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Simultaneous Decompositions of Nitrous Oxide

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A method, utilizing experimental data obtained with a backmix reactor, is presented for the determination of homogeneous reaction rates and heterogeneous reaction rates in systems in which the reaction proceeds by both mechanisms simultaneously. The methods of obtaining the individual reaction rates directly from the measured total reaction rates are developed, and these methods are illustrated for data on the thermal decomposition of nitrous oxide at 700-800°C. Comparison is made between the reaction rates derived from this type of measurement and those derived by previous investigations in which the two reaction mechanisms were observed in separate experiments. The accuracy of the kinetic parameters derived from measurements of the total reaction rate is comparable to that obtained by more traditional experimental methods for high-temperature reaction kinetics.

INTRODUCTION

A chemical reaction occurring simultaneously by parallel homogeneous and heterogeneous paths presents unique problems in investigations of chemical kinetics. The experimental design and the analysis of the data must separate the two contributions to the total observed reaction rate. Otherwise, the data are of little value either for an interpretation of mechanism or for possible design use. Other investigators have usually attempted to measure the homogeneous and heterogeneous contributions separately. However, the method presented here allows the determination of both rate expressions from a single set of experimental measurements.

When there are parallel rate processes, the total rate is the sum of the individual rates; this may be expressed in terms of specific reaction rates per unit volume as

$$r_T = r_H + r''(S/V), \qquad (1)$$

where r''' is the reaction rate per unit catalyst surface. Alternatively, the heterogeneous rate could be expressed in terms of r''', a rate per unit weight of catalyst, and (W/V). In general, r'' is a function of bulk phase reactant concentration, temperature, and catalyst geometry and activity. Usually, r'' is found to be independent of the surface-to-volume ratio S/V, and in this case, r_T will be linearly dependent on S/V. Even in those cases where r'' is not independent of S/V, it is often possible to separate the functional dependence on S/V from the dependence on other variables, i.e.,

$$r'' = \rho_s\phi(S/V), \qquad (2)$$

where ρ_s does not depend on (S/V). Then, Eq. (1) may be written in the form

$$r_T = r_H + \rho_s(S/V)[\phi(S/V)], \qquad (3)$$

and a linear relationship will be obtained between r_T and (S/V) $[\phi(S/V)]$.

Equations (1) or (3) indicate that it should be possible, by varying the surface-to-volume ratio in the case of systems with parallel homogeneous and heterogeneous reaction paths, to obtain individual reaction rates from data on the total reaction prior to fitting any rate equation to the data. Thus, it would not be necessary to devise experiments to measure individual

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reaction rates. Nor is it necessary to determine a complex rate equation to fit the data for the total reaction rate, and then deduce which part of this complex expression is surface dependent by observing the effect of changing surface-to-volume ratio (*1*).

It is our purpose to show that the immediate separation of the data into heterogeneous and homogeneous contributions will allow the experimenter to obtain data of comparable accuracy to those obtained in measurements of individual reaction rates, but without the problems of separating the reactions in the physical system or determining a complex rate expression for the total rate. Mrazek, Knapp, and Block (*2*) employed this technique to evaluate the magnitudes of the rates of simultaneous homogeneous and heterogeneous thermal decompositions of tungsten hexacarbonyl. Their determination of the available surface area was uncertain, however, primarily because of the formation of metallic tungsten, which could also catalyze the reaction.

System and Apparatus

The thermal decomposition of nitrous oxide in the gas phase and on a gold surface was chosen as a system to verify the utility of Eq. (1) in determining the individual reaction rates. The homogeneous reaction has been investigated extensively (*3–11*) and the decomposition on gold has been investigated with the hot wire technique (*12*). Nitrous oxide decomposes at high temperatures by two reactions:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2 \quad \text{primary reaction;} \qquad (4)$$

$$N_2O \rightarrow NO + \tfrac{1}{2}N_2 \quad \text{secondary reaction.} \qquad (5)$$

At the conditions used in this investigation, the calculation of equilibrium conditions showed that these are the only two reactions which occur to a significant extent.

