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The Decomposition of N_2O on Oxide Catalysts

III. The Effect of O_2

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The effect of added O_2 upon the catalysis of the N_2O decomposition at 50–200 Torr pressure has been studied for 31 metallic oxides; 15 oxides are unaffected by O_2. The overall kinetics of the probable series of linked reactions are discussed in detail and the difficulty of deciding unequivocally upon the correct kinetics is demonstrated by reference to calculations upon synthetic data obeying accurately first-order kinetics. The results are discussed with reference to earlier generalizations based upon statistical examination of the decomposition of initially pure N_2O on the same catalysts. It is concluded that the relationships found earlier between the parameters of the N_2O decomposition and those of the isotopic exchange between O_2 gas and surface are still valid. In the case of those oxides insensitive to O_2 the catalytic decomposition is restricted to special small areas of the surface where the adjacent anion vacancies containing trapped electrons (R_2-centers) formed by the desorption of O_2 from the decomposing N_2O are rapidly converted to F-centers by surface migration and are not accessible to gaseous O_2.

INTRODUCTION

Earlier papers in this series (*1*) presented a number of general relationships between the kinetic parameters of the decomposition of N_2O, catalyzed by 40 stable metallic oxides, and the parameters of the exchange of isotopic oxygen between those oxides and O_2 gas. It was proposed that in all cases an important step in the decomposition reaction was the desorption of O_2. One consequence of this mechanism is that it would be expected that all the oxides would be poisoned by O_2. This matter is examined in the present paper as only a few oxides were so tested in the earlier work.

EXPERIMENTAL METHODS

a. Materials

N_2 gas was taken from a cylinder of high-purity "white-spot" material and purified further by vacuum distillation. N_2O and O_2 gas and ^{18}O-enriched O_2 and the oxide samples were those used in earlier work (*1, 2*): 9 of the original, aged, samples were unavailable.

b. Kinetic Measurements

The kinetic measurements were carried out as before (*1*).

For each oxide the procedure was to select a reaction temperature around the middle of the range used in the earlier work, to establish stable conditions by performing several duplicate runs at ca. 200 Torr initial P_{N_2O} and then to perform similar runs with the addition of 100 and 200 Torr O_2 (a) before adding the N_2O, (b) simultaneously with the N_2O and (c) in a few cases after ca. 25% of the N_2O had decomposed. When poisoning by O_2 was apparently established the experiment was repeated using N_2 instead of O_2 to ensure that diffusion or pumping artifacts were absent. In no case did N_2 affect the reaction. The experiments involving the addition of O_2 or N_2 were followed by runs using pure N_2O to confirm that the activity of the catalyst was constant under standard conditions. On most oxides the effect of varying the initial pressure of N_2O was studied at one temperature by performing experiments using pure N_2O at pressures between ca. 50 and 300 Torr.

A few experiments involving the simultaneous measurement of the rate of N_2O decomposition and the rate of ^{18}O exchange between O_2 and the surface were performed at ca. 100 Torr total pressure (50 Torr N_2O) using Ar as an internal standard. A static system of ca. 150 ml capacity, fitted with a capillary leak to the mass spectrometer, was employed as in an earlier work upon O_2 exchange (*3*).

KINETICS

The scheme below includes all the reactions which are likely to be involved in the work under consideration:

$$\underset{n}{N_2O_{(gas)} + e_s^-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{n_1}{N_2O_s^-}, \tag{1}$$

$$\underset{n_1}{N_2O_s^-} \xrightarrow{k_3} N_{2(gas)} + \underset{n_2}{O_s^-}, \tag{2}$$

$$\underset{n_2}{O_s^-} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \tfrac{1}{2}O_{2(gas)} + \underset{n}{e_s^-}, \tag{3}$$

$$\underset{n_2}{O_s^-} + N_2O_{(gas)} \xrightarrow{k_6} N_{2(gas)} + O_{2(gas)} + \underset{n}{e_s^-} \tag{4}$$

With

$$N = n + n_1 + n_2, \tag{5}$$

where N is constant at a given temperature.

