teflon sleeve. The wire was placed 3.1 cm downstream from a fine-porosity, fritted-glass flow distributor in a 4.1-cm-i.d. Pyrex tube.

A Thermo-Systems Inc. (Model 1010A) constant-temperature anemometer maintained the wire at a constant resistance by changing the current through it (maximal current output, 2 A). The high frequency response of this instrument (50 kHz) enabled accurate measurements of the fluctuations in the heat generated by the reaction. The voltage across the bridge was measured by a digital voltmeter (Non-Linear Systems, Series X-2) and
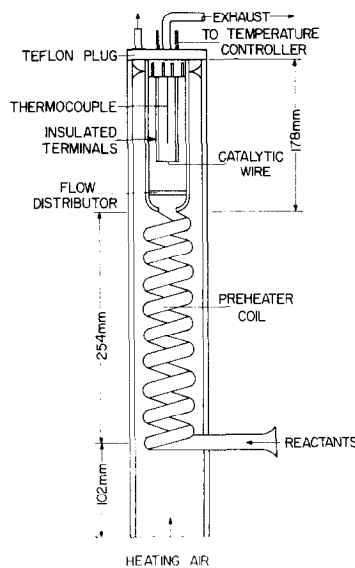


FIG. 2. Details of the reactor.

recorded by a strip chart recorder (Houston Instrument Series 2-3000).

*Procedures.* Each catalytic wire was activated by heating it electrically to about 700°C in a stream of hydrocarbon-free air for 30 min. Then a mixture of approximately 3% $H_2$ in air was passed over the wire, and the current was reduced to maintain a constant wire temperature. After about 1 hr the reaction sustained itself without any electrical heating and was continued for another 8 hr. After this treatment, the wire's cold resistance remained invariant for several months.

At the start of each run, the catalyst was heated to 900°C in a stream of Dry Grade air for 5 min and then kept at 300°C for another 30 min. This "regeneration" step was intended to yield a similar surface at the start of all the experiments.

After the regeneration, nitrogen gas was substituted in the air stream, and the wire was heated electrically to the desired temperature. Oxygen was added to the nitrogen, and the voltage across the wire was recorded. Hydrogen was then added to the stream, and the new level of voltage recorded for about a half-hour. Experience showed that, if oscillations occurred, they develop within 20 min of the start of the run. When oscillations were noted, the run was continued until the frequency, amplitude, and shape of the cycles did not change. A typical run lasted from 2 to 16 hr.

## RESULTS

Oscillations in the isothermal reaction rate were observed in certain cases for wire temperatures in the range of 85 to 150°C for mixtures containing 0.2 to 1.3% (by vol) hydrogen, 21 to 40% (by vol) oxygen, and nitrogen. The lower limit of the hydrogen concentration is the smallest concentration at which the reaction rate can be still measured accurately at the lower temperature. The upper limit of the hydrogen concentration is a limitation of the experimental technique since the method cannot be used when the heat generated by the reaction exceeds the energy required to maintain the wire at the same temperature in a non-reactive environment.

In a special set of preliminary experiments, a Philco (Model 705B-2) thermal microplotter was used to measure the radiant energy emitted from several small spots along the wire (nominal area 0.0013 $mm^2$). The measurements, which are reported in detail in Ref. *(19)*, indicated that the local surface temperature remained constant even when the fluctuations in the reaction rate were very large and that the temperature along the wire was constant and uniform.

Although the time-averaged reaction rate obtained during the oscillations was very reproducible, the shape and period of the oscillations could not be reproduced exactly and were very sensitive to slight
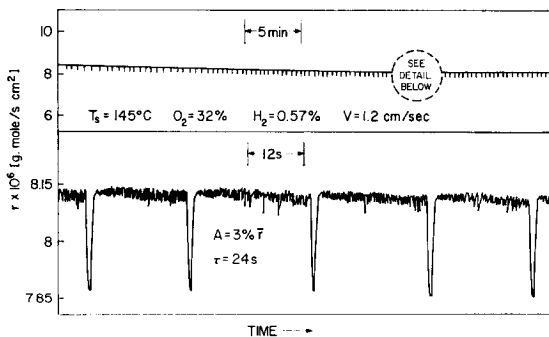


FIG. 3. High-frequency oscillations observed during slow change in average reaction rate.

changes in the history of the wire. The oscillations were usually of low frequency, with periods from 3 to 63 min. They often had more than one peak per cycle and were of the relaxation type.