A backmix reactor was chosen for obtaining the reaction rate data. There are several advantages in using a backmix reactor for catalytic studies (*13–16*): Isothermal operation, the possibility of a wide range of conversions at steady state conditions, minimal resistance to mass transfer from the bulk phase to the catalyst, and the direct calculation of rate without differentiating data or curve fitting with assumed rate equations. For a backmix reactor, the rate of decomposition of nitrous oxide by Eq. (4) is

$$-r_1 = nX(1 - f)/V, \qquad (6)$$

and the rate of decomposition by Eq. (5) is

$$-r_2 = nXf/V \qquad (7)$$

where X is the fraction of N_2O that decomposes, f is the fraction of the decomposition that occurs via reaction (5), n is the feed rate of N_2O, and V is free reactor volume. These expressions are valid only for a perfectly mixed reactor. Evaluation of mixing in the reactor was achieved by monitoring conversion as a function of stirring rate (15). These tests indicated that perfect mixing could be sustained for a surface-to-volume ratio of 1.1436 cm^{-1} and below.

Previous work on the decomposition of nitrous oxide showed that fused quartz has a minor effect, if any, on the reaction (*6, 9, 10*). This was verified by the results of several preliminary experiments in which the surface area of quartz in the reactor was varied. A 71/60 standard taper joint made of clear fused quartz was fashioned into the reactor as shown in Fig. 1. The coldfinger (Fig. 1) was also constructed from clear fused quartz; hot reaction gases entered the coldfinger and were quenched to a temperature of 500°C (at which temperature the decomposition rates are negligible) in less than 1 cm. The stirrer consisted of four curved quartz blades which swept through a radius of approximately 26 mm. The stirrer shaft was a quartz rod and the sleeve for the shaft was a fused quartz tube. No lubricant or sealant was required in the stirrer shaft-sleeve assembly.

The catalyst used in this study, gold with a purity of 99.99%, was in the form of continuous ribbon, 0.003 in. thick and 0.150 in. wide. The gold-wrapped catalyst racks were placed in the support rack

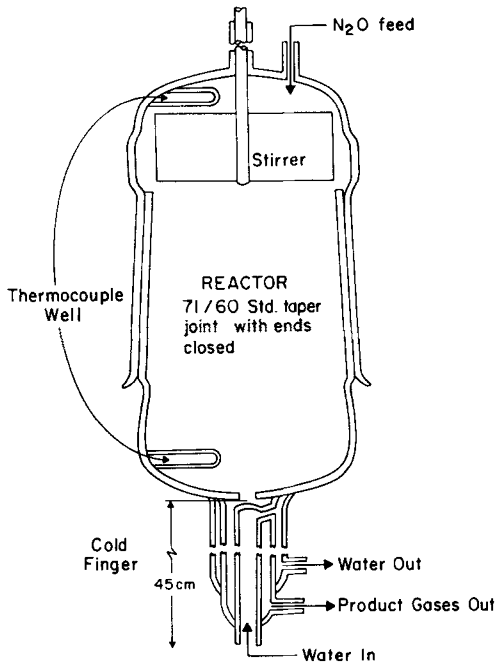

FIG. 1. Outline of backmix reactor.

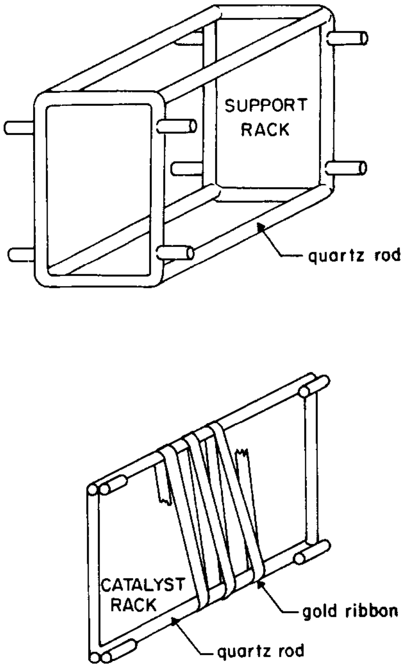

FIG. 2. Catalyst rack and support rack.