The following comments may be made upon these reactions:

Equation (1) may be plausibly inferred from a consideration of mass spectrometric and semiconductivity studies (*3*, *4*) and from direct measurement of adsorption of N_2O (*1*).

Equation (2) has been shown to occur at low pressures (<ca. 1.0 Torr) (*1*, *5*).

Equation (3) is known to be involved in the equilibrium existing between gaseous oxygen and metallic oxide surfaces at reaction temperatures. It is an important step in the isotopic exchange reaction in that system (*2*) and the prime object of the present paper is to discuss whether it is in all cases important in the overall kinetics of the N_2O decomposition.

Equation (4) has only been positively identified upon NiO between 0.05 and 1.0 Torr (*5*) below about 140°C.

The present paper is concerned with reactions at initial P_{N_2O} of at least 50 Torr, and usually in the region of 200 Torr: at these pressures the presence or absence of significant reaction by the individual Eqs. (1), (2), and (4) cannot be directly and separately demonstrated and we must consider the consequences of a generalized kinetic analysis. We are also concerned with the steady state reaction at these higher pressures where such factors as the initial poisoning of reactions (2) and (4), investigated in some detail on NiO at low pressures (5) will not be significant.

In the most general case, when all the above are important in determining the kinetics, we may write at the steady state conditions which determine the equilibrium concentrations of the surface species n, n_1 and n_2. Thus for n:

$$k_1Pn + k_5P_{O_2}{}^{1/2}n = k_6Pn_2 + k_4n_2 + k_2n_1, \tag{6}$$

with similar expressions for n_1 and n_2. We have also, for the observed rate of reaction namely the rate of disappearance of N_2O from the gas phase:

$$-\frac{dP}{dt} = k_1Pn + k_6Pn_2 - k_2n_1, \tag{7}$$

where P = pressure of N_2O at time t.

This set of equations, with Eq. (5), yield finally the rate expression:

$$-\frac{dP}{dt} = NP\left[\frac{k_1k_3(k_6P + k_4) + k_6(k_2 + k_3)(k_1P + k_5P_{O_2}{}^{1/2}) - k_1k_2k_6P}{(k_2 + k_3)\{(k_1 + k_6)P + k_4 + k_5P_{O_2}{}^{1/2}\} + k_1P(k_4 - k_2 + k_6P)}\right]. \tag{8}$$

In view of the great difficulty in obtaining reproducible kinetic results of high accuracy in the systems under discussion this equation is of no practical utility, but it reduces to a more simple form in a number of special cases which are of interest. Thus if we neglect k_6 we have:

$$-\frac{dP}{dt} = NP\left[\frac{k_1k_3k_4}{k_4(k_2+k_3)+k_1P(k_3+k_4)+k_5P_{O_2}{}^{1/2}(k_2+k_3)}\right], \tag{9}$$

which is of the form:

$$-\frac{dP}{dt} = \frac{AP}{C+BP+DP_{O_2}{}^{1/2}} \tag{10}$$

where A, B, C and D are constants.

Similarly if we neglect k_5 and k_6:

$$-\frac{dP}{dt} = \frac{NPk_1k_3k_4}{k_4(k_2+k_3)+k_1P(k_3+k_4)}, \tag{11}$$

while if we neglect k_4 and k_5:

$$-\frac{dP}{dt} = \frac{2NPk_1k_3k_6}{(k_2+k_3)(k_6+k_1)+k_1(k_6P-k_2)}. \tag{12}$$

Both the last two equations are of the form

$$-\frac{dP}{dt} = \frac{AP}{C+BP}. \tag{13}$$

which reduces to a simple first-order equation if $C \gg BP$.