In certain experiments, high frequency oscillations were observed (period, 3–50 sec), with very rapid superimposed fluctuations. These oscillations were accompanied initially by a very slow shift in the time-averaged reaction rate and could be sustained for several hours. A typical example is shown in Fig. 3.

In some cases, especially for the higher hydrogen concentrations, the oscillations had an erratic shape and did not attain a periodic pattern even after 10 to 15 hr. A typical example of this chaotic behavior is shown in Fig. 4.

For oxygen-to-hydrogen ratios 25 to 100, the time-averaged rate was always reproducible. At lower oxygen-to-hydrogen ratios, it was very difficult to reproduce even the time-averaged rate, and the oscillations were usually chaotic.

For oxygen concentrations above 42% (by vol) no sustained oscillations were found, and chaotic behavior was observed for surface temperature below 125°C and hydrogen concentrations exceeding 0.85% (by vol). For oxygen concentration of 40% (by vol) constant states were obtained for hydrogen concentration up to 0.4%, while periodic oscillations occurred for $H_2$ equal to 0.57%. For hydrogen concentrations exceeding 0.85%, the rate was chaotic.

For oxygen concentration of 32% (by vol), oscillations existed for a bounded
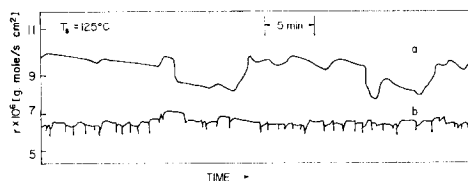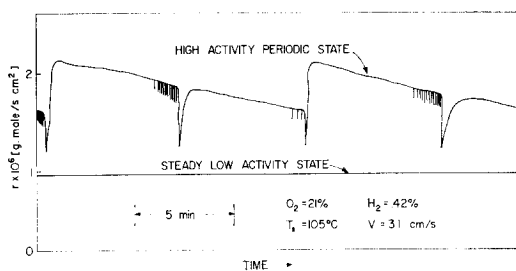
FIG. 5. Time dependence of the rate of two different states, both of which exist at the same operating conditions.

region of hydrogen concentrations. For example, when the surface temperature was 105°C, oscillations were noted for hydrogen concentrations in the range of 0.42 to 0.85% (by vol). For hydrogen concentration of either 0.4% or 1% (by vol), a time-invariant state existed; whereas, for $H_2$ equal to 0.95%, small amplitude chaotic fluctuations occurred. The period and peak-to-peak fluctuations attained a maximal value for hydrogen concentration of about 0.57% (by vol).

For oxygen concentration of 21%, the period of the oscillations increased with hydrogen concentration until about 0.9% (by vol). Above this limiting concentration, the oscillations became chaotic.

For certain operating conditions, two different states could be obtained. The low activity state was attained by slow heating of the wire from 85°C, whereas the high activity state was reached by slow cooling of the wire from 300°C to the desired temperature. For temperatures above 150°C, each of the two states had a constant, time-invariant rate. For surface temperatures below 150°C, however, the rates of the two states were not always constant. In some experiments, the low activity state was constant but the rate of the high activity state was periodic. A typical example of such behavior is illustrated in Fig. 5. In other cases, both states were periodic, with each state having a different shape, amplitude, and period of oscillation. An illustration of



