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Kinetics of N_2O Decomposition on Polycrystalline Platinum[1]

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The kinetics of N_2O decomposition on polycrystalline Pt is studied over a wide range of surface temperatures ($400 < T < 1200°C$) and pressures ($0.01 < P_{N_2O} < 0.50$ Torr) in a steady-state flow system with conversions less than 6% so that differential rates are obtained. It is found that a single Langmuir–Hinshelwood (LH) rate expression correlates all rate data within ±10% at all temperatures and pressures to give a reaction activation energy of 34.9 kcal/mole and a heat of adsorption of N_2O of 21.3 kcal/mole. A simple reaction mechanism which can give this rate expression is also proposed.

INTRODUCTION

The determination of accurate and unique rate expressions for catalytic reactions is important to obtain expressions which can be extrapolated to conditions outside of laboratory measurements, to determine or eliminate reaction mechanisms, and to correlate rate parameters with molecular quantities measured in clean surface experiments. We have previously shown that the kinetics of NH_3 decomposition near atmospheric pressure on polycrystalline Pt (*1*), single-crystal planes of Pt (*2*), and on polycrystalline Fe (*3*) could be fit quantitatively by a simple Langmuir–Hinshelwood (LH) expression. We have also shown that the kinetics of NO decomposition on clean Pt near atmospheric pressures (*4*) could be fit by a simple LH expression.

Nitrous oxide decomposition on noble metal catalysts is important in NO removal in the automotive catalyst (*5*). The reaction between NO and NH_3 has been shown to exhibit oscillations (*6*) in the temperature range 370 to 560°C and reactor pressures 0.2 to 1.0 Torr with N_2 and N_2O as the only products. Similar questions arise for the reaction between CO and NO (*7*) and for the oxidation of CO by NO_2 (*8*), where oscillations have also been reported.

The nitrous oxide decomposition on wires, foils, and supported catalysts has been studied over a variety of catalysts since the first experiment by Hinshelwood and Burk in 1924 (*9–13*). We were unable to find any results of this reaction on Pt, and much of the experimental data are reported over a gold catalyst (*9, 14, 15*). However, a major problem in attempting to extract rate parameters from previous experiments is that the ranges of variables have usually been small (a few hundred degrees variation in temperature and less than a factor of 10 in pressures have been typical).

In this paper we report measurements of steady-state rates of the N_2O decomposition on Pt wires, in the temperature range 400 to 1200°C and at pressures between 0.01 and 0.50 Torr. The objectives of this work are to obtain rates in this simple reaction as accurately as possible in order to obtain adsorption, desorption, and reaction parameters and to test quantitatively the validity of Langmuir–Hinshelwood kinetics.

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EXPERIMENTAL

The apparatus and procedure have been described previously (*16*). The 380-cm^3 reactor was made of stainless steel and was pumped by a mechanical vacuum pump downstream from the reactor. Between the mechanical pump and the reactor, a gate valve was used for reactor pressure control. A flow valve upstream from the reactor controlled volumetric flow rates. Backstreaming oil pump vapors were trapped in a dry ice–acetone-cooled cold trap, so that the background reactor pressure was kept at less than 0.001 Torr. Gas partial pressures were monitored through a leak valve into a quadrupole mass spectrometer (Spectrum Scientific 80). This chamber had a base pressure of 1×10^{-8} Torr and with the leak valve open and the reactor at its normal operating pressure (0.010 to 0.500 Torr), the pressure was 2 to 2.5×10^{-6} Torr. Reactor residence times were varied from 0.4 up to 12 sec, corresponding to volumetric flow rates of 31 to 950 cm^3/sec. The major advantages of this reactor geometry are an accurately known catalyst area, ease of variation of reactor conditions, and applicability of the standard stirred tank formulation for determining absolute reaction rates. Thus, rates are given by the expression

$$r_i = \frac{Q \Delta P_i}{R T_g A_c}, \qquad (1)$$

where r_i is the specific rate of consumption (formation) of reactant (product) species i, ΔP_i is the change in partial pressure of species i between reaction and feed conditions, Q is the volumetric flow rate, A_c the catalyst area, R the gas constant, and T_g the temperature of the gas phase.