Writing the general relationship Equation (10) in the form

$$-\frac{dP}{dt} = \frac{kP}{a+bP+cP_{O_2}{}^{1/2}} \tag{14}$$

and integrating under the conditions that no O_2 is added, i.e., that all the O_2 in the system is formed from decomposed N_2O, we have

$$-\frac{kt}{2.3} = a\log_{10}(f) - \frac{bP_i}{2.3}(1-f) + \frac{cP_i{}^{1/2}}{2^{1/2}}(X), \tag{15}$$

where

$$X = \frac{2(1-f)^{1/2}}{2.3} + \log_{10}\left\{\frac{1-(1-f)^{1/2}}{1+(1-f)^{1/2}}\right\}, \tag{16}$$

$$f = P/P_i \tag{17}$$

and P_i, P, are the pressures of N_2O in the system initially and at time t from the commencement of the reaction. Various special cases, corresponding to Eqs. (11), (12) and (13) above, can be obtained by putting a, b or c (or any two of these) equal to zero in Eqs. (14) and (15). We have used the assumption that $a + bP \ll cP_{O_2}{}^{1/2}$ in our work on this reaction (*1*). Samaha and Teichner (*7*) have found $b = 0$ to hold on NiO under certain circumstances, although an equally accurate representation of their individual runs could be obtained from an equation of the form

$$-\frac{dP}{dt} = \frac{k'P}{a'+b'P_{O_2}}.$$

We have reported similar observations (*1*) upon CuO, MnO_2, Rh_2O_3 and IrO_2. This difficulty of deciding upon the correct reaction mechanism by choosing between the plots of experimental data in the form of various integrated rate expressions, particularly when these contain several disposable parameters, is well known. In the present series of papers the experimental procedure is such that irregularities in the data occurring in the first minute or so would be ignored (because, for example, of possible variation in reaction rates on admission of N_2O to a freshly outgassed catalyst). Further, since the reaction products accumulate in the system the reaction rate (in spite of a rate of gas circulation which, at the beginning of the reaction is several times greater than that at which a dependence of reaction rate upon circulation speed becomes detectable) will inevitably show an apparent decrease towards the end of each experiment, as the partial pressure of N_2O becomes low. For this reason we [as well as other workers (*8*)] have not normally been concerned with data beyond about 50% conversion.

With these practical considerations in mind we consider further the consequences of attempting to fit experimental data to Eqs. (14) and (15) or to any more simple rate expression derived from them by putting a, b or $c = 0$.