(Fig. 2) and the entire arrangement was set in the reactor. The amount of catalyst in the reactor could then be varied by changing the number of gold-wrapped catalyst racks in the support rack.

Reactor temperatures were measured with two chromel–alumel thermocouples in direct contact with the reaction gases. Radiation influences on the thermocouple beads were accounted for by correlating their temperatures with the temperature of a chromel–alumel thermocouple, shielded with two concentric cylinders of shiny gold foil, which was placed in the center of the reactor. The temperature indicated by this shielded thermocouple was found to be independent of its position and orientation in the reactor.

The feed rate of reactant (medical grade nitrous oxide) was measured with a rotameter calibrated with a wet test meter. Analysis of the reaction products was accomplished with a gas chromatograph for which the column was packed with Chromosorb 102 and coiled into a helical configuration so that it could be immersed in a small Dewar flask. The column temperature was kept at −80°C (dry ice–acetone bath) to effect the separation of nitrogen and oxygen. After the oxygen had eluted, the column was placed in a water bath at 35°C for elution of nitrous oxide. Because nitric oxide combines rapidly and completely with oxygen at room temperature (*17–19*), any nitric oxide formed in the reactor was oxidized to nitrogen dioxide in the coldfinger ($T \simeq 15°C$). Consequently, no nitric oxide was detected in any of the runs. Because the shapes of the nitrogen dioxide peaks were undesirable for quantitative analysis, the extent of the secondary reaction was calculated by examining the ratio (moles N_2/moles O_2) in the product.

REDUCTION OF EXPERIMENTAL DATA

The chromatographic analyses gave the values of the ratios (moles N_2/moles O_2) and (moles O_2/moles N_2O), and the quantities f and X which appear in equations 6 and 7 were obtained by simple stoichiometric relationships. In addition, the concentrations of all species could then be obtained from the material balance and the ideal-gas law. Thus, one can calculate the rates of reaction for the primary and secondary reactions as shown in Eqs. (6) and (7). At this point, it must be assumed that these represent total reaction rates, i.e., each reaction may possibly occur by simultaneous homogeneous and heterogeneous paths.

The experimental data for the primary reaction were then expressed as plots of total observed reaction rate as a function of the concentration of nitrous oxide for various values of the surface-to-volume ratio. These data are shown in Fig. 3 for a temperature of 800°C. Further data are given by Halladay (*20*). A "best fit" curve was put through each set of points and cross-plots were made which expressed the reaction rate, at constant concentration of nitrous oxide and constant temperature, as a function of the surface-to-volume ratio (Fig. 4). The linear portions of these plots show the range of the existence of a first-order dependence of rate on the amount of catalyst. The nonlinearity at the upper end of these curves is a result of imperfect mixing. Consequently, none of the data for S/V above 1.1436 cm^{-1} were used in subsequent calculations of heterogeneous or homogeneous rates.

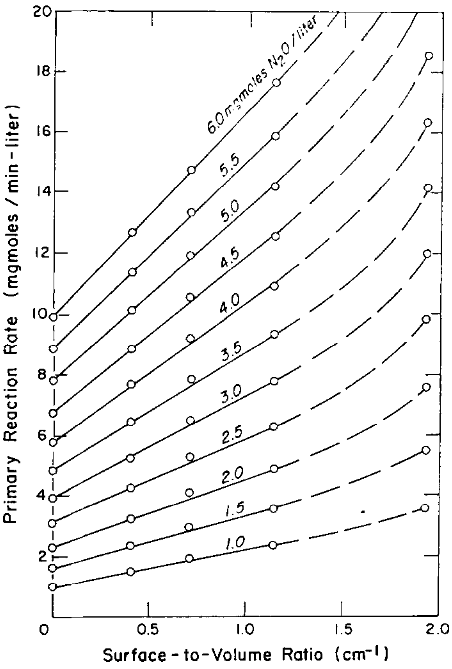

FIG. 4. Variation of primary reaction rate with surface-to-volume ratio at 800°C.