The catalyst used in these experiments is a 0.025-cm-diameter, high-purity (Matheson 99.99&) platinum wire filament, 6 to 10 cm long (surface area ≈ 0.6 cm^2) mounted onto heavy tungsten leads. Temperatures were measured by a Pt–Pt 13% Rh thermocouple spot-welded to the center of each wire. An optical pyrometer was periodically used for calibration of the temperatures measured. Temperatures measured are regarded as accurate to ±4°C. An important question in these experiments is the chemical state of the platinum surface of which the only direct indication is reproducibility of our data. But we have reported previously (*17*) that there is no evidence of oxide on Pt under conditions similar to the ones used in this study. Auger electron spectroscopy studies on an identical Pt ribbon (*16*) indicated that after exposure to O_2 at 1300°C and 0.010 Torr for over 15 min the surface was free of sulfur and metals, while carbon concentrations were a few percent of a monolayer. In the present work, the Pt wire is initially heated in O_2, typically at 0.010 to 1.0 Torr and 1300°C, for 1 h. Following this treatment, reaction rate data are reproducible over long periods of time and on different wires. Also, since oxygen is one of the products of N_2O decomposition, the surface is continuously cleaned of contaminants such as carbon or sulfur species. Examination of samples by SEM showed that catalytic etching is negligible (*6, 16*) under these conditions, and the surface area is unchanged.

All gases were of standard purity (Matheson N_2O-99.9%, Chemetron O_2-99.9%) and were used with or without further purification. Occasional purification included a dry ice–acetone-cooled cold trap for condensables, molecular sieves, and activated charcoal.

After the initial steady-state reactant partial pressure was obtained, reaction was initiated by electrically heating the filament to the desired temperature. Steady-state temperatures were attained very rapidly and the species pressures approached the new steady-state values within 4 sec. In some of these experiments, the temperature was controlled by a minicomputer connected to our system through a programmable power supply.

Reactor pressures were calibrated against mass spectrometer readings using known pressures of pure gases or mixtures of them in the reactor. These pressures were measured by McLeod and thermocouple gauges. Mass spectrometer readings were proportional to partial pressures over the entire range of pressures reported here. Masses 28, 30, 32, and 44 were monitored during these experiments.

Data were reproducible to within ±5% on a given wire, and to within ±10% on three different wires over a long period of time.

RESULTS

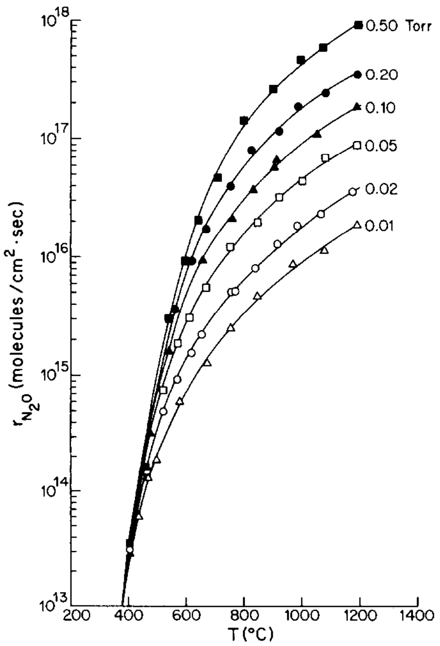

FIG. 1. N_2O decomposition rate vs temperature for N_2O pressures between 0.01 and 0.50 Torr. The solid lines are fits to data using an LH rate expression, Eqs. (2), (5), and (7).

