

Catalytic Decomposition of N₂O and Oxygen Desorption Spectra on NiO

IAN D. GAY

*Department of Chemistry, Simon Fraser University, Burnaby 2,
British Columbia, Canada*

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Desorption spectra have been obtained for oxygen desorbing from NiO after adsorption of O₂ and after catalytic decomposition of N₂O. Three different binding states can be produced by adsorption of O₂ under various conditions, and a fourth during decomposition of N₂O. An attempt is made to relate the kinetics of N₂O decomposition to the nature of the binding of adsorbed oxygen.

INTRODUCTION

It has been suggested by Charman, Dell, and Teale (1) on the basis of adsorption kinetics, that there are three and possibly four modes of adsorption of oxygen on pure NiO. In addition, Gay and Tompkins (2) have suggested that the low temperature decomposition of N₂O on NiO involves adsorbed oxygen in a state which does not correspond to one of those reached by adsorption of O₂. It appears reasonable to suggest that the various different modes of oxygen adsorption are associated with different energies of binding of the oxygen to the surface. This hypothesis is examined here by the technique of desorption spectrometry.

EXPERIMENTAL

Nickel oxide was prepared by igniting reagent grade nickel nitrate at 850°C for 9 hr in a nickel crucible. The supplier's analysis showed the following metallic impurities in the nitrate: .002% Co, .001% Fe, .001% Cu, and .002% Pb. This oxide had an area of 2.45 m²/g by the BET method assuming an area of 19.5 Å² per krypton atom. A sample of .88 g was used in these experiments, giving a total area of 2.15 m². This area remained constant within 2% over the entire course of the experiments. There was no evidence of

gross instability of area, as reported by Eaton and Winter (3), notwithstanding several hundred heatings and coolings through the Neel point. Oxygen was prepared by the thermal decomposition of potassium permanganate, or in some experiments was 99.98% pure oxygen from a cylinder (Fisher). Nitrous oxide of 98% purity (Matheson) was purified by repeated vacuum distillations.

Experiments on adsorption of O₂ and decomposition of N₂O were carried out in a static system of approximately 350 cm³ volume similar to that used previously (2), and desorption spectra were obtained by connecting to the cell the apparatus shown in Fig. 1. The NiO was protected from grease and mercury vapors by a trap maintained at -78°C. Desorption spectra were obtained by evacuating the cell at room temperature, then closing S₁ and pumping via the capillary, S₃ and S₂, while raising the temperature. The thermistors were connected in the Wheatstone bridge circuit so as to measure the pressure drop across the capillary, thus giving a signal proportional to the rate of flow of gas through the capillary; the bridge out of balance signal was recorded on a strip chart recorder, as was the signal from a thermocouple within the NiO bed. The capillary had a conductance of approxi-

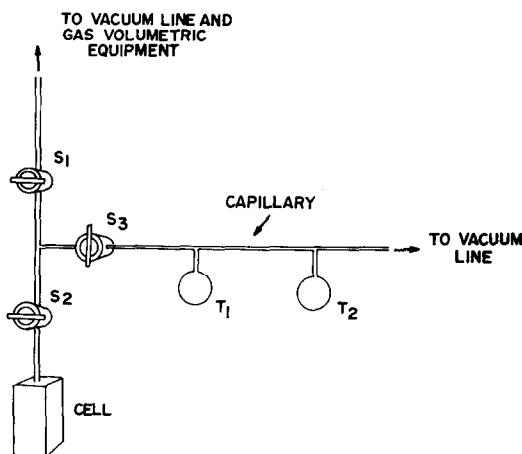


FIG. 1. Apparatus used for obtaining desorption spectra. S_1 , S_2 , S_3 — stopcocks; T_1 , T_2 , thermistors.

mately .01 liter/sec for O_2 at room temperature, and the maximum usable pressure sensitivity was about 10^{-3} Torr full scale, giving a minimum detectable gas evolution rate of approximately 3×10^{12} molecules/sec. The flow measuring system was calibrated by releasing a known amount of gas from the cell by gradual opening of S_2 . It was found that the area under the recorded curve was linear in amount of gas for calibrations with 3×10^{15} to 2×10^{17} molecules. Amounts adsorbed in experiments ranged up to 6×10^{17} molecules. Maximum gas flow rates in the calibration peaks were in the range 1.4×10^{14} to 1.0×10^{15} molecules/sec, compared with rates of up to 6×10^{14} molecules/sec in desorption experiments. The cell, which was constructed of silica, was heated by an external tube furnace. In isothermal experiments, the furnace was regulated by an electronic controller which kept the temperature constant and reproducible to $\pm 1/4^\circ C$. For desorption spectra, the furnace was connected to a motor-driven Variac, which could produce approximately linear temperature sweeps in the range of 5 to $15^\circ/\text{min}$. Most spectra were taken at $10^\circ/\text{min}$, and the instantaneous rate was normally between 9 and $11^\circ/\text{min}$ from 60 to $700^\circ C$.