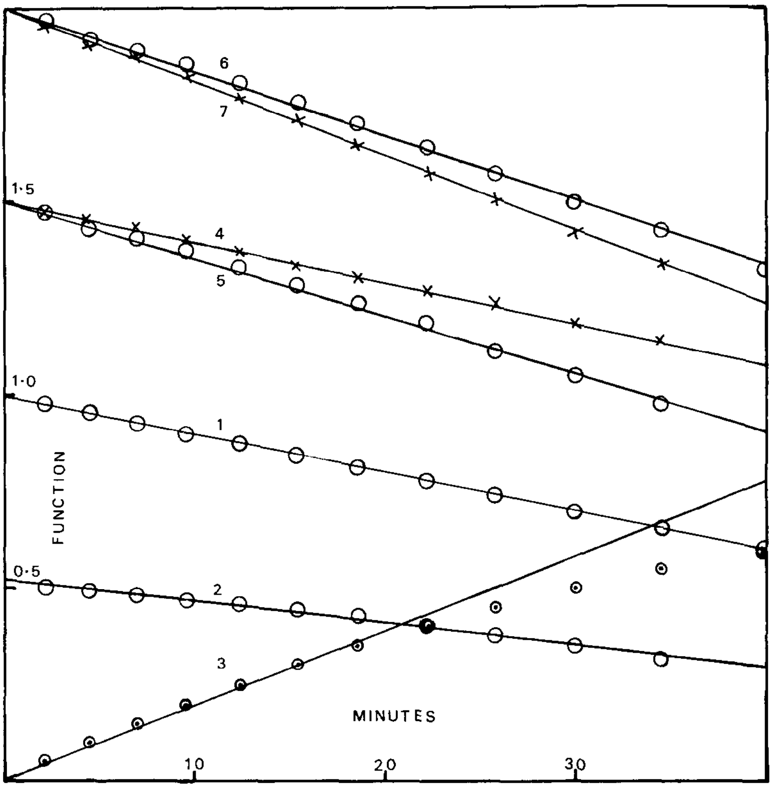

FIG. 1. The functions in Eq. (15) applied to data accurately obeying first-order kinetics. (1) $\mathrm{Log}_{10}(f)$; (2) $0.5 + X$; (3) $1 - f$; (4) $1.5 + \log_{10}(f) + 0.1\,X$; (5) $1.5 + \log_{10}(f) + 1.0\,X$; (6) $2.0 + \log_{10}(f) + 1.0\,X - 0.1\,(1 - f)$; (7) $2.0 + \log_{10}(f) + 1.0\,X - 0.25\,(1 - f)$.

We plotted the first 60% of an imaginary experiment wherein the data obeyed strictly a first-order expression with $t_{1/2}$ = 30 min. This is the plot of $\log_{10}(f)$ vs time, line (1) in Fig. 1, and corresponds to $b = c = 0$ in Eqs. (14) and (15). From this plot we calculated X [Eq. (16)] for each value of t; line (2) shows the plot of X against time. It is seen that, except for the points at $t = 0$ and 2 min, X is reasonably linear with respect to time over at least 50% of the reaction (i.e., at least to 35 min). Line (3) shows $(1 - f)$ plotted against time: this, as expected, is not linear but nevertheless the deviation from linearity up to ca. 30 min is such that up to at least $bP_i/2.3 \approx 0.25a$ or $\approx 0.25c\ P_i^{1/2}/2^{1/2}$ the resulting plot of Eq. (15) would be experimentally as linear as that of log (f) vs time. Clearly these facts mean that data which accurately fit a first-order expression will, over a wide range of ratios of $a{:}b{:}c$, also fit Eq. (15) within experimental error over at least the first 50% or so of the reaction. This is confirmed by lines (4) (5) (6) and (7) of Fig. 1. (Certain of these plots have been shifted along the vertical axis for clarity, as indicated in the caption to Fig. 1. Similarly in all cases the values of the functions at $t = 0$ have not been plotted: however, all lines except (2) pass through the correct value at zero time.) The converse also applies, that is (for example) data which accurately obey Eq. (15) will, over a wide range of ratios $a{:}b{:}c$, also apparently fit a simple first-order plot. Figure 2 shows typical results for two oxides poisoned by O_2.

It has been reported by other workers (*5, 8*) that data upon the present reaction at a constant temperature yield a pseudo-first-order rate constant, k_a, from a plot of log (P) vs time and that over a limited range of initial N_2O pressures:

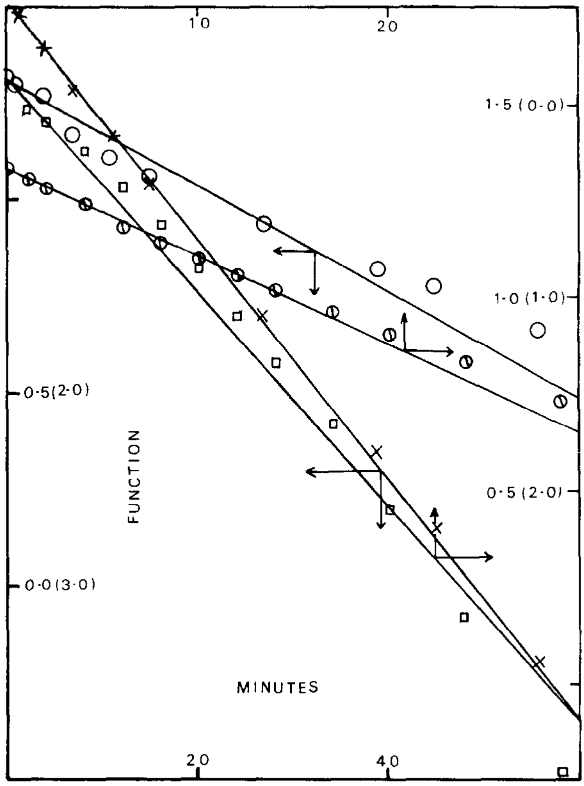

FIG. 2. Data for two oxides poisoned by O_2. (⦸, □) $\log_{10}(f)$ and X for Er_2O_3 at 615°C: $P_i = 215$ Torr; (○, ×) $\log_{10}(f)$ and X for MgO at 500°C: $P_i = 208$ Torr. ($\log_{10}(f)$ in arbitrary units; scale for X in parentheses).