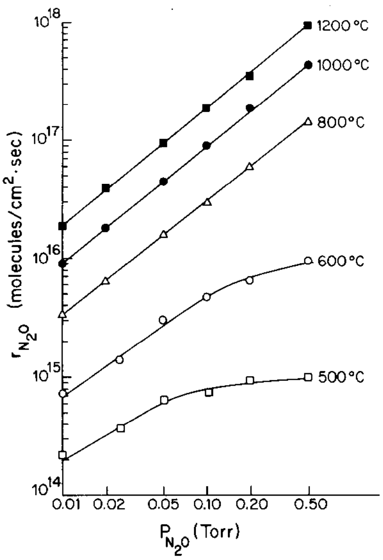

FIG. 2. N_2O decomposition isotherms showing the shift from first-order kinetics to zeroth-order kinetics as P_{N_2O} increases.

In Fig. 1, the rate of N_2O decomposition versus Pt wire temperature is shown for nitrous oxide pressures between 0.01 and 0.50 Torr. At low temperatures the rate at all pressures follows an asymptote, showing that the reaction is zeroth order with respect to P_{N_2O}. At high temperatures the rates drop below the asymptote and become dependent on pressure. Figure 2 shows a plot of rate versus P_{N_2O} for temperatures shown. Data points in the isotherms are points from Fig. 1 if they coincide with the temperature chosen; otherwise, rates were interpolated from rates just above and below that temperature. This plot indicates an order of 1.01 ± 0.05 at high temperatures (1000 to 1200°C) and shows that the N_2O decomposition rate becomes independent of pressure at low temperatures (500°C) as P_{N_2O} increases. These pressure and temperature dependences indicate that the rate, in pure nitrous oxide, is given by a Langmuir–Hinshelwood rate expression

$$r_{N_2O} = \frac{k_R K_{N_2O} P_{N_2O}}{1 + K_{N_2O} P_{N_2O}}, \tag{2}$$

where k_R is usually interpreted as the reaction rate coefficient

$$k_R = k_{0,R} \cdot \exp(-E_R/RT) \tag{3}$$

and K_{N_2O} the adsorption equilibrium constant for N_2O,

$$K_{N_2O} = K_{0,N_2O} \exp(E_{N_2O}/RT), \tag{4}$$

with E_R and E_{N_2O} the activation energy for reaction and the heat of adsorption of N_2O, respectively. The Arrhenius forms of k_R

and K_{N_2O} are examined in Figs. 3 and 4. Figure 3, obtained from data points on the zero-order asymptote of Fig. 1, gives a straight line for a rate variation by a factor of 100. The slope and intercepts yield

$$k_R\left(\frac{\text{molecules}}{\text{cm}^2\ \text{sec}}\right) = 9.9 \times 10^{24} \exp\left(\frac{-34{,}900}{RT}\right). \quad (5)$$

A plot of log $[r_{N_2O}/P_{N_2O}]$ versus $1/T$ for high-temperature rates is shown in Fig. 4. While the variation in r_{N_2O}/P_{N_2O} is only over a factor of 7, data follow the Arrhenius form with

$$k_R K_{N_2O}\left(\frac{molecules}{\text{cm}^2\ \text{sec}\cdot\text{Torr}}\right) = 2.1 \times 10^{20} \exp\left(\frac{-13{,}600}{RT}\right) \quad (6)$$

or

$$K_{N_2O}\ (\text{Torr}^{-1}) = 2.1 \times 10^{-5} \exp\left(\frac{21{,}300}{RT}\right) \quad (7)$$

to give a calculated heat of adsorption of N_2O, E_{N_2O}, of 21,300 cal/mole. Solid lines in Figs. 1 and 2 are those calculated from Eq. (2) with parameters from Eqs. (5) and (7). Rates over a factor of 10^4 can be fitted by these expressions with no systematic deviations.

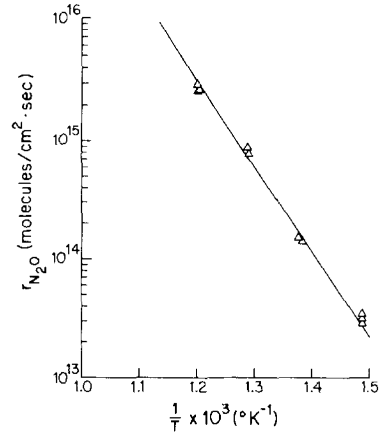

FIG. 3. Arrhenius plots for data points on the zero-order asymptote of Fig. 1.