After preparation, the NiO was placed in the cell and outgassed at $750^\circ C$ for 2 days. After such an outgassing, the sample

could be cooled and isolated by S_2 for up to a day with no detectable desorption in a subsequent temperature sweep to $750^\circ C$. This indicates that not more than about 10^{-4} of the surface sites become covered by desorbable gases on moderately prolonged exposure to the residual gases in the vacuum system. After exposure to O_2 or N_2O , at least overnight degassing at $700^\circ C$ was required to give a blank desorption spectrum. A portion of the oxygen was always strongly enough bound that its evolution was not rapid at $750^\circ C$.

RESULTS

Whenever the NiO surface was exposed to O_2 or N_2O , a subsequent desorption spectrum showed a high temperature desorption peak with a maximum between 650 and $750^\circ C$. This peak was generally broad and not well reproducible, probably due to minor variations in outgassing conditions. A small shoulder at $500^\circ C$ was a regular feature. In addition to this peak, various peaks were found at lower temperatures, depending on experimental conditions.

Exposure of the NiO to O_2 at room temperature and pressures of 0.1 to 1.0 Torr resulted in fairly rapid adsorption of about 4.6×10^{16} molecules of O_2/m^2 of surface, a coverage of somewhat less than 1%.* This adsorption which was complete in 30 min was followed by a slower adsorption, leading to uptake of a further 10^{16} molecules/ m^2 in a day. Part of this gas could be removed by pumping at room temperature; the remainder produced a desorption spectrum showing a small peak at $70^\circ C$, together with the above mentioned high temperature peak. A typical desorption spectrum is shown in Fig. 2a. The low temperature peak typically represented evolution of about 10^{16} molecules/ m^2 . The area of the high temperature peak could not be accurately measured, because desorption was not complete at $750^\circ C$, but it appeared that the area was of the correct magnitude

* $1 m^2$ of the (100) surface of NiO exposes 1.1×10^{19} Ni ions.

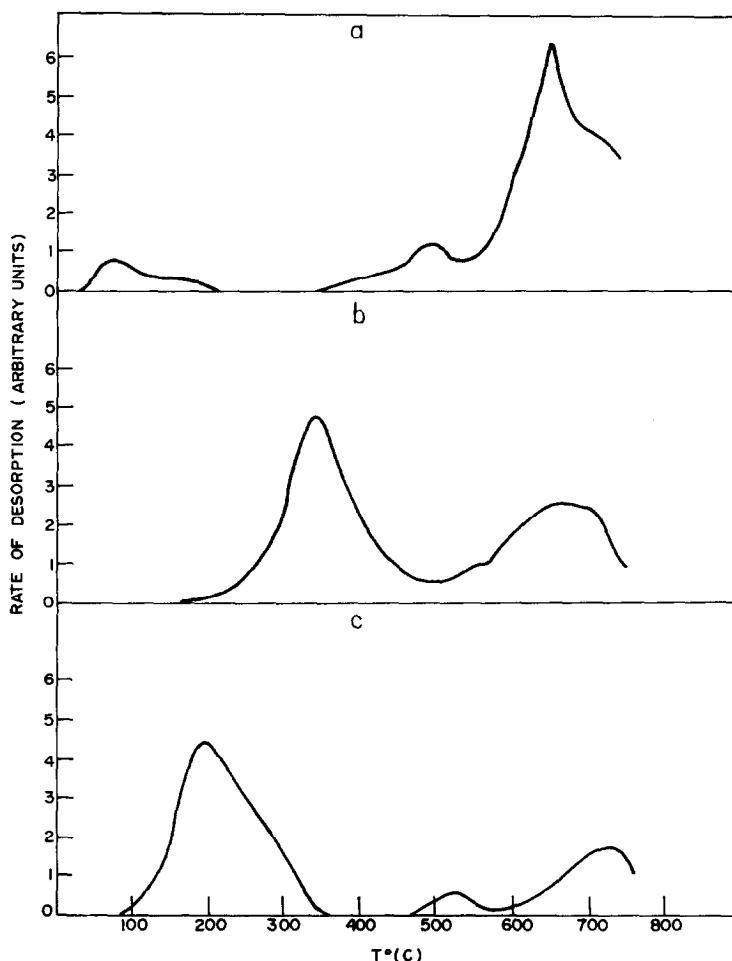


FIG. 2. Typical desorption spectra (a) after adsorption of O₂ at 25°C, (b) after adsorption of O₂ at 200°C, and (c) after decomposition of N₂O at 100°C. Rate units are the same for (a), (b), and (c).