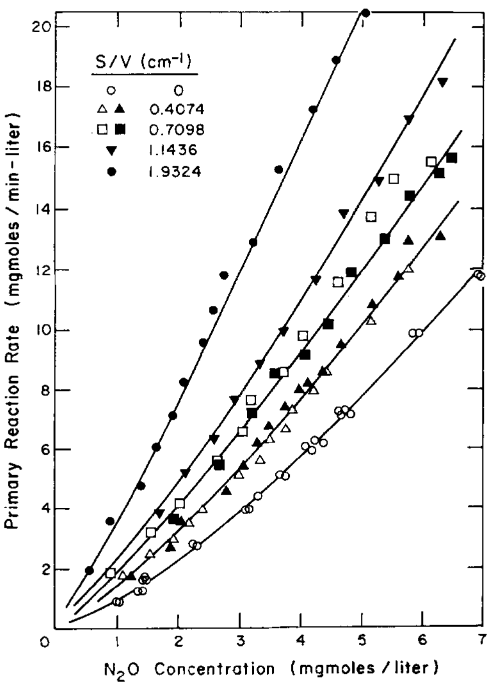

FIG. 3. Variation of primary reaction rate with N_2O concentration at 800°C.

It should be noted that, while the rate of the homogeneous portion of the primary reaction could have been obtained from Fig. 4 by extrapolation to $S/V = 0$, the homogeneous reaction was measured independently as a check. These data appear in Fig. 3 as the curve for $S/V = 0$, and the comparison between values obtained by direct measurement and values obtained by extrapolation can be seen in Fig. 4.

As developed previously, the linear portions of the curves shown in Fig. 4 have intercepts of r_H and slopes of r'' [cf., Eqs. (1) and (3), with $\phi(S/V) = 1$]. The slopes, or surface reaction rates per square centimeter of gold foil, were then plotted against the concentration of nitrous oxide, revealing a first-order dependence of rate on the concentration of nitrous oxide in the bulk gas (Fig. 5). The heterogeneous rate equa-

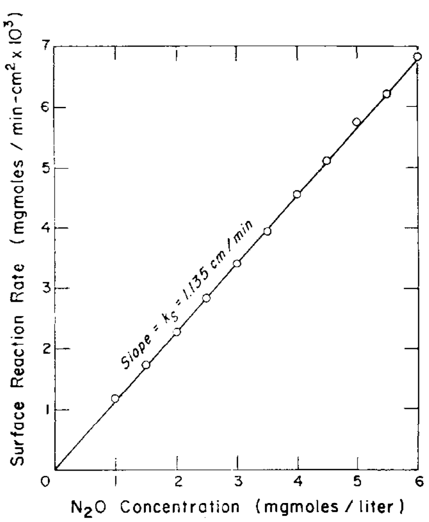

FIG. 5. Variation of surface reaction rate with N_2O concentration at 800°C.

tion for the primary reaction can then be written as

$$-r''(S/V) = k_s C_{N_2O}(S/V). \qquad (8)$$

The values of k_s were calculated from the slopes of lines such as that shown in Fig. 5 for 800°C.

The data for the secondary reaction could have been reduced in a similar manner to separate the homogeneous and heterogeneous contributions. However, as can be seen in Fig. 6, the rate of the secondary reaction did not vary with the amount of catalyst. Therefore, as the secondary reaction is apparently not catalyzed by gold, the measurements yielded the homogeneous reaction rate directly, and subsequent data reduction was not necessary.