DISCUSSION

Although it is generally difficult to demonstrate that any particular rate equation gives the "best" fit to experimental data, our rate expression, Eq. (2), with parameter values from Table 1, fits all of our data points in pure N_2O to within ±10%. This expression is thus valid over a factor of 50 in reactor pressure, temperatures between 400 and 1200°C, and rates varying by a factor of 10^4. This expression is therefore an adequate representation of the experimental results, although any temperature dependencies of preexponential factors would be averaged in Arrhenius plots. Also, the only products observed at all times and under any conditions were molecular nitrogen and molecular oxygen.

This rate expression has the simple Langmuir–Hinshelwood form of a unimolecular reaction without product inhibition;

$$N_2O + S \underset{k_d}{\overset{k_a}{\rightleftarrows}} N_2O - S, \quad (8)$$

$$N_2O \xrightarrow{k_R} N_2 + O - S, \quad (9)$$

$$2O - S \underset{k_a'}{\overset{k_d'}{\rightleftarrows}} O_2 + 2S \quad (10)$$

TABLE 1

Comparison of N_2O, NO, and NH_3 Adsorption and Reaction Parameters on Polycrystalline Pt

Reactant	E_i (cal/mole)	$K_{0,i}$ (Torr^{-1})	E_R (cal/mole)	$k_{0,R}$ (moles/cm^2 · sec)	T (ϑ = 0.5) (°C)
N_2O	21,300	2.1×10^{-5}	−34,900	9.9×10^{24}	710
NO	8,250	6.95×10^{-4}	−13,500	7.95×10^{19}	300
NH_3	16,700	4.35×10^{-5}	−21,000	2.27×10^{23}	560

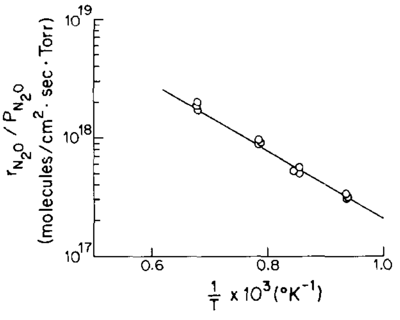

FIG. 4. Arrhenius plot for high temperatures where the rate is first order in N_2O pressure.

in which S is an empty site on the catalyst surface, $N_2O - S$ and $O - S$ are the absorbed species of N_2O and O_2, respectively, k_a and k_a' are adsorption rate constants, k_d and k_d' are desorption rate constants, and k_R is the reaction rate constant. If adsorption–desorption equilibrium is assumed for N_2O and O_2, and the surface coverage (fraction of saturation density) of O_2 on the catalyst surface is small, then we obtain Eq. (2), where

$$K_{N_2O} = \frac{k_a}{k_d}.$$

If the assumption of small coverages of oxygen on the catalyst surface is dropped and competitive adsorption of N_2O and O_2 on the surface is assumed, an additional term in the denominator of Eq. (2) has to be added, so that Eq. (2) becomes

$$r_{N_2O} = \frac{k_R(k_a/K_d)P_{N_2O}}{1 + (k_a/K_d)P_{N_2O} + (K_a'/k_d')^{1/2}P_{O_2}{}^{1/2}} \quad (11)$$

and oxygen inhibition under certain conditions may be expected. We did observe inhibition by oxygen for conversions of N_2O between 9 and 28%, but no studies on oxygen inhibition were carried out. Thus, the lack of such data cannot exclude competitive adsorption of N_2O and O_2 on polycrystalline platinum catalysts.

There have also been several studies of the interaction of oxygen with Pt published (*18–20*). For instance, Amirnazmi and Boudart (*18*) have suggested the formation of a surface oxide PtO_2, during their experiments on NO decomposition over Pt. However, as noted previously, we have found no evidence of oxide on Pt at pressures in the order of 10^{-2}–10^{-1} Torr, very low conversions, and oxygen-free feed streams, at any temperature (*17*).