to account for the remainder of the gas adsorbed.

At temperatures of 150°C and above, a second type of O₂ adsorption was found which was characterized by slow adsorption, following approximately Elovich kinetics. Coverages of up to 3×10^{17} molecules/m² or about 5% could be reached in 1–2 days at pressures up to 0.2 Torr. The desorption spectra of this oxygen showed a peak at 320–360°C in addition to the high temperature peak. At the higher coverages, these peaks tended to merge. Typical desorption spectra are shown in Fig. 2b. The 340°C peaks typically represent coverages of $2\text{--}8 \times 10^{16}$ molecules/m², i.e., a few percent of the surface. It

appears that this mode of adsorption poisons the surface for low temperature O₂ adsorption, since cooling to room temperature produced no further oxygen uptake, nor was a 70°C peak found in the desorption spectra.

Exposure of the NiO to N₂O at temperatures above 50°C led to catalytic decomposition of the N₂O, some of the oxygen being retained on the catalyst and the remainder appearing as gas phase O₂. A desorption spectrum, taken after completion of a catalytic decomposition and after pumping off reaction products at room temperature, showed a peak at about 200°C in addition to a high temperature peak. A typical spectrum is shown in Fig. 2c. The

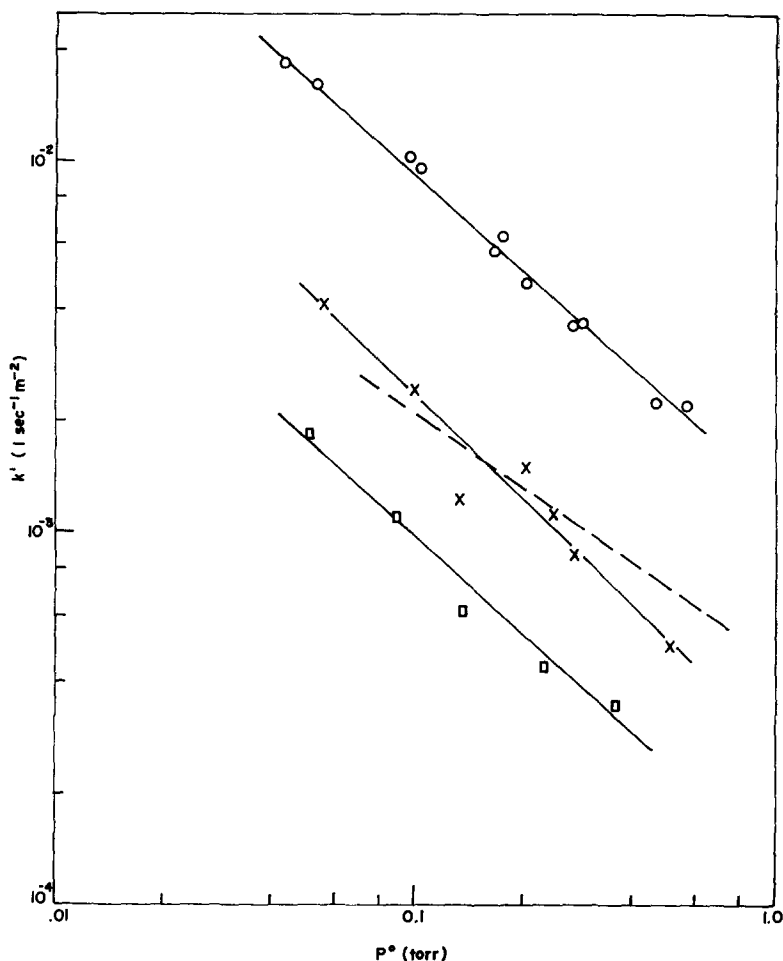


FIG. 3. Reduced rate constants for N_2O decomposition. \circ $150^\circ C$, \times $100^\circ C$, \square $75^\circ C$; dashed line results of Ref. (2).

results of Gay and Tompkins (2) show that under the conditions used here the amount of gas phase N_2 produced is equivalent to the whole of the N_2O introduced; thus, the desorption peaks arise from adsorbed oxygen. It can be seen that the low temperature O_2 adsorption is again poisoned.