RESULTS AND DISCUSSION

Homogeneous Reactions

The data for the primary reaction, $N_2O \rightarrow N_2 + \frac{1}{2}O_2$, can be represented by the equation

$$-r_{H1} = k_1 C_{N_2O}^2/(1 + k_2 C_{N_2O}). \qquad (9)$$

The constants k_1 and k_2 were determined by linear regression after rearranging Eq. (9) into the form

$$C_{N_2O}^2/-r_{H1} = (1/k_1) + (k_2/k_1)C_{N_2O}. \qquad (10)$$

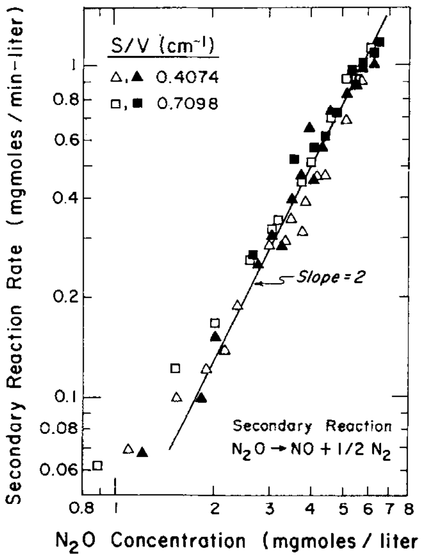

FIG. 6. Some secondary reaction rate data at 800°C.

The values determined for k_1 and k_2 are given in Table 1, and the agreement with the data is illustrated by the curve and data points for $S/V = 0$ in Fig. 3.

The data for the secondary reaction, $N_2O \rightarrow NO + \frac{1}{2}N_2$, appear to follow a second-order rate equation,

$$-r_{H2} = k_3 C_{N_2O}^2. \qquad (11)$$

Some of these data are shown in Fig. 6. Because of the scatter in the values for the rate of the secondary reaction (to be discussed later), there is some uncertainty as to the correct rate equation, and the values for k_3 (cf., Table 1) should probably be regarded as estimates.

The rate expressions for r_{H1} and r_{H2} can both be derived from the assumption of a bimolecular collision mechanism in which the steady-state approximation for the activated species N_2O^*, is made. The rate equation and mechanism proposed for the primary homogeneous reaction are the same as those proposed in most previous studies (*4, 9, 10*). Additional evidence for the collisional mechanism has been provided by studies on the effect of foreign molecules (*3, 10*). The increase in reaction rate with increasing concentrations of SO_2, CO_2 and CF_4 has been explained by hy-

TABLE 1
RATE CONSTANTS AND ARRHENIUS EQUATIONS

Constant	Temperature			Arrhenius equations
	973°K	1023°K	1073°K	
$k_1 \frac{\text{liter}}{\text{mgmole-min}}$	0.0279	0.242	1.43	$10^{16.39} \exp\left[\frac{-81{,}800}{RT}\right]$
$k_2 \frac{\text{liter}}{\text{mgmole}}$	0.184	0.467	0.723	$10^{5.69} \exp\left[\frac{-28{,}400}{RT}\right]$
$k_3 \frac{\text{liter}}{\text{mgmole-min}}$	—	0.0059	0.032	$10^{14.3} \exp\left[\frac{-72{,}400}{RT}\right]$
$k_s \frac{\text{cm}}{\text{min}}$	0.213	0.540	1.135	$10^{7.13} \exp\left[\frac{-34{,}600}{RT}\right]$

pothesizing that a collision between N_2O and a foreign molecule can produce an activated species N_2O^* just as if a collision had occured between two N_2O molecules.

Previous investigators customarily expressed the rates they observed for the primary reaction in terms of a pseudo first order rate constant k_f. Johnston (*9*) has compiled, averaged, and summarized most of the data recorded before 1950. In 1959, Graven (*5*) reported values of k_f for high temperatures. Their results and those of this study are compared in Fig. 7, revealing good agreement of rates and of activation energies.