$$\log k_a = k_1 - k_2 \log (P). \tag{18}$$

Following from Fig. 1 and the above paragraphs we could reasonably assume that in the work reported as obeying Eq. (18) the data would be equally well represented by the expression:

$$-\frac{dP}{dt} = \frac{k_t P}{1 + f(P)}, \tag{19}$$

where k_t is the true rate constant and $f(P)$ is some function of P.

This is to be compared with the approximate constant, k_a given by:

$$-\frac{dP}{dt} = k_a P. \tag{20}$$

We have

$$-\frac{1}{P} \cdot \frac{dP}{dt} = k_a$$

and

$$-\frac{1 + f(P)}{P} \cdot \frac{dP}{dt} = k_t \tag{21}$$

so that

$$k_a[1 + f(P)] = k_t$$

or

$$k_a = \frac{k_t}{1 + f(P)} - k_t[1 - f(P)] \tag{22}$$

if $f(P)$ is $\ll 1$.

A relationship of the type of Eq. (22) could well approximate over a limited range of P to Eq. (18), where k_1 and k_2 are temperature-dependent constants.

In confirmation of this view we consider some of our own results. Figure 3 shows for an oxide, ThO_2, poisoned by O_2, a plot of k_a, and of $\log_{10} k_a$ defined as above, against P_i and $\log_{10} P_i$ over the range 50–300 Torr: clearly either Eq. (18) or (22) with $f(P)$ = constant XP will fit the observations.

This would appear to demonstrate a deactivation of the surface in the way discussed by Read (*8*). However, if the same kinetic data are plotted according

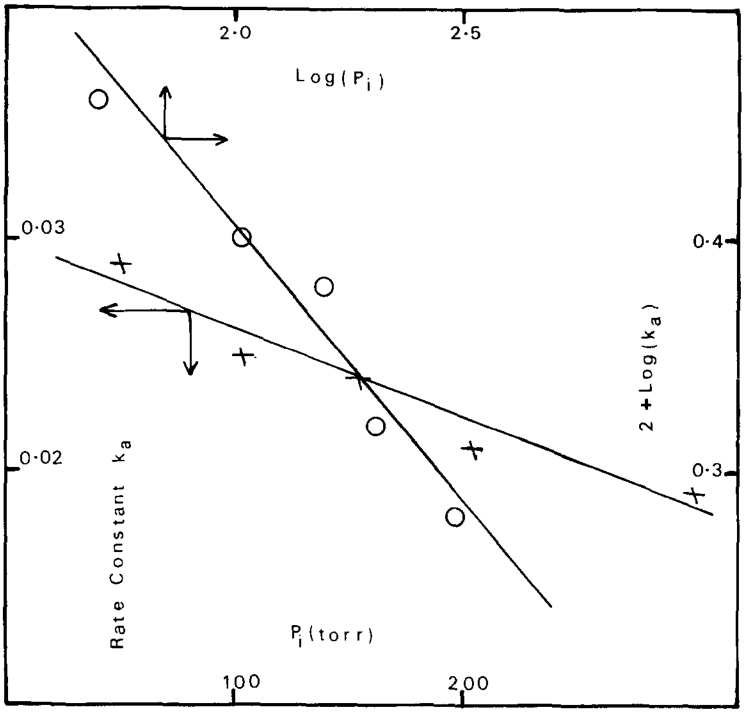

FIG. 3. Data for ThO_2 at 565°C according to Eqs. (18) and (22).

to Eq. (15), with $a = b = 0$, the rate constants are all equal to 0.088 ± 0.002. [Both the log (P) vs time plots and those according to Eq. (15) are of good linearity.] Figure 4 shows a similar plot for Fe_2O_3, an oxide also poisoned by O_2; here the rate constants from Eq. (15) with $a = b = 0$ are all equal to 0.018 ±0.0015.