Another approach to the N_2O decomposition reaction scheme has been the assumption of an oxygen transfer redox mechanism (*21*). But, although we have tried to predict Eq. (2) by such a mechanism, all our attempts have failed.

The N_2O decomposition reaction has been studied over a wide range of pressures, from a few Torr up to 70 atm, and over a variety of catalysts (*9–15*). Nagasubramanian *et al.* (*10*) report that on titanates of Mn, CO, and Ni the N_2O decomposition rate depends on P_{N_2O}, being first order with respect to P_{N_2O} at pressures less than 50 Torr, and $r_{N_2O} = kP_{N_2O}/P_{O_2}^{1/2}$ at pressures greater than 200 Torr. Viswanathan (*11*) distinguishes two different kinetics over oxide catalysts, where desorption of O_2 is rate controlling at high pressures and adsorption of N_2O is rate controlling at low pressures. This paper is the first report on N_2O decomposition over a platinum catalyst at pressures less than 1 Torr. In these studies, the reaction step is the rate-controlling one. Although we were unable to find any data of N_2O decomposition on Pt, there is a great deal on gold catalysts. Surprisingly, we found that the reaction activation energy in our experiments was 34,900 cal/mole, compared to 33,875 cal/mole in (*9*), 30,900 cal/mole in (*14*), and 34,600 cal/mole in (*15*) under different conditions and over a gold catalyst. This suggests that this process is not sensitive to the detailed electronic structure of the surface.

The coverage of $N_2O - S$ is equal to unity at low temperatures (zeroth-order regime) and proportional to P_{N_2O} at high temperatures (first-order regime).

In Table 1, adsorption and reaction parameters are reported for the decomposition of N_2O, NO, and NH_3 on polycrystalline Pt at pressures in the order of 0.5 Torr (this work, *1*, *4*). In this table we see that while a fit of the reaction kinetics of the NO decomposition to a Langmuir–Hinshelwood rate expression yielded a weakly bound state of NO (*4*), similar fits of the reaction kinetics of the N_2O and NH_3 decompositions yielded tightly bound states of N_2O and NH_3 (this work, *1*). Table 1 also indicates that the decomposition rate of NO is smaller than that of either N_2O or NH_3 at the same temperatures and pressures. In particular, at temperatures greater than 550°C N_2O and NH_3 decompose 50 to 100 times faster than NO does (*16*).

For a single state with coverage-independent parameters, the adsorption equilibrium constant K is given by the expression

$$K = \frac{S_0}{k_{d_0}\sqrt{2\pi MRT}\, n_0} \exp(\Delta H/RT)$$

with the heat of adsorption ΔH being approximately the desorption activation energy E_d. Trying to see whether the preexponential term of K_{N_2O} is reasonable, we assume $S_0 = 1$, $k_{d_0} = 10^{13\pm1}$ sec^{-1}, and $\Delta H \approx 21{,}300$ cal/mole for the N_2O decomposition, and we obtain

$$K_{N_2O}(\mathrm{Torr}^{-1}) = 1 \times 10^6 \frac{S_0}{k_{d_0}} \exp(\Delta H/RT) \approx 10^{-7\pm1} \exp\left(\frac{21{,}300}{RT}\right),$$

which is similar to Eq. (7).

Note that at high temperatures the N_2O decomposition rate is of the same order of magnitude as the reaction between NO and NH_3 (*22*), so that the decomposition of N_2O may be important in the kinetics and dynamics of this bimolecular reaction between NH_3 and NO under these conditions.

SUMMARY

N_2O decomposition rates have been measured over a polycrystalline Pt catalyst, at pressures between 0.01 and 0.50 Torr and in the temperature range of 400 to 1200°C, with a precision comparable to that usually attained in homogeneous kinetics. All of these results can be correlated with a single rate expression of the Langmuir–Hinshelwood form. This is further evidence that it is not necessary to invoke surface heterogeneities or coverage-dependent parameters to fit the rate quantitatively over wide ranges of variables.

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