FIG. 4. Chaotic variation of rate with time: (a) $O_2$, 40%; $H_2$, 0.57%; $v$, 3.1 cm/sec; (b) $O_2$, 21%; $H_2$, 0.85%; $v$, 1.2 cm/sec.
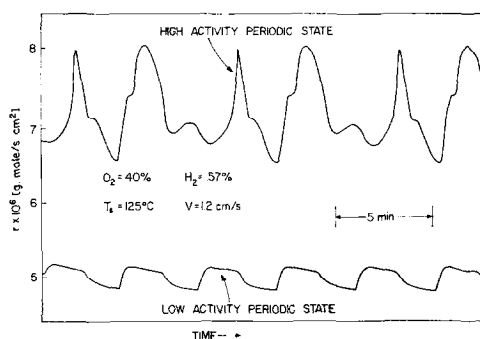
FIG. 6. Time dependence of the rate of two oscillating states, both of which exist at the same operating conditions.

this phenomenon is shown in Fig. 6. The occurrence of the oscillating states in the region of steady-state multiplicity was reproducible, and it was possible to shift from one state to another.

Changes in surface temperature had a pronounced influence on the shape, frequency, and magnitude of the oscillations. Figure 7 illustrates a case in which the temperature affected even the number of peaks per cycle. Although a single peak per cycle existed for surface temperatures of 85 and 145°C, two and three peaks per cycle occurred for surface temperatures of 105 and 125°C, respectively. This
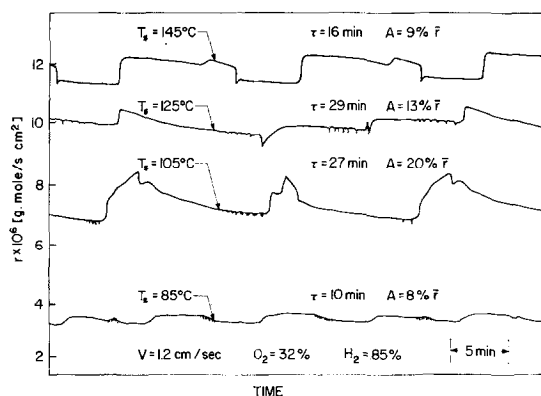
change in the shape of the oscillations is responsible for the initial increase and subsequent decrease in the period of the oscillations with increasing surface temperature.

The temperature usually had a marked influence on the period and magnitude of the oscillations (Fig. 8). At low velocity (1.2 cm/sec) and high oxygen concentration (40%), the period tended to decrease with increasing temperature. However, at higher gas velocity (3.1 cm/sec) and lower oxygen concentration, the opposite influence was noted. For oxygen concentration of 32%, both tendencies could be observed, and, in certain instances, the period attained a local maximum for some intermediate temperature (Fig. 8).

Because of their intricate shapes, the oscillations cannot be completely characterized by a single statistic. We report in this work the amplitude of the peak-to-peak fluctuations, $A$, as a measure of their magnitude. In general, changes in the temperature affected both the period and
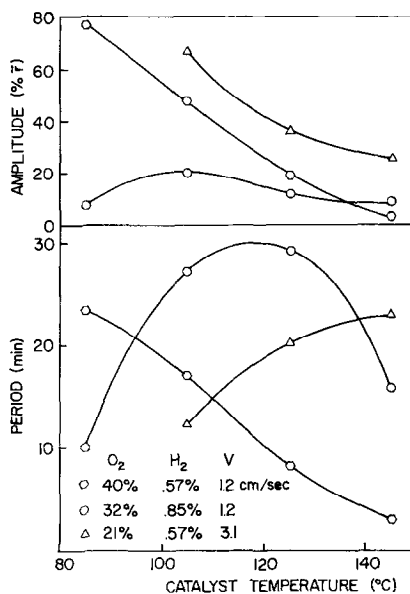


FIG. 7. Influence of catalyst on the oscillations of the reaction rate. $O_2$, 32%; $H_2$, 0.85%; $v$, 1.2 cm/sec.