The kinetics of N_2O decomposition were studied at 75, 100, and $150^\circ C$ in the pressure range 0.05 to 0.5 Torr. The kinetics are found to be those previously reported (2); viz., first order reaction in any given experiment, together with a linear dependence of the logarithm of the rate constant on the logarithm of initial pressure of N_2O . It is found that the quantity

of O_2 desorbed in the $200^\circ C$ peak is a linear function of the logarithm of initial N_2O pressure. Figure 3 shows reduced rate constants (experimental first order constants times system volume divided by catalyst area) as a function of initial pressure. Figure 4 shows amount of O_2 desorbed in the $200^\circ C$ peak as a function of initial N_2O pressure. It can be seen from Fig. 4 that the area of the $200^\circ C$ desorption peak extrapolates to zero at a pressure of about 0.025 Torr at all temperatures. If a dose of N_2O was admitted at a lower pressure than this, there was an initial rapid pressure rise, due to the decomposition, followed by a pressure decrease due to adsorption of the O_2 produced. Only a high

temperature (600°C) peak is found in the desorption spectrum in this case. This indicates that at least part of the high temperature oxygen comes from adsorption of O₂, and not from the reaction N₂O(g) → N₂(g) + O(a). It can be seen that the rate constants at 100°C are in close agreement with those of Gay and Tompkins (2), although their temperature and pressure dependence is somewhat stronger. The activation energy obtained from these rate constants is 8.7 kcal/mole with no significant pressure dependence.

DISCUSSION

A. Desorption Kinetics

The rate of desorption of gas for a linearly increasing temperature can be written as

$$-\frac{d\theta}{dt} = A\theta^n \exp[-E/R(T_0 + \alpha t)], \quad (1)$$

where n is the order of the reaction, A the preexponential factor, E the activation

energy for desorption (which can in general be a function of θ), T_0 the initial temperature, α the temperature sweep rate, and t the time. Equation (1) can be integrated (4) in terms of the exponential integral for the case when E is independent of θ . In the present work, however, (1) has been integrated numerically, and the numerical solutions least-squares matched to the experimental desorption spectrum as described elsewhere (5, 6). This has the advantages of correctly using experimental temperature-time information, when the sweep is not exactly linear, and of permitting an analysis in which E is a function of θ . Kinetic analysis has been attempted for the 300°C peak produced by high temperature O₂ adsorption and the 200°C peak found after N₂O decomposition. Analyses were performed for both first and second order desorption and for E independent of and a linear function of θ . In both cases, second order kinetics gave the better fit, and the experimental data were reproduced