These observations are typical of those obtained by us upon all the oxides poisoned by O_2 (see Table 1), and provide some confirmation of the validity of our earlier interpretation of the kinetics and of the use of Eq. (15) with $a = b = 0$. They show no evidence of deactivation in the manner proposed by Read. We do not

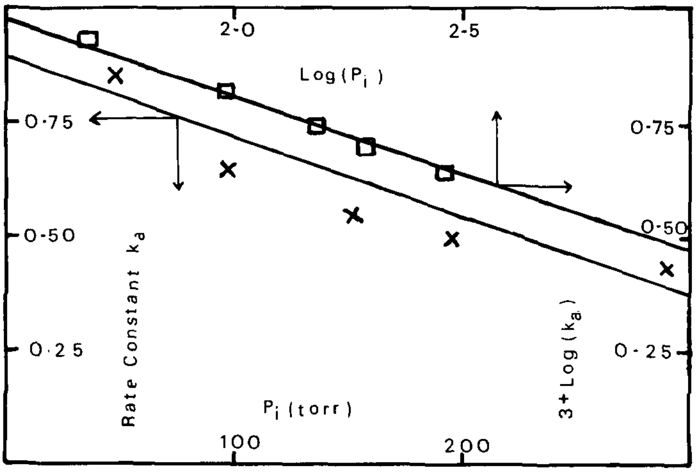

FIG. 4. Data for Fe_2O_3 at 425°C according to Eqs. (18) and (22).

TABLE 1
EFFECT OF ADDED OXYGEN UPON N_2O DECOMPOSITION

No effect	Retardation
CaO	MgO
SrO	NiO
(NiO)[a]	MnO_2
ZnO	SnO_2
TiO_2	ThO_2
HfO_2	IrO_2
CeO_2	Fe_2O_3
Al_2O_3	Cr_2O_3
Y_2O_3	Rh_2O_3
La_2O_3	Ga_2O_3
Nd_2O_3	In_2O_3
Sm_2O_3	Sc_2O_3
Gd_2O_3	Eu_2O_3
Dy_2O_3	Er_2O_3
Yb_2O_3	Tm_2O_3
	L_2uO_3
	Ho_2O_3

[a] Freshly prepared samples: see text.

think that our present remarks should be extended to the reaction at very much lower pressures, studied by Gay and Tompkins (*5*). Here it is well established, both by those workers and by other studies (*1, 11*), that there is indeed some saturation of isolated surface anion vacancies on admission of N_2O to the freshly outgassed catalyst. This causes the $N_2:O_2$ ratio in the product to be much greater than the theoretical value of 2 during the initial stages, and the accompanying loss of catalytic activity has been adequately accounted for in the case of NiO (*5*). This type of deactivation is, however, not detectable experimentally at the much higher pressures used in the present study on oxides poisoned by O_2.

In the case of oxides not poisoned by O_2 we assume, for reasons discussed later, that the correct kinetic expression is Eq. (11), i.e., that $c = 0$ in Eqs. (14) and (15). We then find, in agreement with the argument presented above, that a plot of log (P) vs time gives rate constants, k_a, which decrease with increasing P_i. A plot of k_a vs P_i is in all cases approximately linear, from which a/b [Eq. (14)] may be evaluated. Use of this ratio in Eq. (15) then gives true rate constants which are independent of P_i within the limits of experimental error. The plots of log (f) and of log $(f) - (bP_i/a)(1 - f)$ are of similar linearity in all cases up to at least 50% conversion. Thus in the case of oxides not poisoned by O_2 there is also no evidence of deactivation by N_2O at the pressures employed here.

RESULTS

The oxygen-poisoning experiments are summarized in Table 1.