FIG. 8. The influence of catalyst temperature on the amplitude and period of oscillations.
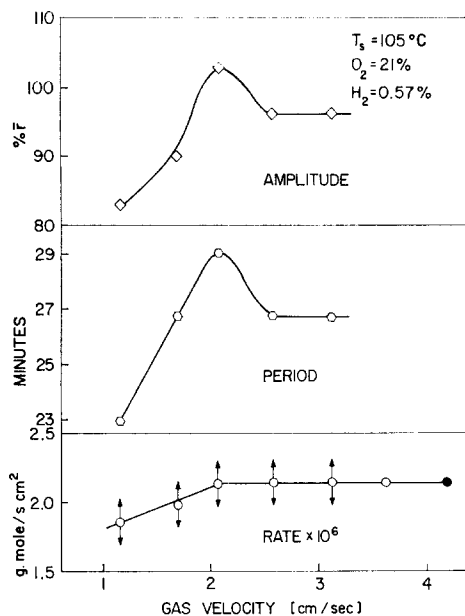
the peak-to-peak fluctuations in a similar fashion. Thus, when the period decreased with temperature, so did the amplitude. A few exceptions to this rule were observed, such as the case shown in Fig. 8 for 21% and 0.57% $H_2$.

Figure 9 describes the dependence of the time-averaged reaction rate, as well as the period and magnitude of the oscillations on the linear gas velocity. The corresponding graphs of the instantaneous rate vs time are shown in Fig. 10. The data indicates that the time-averaged rate increased with linear gas velocity, attaining a constant value for velocities larger than approximately 2 cm/sec. For higher linear velocities, the reaction rate was controlled by the kinetics and was not affected by the external mass-transfer resistance.

Oscillating states are described in Fig. 9 by open circles with superimposed arrows. These oscillating states were observed both when the mass-transfer resistance affected the time-averaged rate (gas velocity less than 2.1 cm/sec), as well as

when the transport resistance is negligible. When the gas velocity was increased to 3.6 cm/sec, the oscillations became chaotic (denoted by an open circle in Fig. 9). For linear velocities exceeding 4 cm/sec, the oscillations disappeared, and a time-invariant steady state was attained (denoted by a solid circle in Fig. 9).

The data plotted in Fig. 10 indicate that the linear velocity had a rather minor influence on the shape of the isothermal oscillations, and three peaks per cycle were observed in all cases. The period of the oscillations was in the range of 23 to 29 min, and the maximal value was attained when the linear gas velocity was 2.1 cm/sec. The peak-to-peak amplitude of the oscillations was only slightly affected by the changes in the velocity and was in the range of 83 to 103% of the time-averaged rate.

When the reaction rate was periodic, replacement of the nitrogen by argon increased the period but did not affect the average reaction rate. After 1 to 2 hr of operation with argon, the rate became constant. Changing the inert gas back to
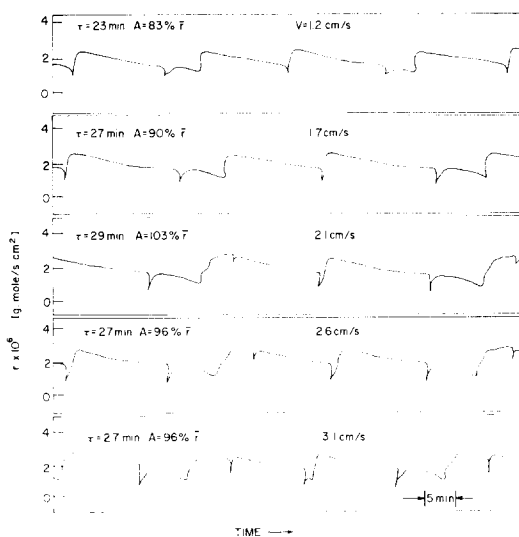


Fig. 10. Time traces of the instantaneous rate corresponding to the cases shown in Fig. 9.

nitrogen did not restore the oscillatory behavior. Oscillations were attained, however, after reactivation of the wire by the procedure described in the Methods section. When the shift from argon to nitrogen was made no later than 30 min after argon replaced the nitrogen, the system returned to the original oscillatory state (same wave form and peak-to-peak amplitude but, generally, a larger period). When helium replaced nitrogen, the rate always became time invariant within 5 to 10 min. Oscillations in the rate were never observed when helium was the inert gas under the operating conditions which produced oscillations for the mixture containing nitrogen.