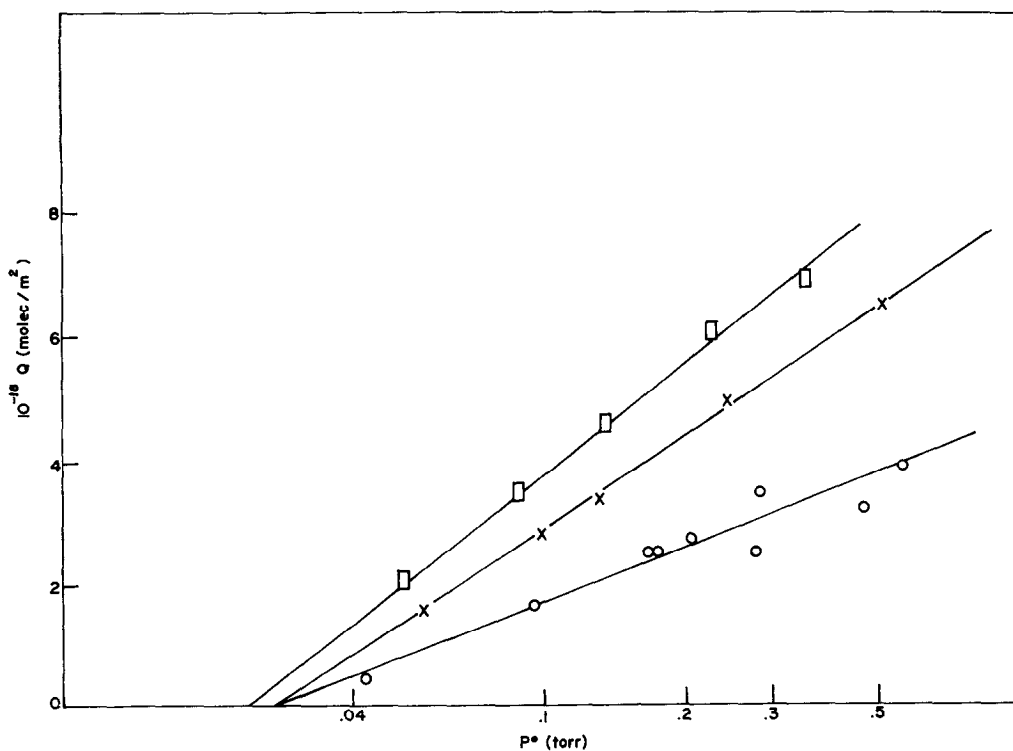


FIG. 4. Oxygen desorbed in 200°C Peak after N₂O decomposition at various temperatures and pressures. ○ 150°C, × 100°C, □ 75°C.

within a reasonable estimate of experimental error with E independent of θ . When E was allowed to vary linearly with θ , the resulting three-parameter equation typically gave a 20% smaller root mean square deviation. In this case the parameters were strongly coupled and less consistent, indicating that the precision of the data is not sufficient for a three-parameter fit. A similar conclusion was reached in attempting to fit the data by assuming a range of sites of varying E , each of which individually obeyed Equation (1). Fits were attempted in which the distribution of initial population with respect to energy was gaussian, exponential, or rectangular, with the position and width of the distribution variable, and assuming the same A value on all sites. For these three-parameter fits, strong coupling was again found along with only a small improvement in standard deviation compared with Equation (1).

Fits of the various peaks from N_2O experiments gave E values of about 10, 12, and 16 kcal/mole for decompositions at 75, 100, and 150°C, respectively, with individual runs varying by as much as 2 kcal/mole from the figures quoted above. The A values, for second order fits, depend on the coverage taken for $\theta = 1$. If one assumes 10^{19} O atoms/m² for $\theta = 1$, the corresponding A values are 10^5 , 10^6 , and 10^8 sec⁻¹ with variations of as much as a factor of 10 from one run to another.

These preexponential values are unreasonably low (7) even on the assumption that both adatoms and desorption complex are mobile. The three-parameter fits involving a distribution of population with respect to desorption energy produced A values 2-3 orders of magnitude higher, and in this sense are more satisfactory, although A should be at least of the order of 10^{20} from simple transition state theory. If a "reasonable" A value is imposed on the data, the best fit is obtained with an energy distribution 8-10 kcal wide centered at about 40 kcal. The standard deviations resulting are, however, 2-3 times larger than those arising simply from the best fit of Equation (1). This would appear

to be another example of the well known (8) phenomenon of abnormally low pre-exponentials for desorption.

Similar uncertainties were found in the determination of the kinetic desorption parameters for the 340°C peak arising from O_2 adsorption. Simple fitting of Equation (1) gives values of E and A of about 23 kcal/mole and 10^8 sec⁻¹, with fluctuations between experiments similar to those reported above.

B. Kinetics of the N_2O Decomposition

The data of Fig. 4 convincingly support the assumption of Gay and Tompkins that a quantity of oxygen is deposited on the catalyst which is a linear function of the logarithm of initial N_2O pressure. The assumption that the rate of decomposition depends exponentially on this oxygen coverage then reproduces the kinetics (2).

It was proposed in (2) that the amount of this oxygen was determined by a single rate process which obeyed Elovich kinetics. It is apparent in Fig. 4; however, that the oxygen coverage decreases with increasing temperature and must hence be governed either by equilibrium or at least competing rate processes. The simplest assumption to account for lower coverages at higher temperatures is that interaction of N_2O with the catalyst takes place from a physically adsorbed layer, whose concentration decreases with temperature.

A more difficult aspect of Fig. 4 is that the slopes of the lines also decrease with temperature. Elovich models (2) or any simple equilibrium model, such as the Temkin isotherm (9) which relies on linear variation of adsorption energies with coverage, will produce coverage vs. $\ln P$ plots whose slope is proportional to the absolute temperature. The slopes in Fig. 4 are more nearly proportional to $1/T$. It does not appear possible to offer a simple explanation of this at present.

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