DISCUSSION

Our earlier work (*1*) has established a close correlation, on a statistical basis, between the kinetic parameters of the N_2O decomposition and those of the isotopic exchange of oxygen between the oxide surface and gaseous oxygen. Similar relationships have been found by us between the exchange reaction and the decomposition of NO on the same series of oxide catalysts (*9*). In the latter case the decomposition is retarded by O_2 gas in the manner to be expected from a simple kinetic analysis (*10*). There is therefore no reason to doubt the reality and significance of the relationships found in the case of N_2O. It was, however, unexpected that cases of nonpoisoning by added O_2 gas should be encountered.

There is no need to consider altering the earlier proposals for the mechanism on oxides which are affected by added O_2. In discussing a modified mechanism for the oxides not poisoned by O_2 we shall assume that the denominators in the various rate expressions are relatively unaffected by temperature and look to the numerators to provide a reason for the overall correlation of the activities of all the oxides with the parameters of the oxygen exchange reaction. This assumption is probably reasonable in view of the algebraic form of the denominators and bearing in mind that, for oxides poisoned by O_2, the assumption is justified by the correlation which has been found.

It could be argued, in the case of oxides not poisoned by O_2, that reaction (3) above plays no part in the kinetic scheme, thus leading to Eq. (12). This would fit all the accessible kinetic facts but would destroy the basis for the statistical relationships unless it so happened that k_6 possessed kinetic parameters closely similar to those of k_4 on all these oxides. Since reaction (3) is undoubtedly occurring on all oxides at the temperatures used in the N_2O decomposition studies this argument would also imply that the N_2O decomposition was occurring on sites not accessible to molecular gaseous O_2 [for reaction (3)]. In terms of surface defects we can probably write Eqs. (3) and (4) in the following way:

$$2(\mathrm{O}^-|\square_s^-) \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \mathrm{O}_{2(\mathrm{gas})} + (\mathrm{e}^-|\square_s^-)(\mathrm{e}^-|\square_s^-) \tag{23}$$

and

$$(\mathrm{O}^-|\square_s^-) + \mathrm{N_2O}_{(\mathrm{gas})} \rightarrow \mathrm{O}_{2(\mathrm{gas})} + \mathrm{N}_{2(\mathrm{gas})} + (\mathrm{e}^-|\square_s^-), \tag{24}$$

where the right side product in the first case is an R_2-center (adjacent anion vacancies containing trapped electrons) and in the second case an F-center. The last equation is probably the result of two reactions:

$$(\mathrm{O}^-|\square_s^-) + \mathrm{N_2O}_{(\mathrm{gas})} \rightarrow \mathrm{N}_{2(\mathrm{gas})} + (\mathrm{O_2}^-|\square_s^-), \tag{25}$$

$$(\mathrm{O_2}^-|\square_s^-) \rightarrow \mathrm{O}_{2(\mathrm{gas})} + (\mathrm{e_s}^-|\square_s^-). \tag{26}$$

It appears unlikely that either of these would give rate constants closely similar to k_4.

We therefore reject this argument and consider that in the case of oxides not poisoned by O_2 gas the correct mechanism is given by Eq. (11), because k_5 and k_6 are unimportant. This implies that the N_2O reaction scheme on these oxides involves R_2-centers not readily accessible to O_2 gas via k_5 (because for example of particular spatial arrangements) but that even so the value of k_4 on these special sites is closely similar to that prevailing on the bulk of the surface. In this case the R_2-centers formed by k_4 must be very rapidly destroyed by surface migration so that k_5 cannot occur:

$$(\mathrm{e}^-|\square_s^-)_1(\mathrm{e}^-|\square_s^-)_2 + (\mathrm{O}^{2-}|\square_s^-)_3 \rightarrow (\mathrm{e}^-|\square_s^-)_1 + (\mathrm{O}^{2-}|\square_s^-)_2 + (\mathrm{e}^-|\square_s^-)_3 \tag{27}$$

or

$$(\mathrm{e}^-|\square_s^-)_1(\mathrm{e}^-|\square_s^-)_2 + (-|\square_s^-)_3 \rightarrow (\mathrm{e}^-|\square_s^-)_1 + (-|\square_s^-)_2 + (\mathrm{e}^-|\square_s^-)_3, \tag{28}$$