## DISCUSSION

The occurrence of similar oscillations in the reaction rate, when the time-averaged isothermal reaction rate was either dependent or independent of the linear velocity (Fig. 9), indicates that this phenomenon is caused by the chemical reaction and not by an interaction between the kinetics and the mass-transfer resistance. The strong sensitivity of the oscillations (amplitude, wave form, and period) to the past history of the wire and to the method of activation is another indication of the chemical nature of this behavior.

Several previous studies of oscillations during the oxidation of hydrogen on platinum catalysts were conducted so that the changes in the rate induced changes in the temperature of the catalytic surface (1–3, 6). Our experiments with a constant-temperature wire indicate that the oscillations are not induced by temperature fluctuations as speculated in Ref. (17). The very low frequency of the oscillations (on the order of 0.05 min$^{-1}$) precludes the possibility that very fast local temperature fluctuations are causing this phenomenon. The disappearance of the oscillations for

large linear velocities (Fig. 9) is an intriguing result, for which we have no satisfactory explanation.

Slinko et al. (6) also measured oscillations on platinum wires of the same diameter we used, but obtained different results. For example, they found oscillations only in the temperature range of 135 to 210°C, which is higher than that which we found. We cannot explain the difference but note that, when Slinko et al. carried out experiments on a thin platinum foil, oscillations were obtained in the range of 75 to 150°C, which agrees with our findings. Slinko et al. claim that the amplitude and period of the oscillations decrease with increasing surface temperatures. We found that this was not always the case (Fig. 8). Moreover, Slinko et al. claim that the oscillations occurred in the region "in which the reaction rate was inhibited by hydrogen." The oscillations reported in this paper occurred in the region in which the reaction rate increased monotonically with increasing hydrogen concentration (19).

Several models have been proposed in the literature to explain the occurrence of oscillatory states. All these models predict simple periodic behavior with one peak per cycle. The intricate wave form encountered in some of our experiments, with several peaks per cycle, cannot be explained by any of the proposed models and points out the inadequacy of these models. Further development of theoretical models requires a better understanding of the detailed reaction steps on the surface and the influence of the surface structure on the kinetics.

The time-averaged reaction rate is usually of the order of $3 \times 10^{-6}$ g mole/sec cm² which corresponds to a turnover number of about 2000 per second. In spite of this rather high rate of reaction, the overall reaction rate oscillates at a very low frequency, with a period of about

20 min. It is of interest to determine the mechanism which synchronizes the many surface sites on the wire (on the order of $10^{13}$), so that the oscillations in the overall rate can be measured. In fact, it is tempting to speculate that the chaotci behavior is the result of imperfect synchronization of many sites and that, in certain cases, the constant overall rate is an average of many random localized fluctuations.

Recently, many theoretical advances have been made in the modeling of chaotic behavior. However, before applying these tools to the analysis of the behavior illustrated in Fig. 4, additional information is needed about the physical and chemical causes of this behavior. It is well known that the surface of platinum wires and gauzes is changed by chemical reactions occurring on it (20, 21). Thus, it is possible that the chaotic behavior is the result of slow changes in the structure of the surface.

Our repeated observations of the shift to a constant-rate state when either argon or helium was substituted for nitrogen is most puzzling. Most previous investigators used nitrogen as an inert diluent when they observed oscillations during the oxidation of hydrogen on platinum (1–3, 6). Thus, the presence of nitrogen may be essential for the oscillations of this reacting mixture over platinum catalysts. Boudart et al. (7), however, observed oscillations during the oxidation of hydrogen over supported platinum catalysts at pressures of 1 to 2.5 kPa, using either helium or argon as diluents. There is a definite need for additional experimental work to clarify the role of the inert gases on the periodic behavior.

Our experiments focus attention on several interesting phenomena which cannot be explained at present. The understanding of the causes of the oscillations should facilitate the finding of new reactions for which oscillations occur. This should be

of both scientific and practical interest since, when several competing reactions occur simultaneously, oscillations may enhance the yield of desired products. The sensitivity of the oscillations to the detailed structure of the catalytic surface means that they can also be used to characterize the state of the surface.

## ACKNOWLEDGMENT

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