The results of this study indicate that the formation of nitric oxide by the secondary reaction has a second-order dependence on C_{N_2O} over the entire composition range (cf., Fig. 6). However, previous investigators (*3*, *4*, *9–11*) have proposed quite different rate equations, and these investigators do not agree either with each other or with the results of this work. Thus, the order and mechanism of the secondary reaction have not been adequately defined, either in this study or in other studies. The data of this study are very scattered due to the indirect method of determining the extent of the secondary reaction. Consequently, the values for the rate constant k_3, the activation energy, and the order of the reaction should be regarded as estimates only. More complete and reliable data are needed for a confident description of nitric oxide formation.

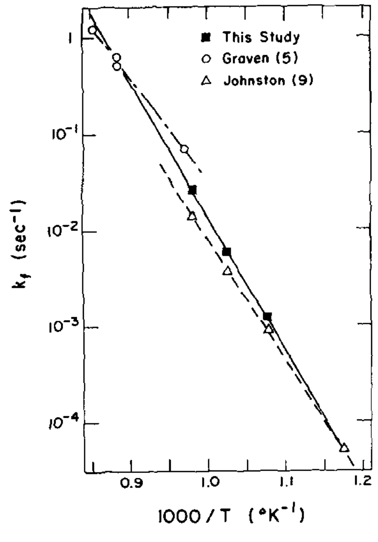

FIG. 7. Arrhenius plot comparing pseudo first-order homogeneous rate constants.

Heterogeneous Reaction

The rate equation for the heterogeneous reaction can be derived by assuming a mechanism which begins with the adsorption of a molecule of nitrous oxide on an active site on the surface of the gold, followed by decomposition of the adsorbed species. The rate of decomposition is proportional to the number of adsorbed nitrous oxide molecules. Use of the lower end of the Langmuir adsorption isotherm (*21*, *22*) to describe the relationship between the number of adsorbed nitrous oxide molecules and the concentration of nitrous oxide in the gas phase will yield Eq. (8) as the rate equation for the heterogeneous reaction.

The adsorption mechanism for the reaction on gold is suggested not only by the

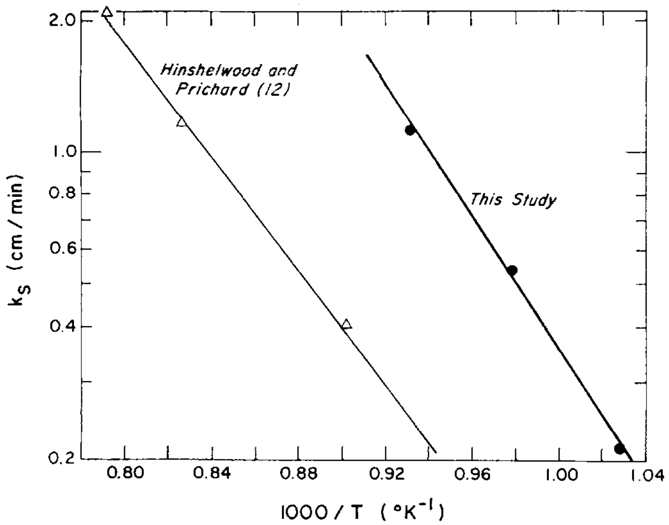

FIG. 8. Arrhenius plot comparing heterogeneous rate constants.

convenience of explaining the observed first order behavior with the Langmuir adsorption isotherm, but also by the results of studies using platinum for a catalyst rather than gold (*23–27*). The catalytic activity of platinum is poisoned by adsorbed oxygen, thereby preventing nitrous oxide from reaching the active sites. This behavior substantiates an adsorption mechanism for the decomposition of nitrous oxide on platinum.

The constants obtained from this study are compared with those of Hinshelwood and Prichard (*12*) in Fig. 8, showing good agreement of the activation energies but poor agreement of the magnitudes of k_S. The most probable explanation for the difference is that the two gold surfaces were different. However, it is possible that failure to account for the effect of radiant heat transfer on temperature measurement could account for the difference. Without a more complete description of the means of temperature measurement by previous investigators, no definite statement as to the cause of the differences shown in Fig. 8 can be made.

Random Errors and Reproducibility

Estimated maximum errors in the measured variables were used in a standard method for computing the maximum possible resultant error in the calculated parameters (*28*). The results of these computations are summarized in Table 2. With the exception of the errors in k_3 and E_3, the errors are similar in magnitude to those obtained in other high-temperature kinetics investigations. The large maximum errors in k_3 and E_3 are due to the indirect method of determining the extent of the secondary reaction, i.e., examining the ratio of moles N_2 to moles O_2, rather than analyzing for NO_2 directly. The variable which had the largest effect on the other observed rates and rate constants was temperature. The estimated maximum error in the temperature was ±2.5°C.

It should be noted that the values given in Table 2 represent maximum errors, not the actual confidence level of the experimental data. That the experimental error is actually quite a bit smaller than these maximum values was illustrated by repeating some sets of data, both to check on

TABLE 2
MAXIMUM ERRORS IN CALCULATED PARAMETERS

Parameter	Total error (%)	Error in E (%)
$-r_{H1}$	12.47	13.2
k_1	15.31	12.79
k_2	8.14	16.92
k_3	48.8	61.7
k_S	13.18	20.9

the reproducibility of the data and to extend it into a region of larger nitrous oxide concentration. Examination of the repeated runs, some of which are shown in Fig. 3 for $S/V = 0.4074$ and $S/V = 0.7098$, reveals that the repeated runs fall within 5–8% of the first run at the same conditions, and all the points are within 5% of the line of "best fit."

CONCLUSIONS

This work demonstrates that the rate of a chemical reaction occurring by simultaneous homogeneous and heterogeneous paths can be resolved into the two contributing reaction rates prior to fitting any rate equation to the data. Indeed, the experimental technique of observing the variation in total reaction rate with the amount of catalyst surface could be applied even in a case where the reaction was catalyzed by the material of which the reaction vessel was constructed. In this case, the homogeneous reaction rate can be determined by extrapolation of the data to a surface-to-volume ratio of zero.

For the decomposition of nitrous oxide, the technique yielded rate expressions, rate constants, and activation energies which compare well with those from previous studies of the individual reactions. Most important, for the primary reaction the accuracy was comparable to that obtained by other experimental methods for high-temperature reaction kinetics.

ACKNOWLEDGMENT

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NOMENCLATURE

Symbol	*Significance*
C (subscripted)	Concentration, mg moles/liter
E	Activation energy, cal/g mole
f	Moles NO formed per mole N_2O decomposed
k (subscripted)	Rate constant in homogeneous mechanism
k_f	Pseudo first-order homogeneous rate constant, time^{-1}
k_s	Observed heterogeneous rate constant
n	Feed rate of nitrous oxide, mgmoles/min
$-r$ (subscripted)	Rate of decomposition of indicated species, moles/time-volume
R	Universal gas constant, 1.987 cal/gmole-°K
$-r_1$	Rate of decomposition of nitrous oxide via $N_2O \rightarrow N_2 + \frac{1}{2}O_2$, primary reaction, moles/time-volume
$-r_2$	Rate of decomposition of nitrous oxide via $N_2O \rightarrow NO + \frac{1}{2}N_2$, secondary reaction, moles/time-volume
$-r''$	Rate of decomposition of nitrous oxide, moles/time-surface area
$-r'''$	Rate of decomposition of nitrous oxide, moles/time-weight of catalyst
r_H	Homogeneous reaction rate, moles/time-volume
r_{H1}, r_{H2}	Values of r_H for primary and secondary reactions respectively, moles/time-volume
r_T	Total reaction rate, moles/time-volume
S	Amount of catalyst, usually expressed as surface area
T	Temperature (°K unless indicated otherwise)
V	Void volume in reactor
W	Amount of catalyst, weight
X	Fractional decomposition of N_2O
ρ_s	The concentration dependent term in the heterogeneous reaction rate
$\phi(S/V)$	Functional dependence of reaction rate, r'', on surface-to-volume ratio

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