where $(-|\square_s^-)$ is a vacant surface anion site and the subscripts identify the different sites, such that sites 1 and 2 are nearest-neighbors and 1 and 3 are not. We have already remarked (*1*) that regeneration of F-centers from R_2-centers by some such means is an essential part of our reaction scheme on all oxides. We think it is reasonable to speculate that in the case of oxides unaffected by O_2 the three sites involved in reactions (27) or (28) are always the same three, for example located at a particular crack in, or edge of, a crystal plane, where the local conditions are such as to promote very ready and rapid switching between just those three sites. However, from these triad sets (or rather from sites 1 and 2) the rate (and activation energy) of k_4 cannot be materially different from the value on the bulk of the surface, or at least, over the set of oxides not poisoned by O_2, it bears a sufficiently close and regular relationship to the average surface value so that the statistical regularities discussed in Parts I and II (*1*) are preserved. It was confirmed, by adding some heavily ^{18}O-enriched O_2 gas to N_2O which was decomposing over oxides not poisoned by O_2 and monitoring the O_2 peaks in a mass spectrometer, that the O_2-exchange reaction rate (with the whole of the oxide surface within experimental error) was not affected by the simultaneous occurrence of the N_2O decomposition. Thus reaction k_5 is unaffected on the main part of the oxide surface. This experiment was performed on Al_2O_3, CaO, TiO_2 and Gd_2O_3 and indicates that on these oxides and presumably therefore on all oxides not poisoned by O_2, the N_2O reaction is confined to special areas of the surface, very small in extent, not readily accessible to gaseous O_2. This is a modification of the view expressed earlier (*1*) that on all oxides there were no specific active sites for the

N_2O decomposition. It is highly likely that whether or not a particular oxide catalyst sample is subject to poisoning by O_2 is very much a matter affected by pretreatment. Thus we have found (unpublished work, see Table 1) that freshly prepared NiO formed by ignition of either the nitrate or the carbonate *in vacuo* is not poisoned by O_2; both samples were rendered sensitive to O_2 by keeping them in contact with ca. 200 Torr O_2 gas at 600°C for 200 hr. Samaha and Teichner (*7*), on the other hand, report that NiO of high surface area prepared from the hydroxide *in vacuo* (and containing some residual H_2) loses its sensitivity towards O_2 on repeated use. Similarly Read (*8*) has recently made a detailed study of the reaction on Nd_2O_3, Er_2O_3 and Dy_2O_3, obtaining results which differ from our own in some respects, and considers the difference as being possibly due to pretreatment. Our own oxides, having been repeatedly used over a period of years for a succession of catalytic investigations (*1–3, 9, 10*), could well have a different surface topography from that possessed by relatively fresh preparations.

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REFERENCES

1. WINTER, E. R. S., *J. Catal.* **15,** 144 (1969); **19,** 32 (1970).
2. WINTER, E. R. S., *J. Chem. Soc. (London)* **1968,** 2899; **1969,** 1832.
3. WINTER, E. R. S., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 10, p. 196. Academic Press, New York, 1958.
4. WAGNER, C., AND HAUFFE, K., *Z. Elektrochem.* **44,** 172 (1938).
5. GAY, I. D., AND TOMPKINS, F. C., *Proc. Roy. Soc., Ser. A* **293,** 19 (1966).
6. RHEAUME, L., AND PARRAVANO, G., *J. Phys. Chem.* **63,** 264 (1959).
7. SAMAHA, E., AND TEICHNER, S-J., *Bull. Soc. Chim. Fr.* **1966,** 667.
8. READ, J. F., *J. Catal.* **28,** 428 (1973).
9. WINTER, E. R. S., *J. Catal.* **22,** 158 (1971).
10. WINTER, E. R. S., *J. Catal.* **34,** 440 (1974).
11. CIMINO, A., BOSCO, R., INDOVINA, V., AND SCHIAVELLO, M., *J. Catal.* **5,** 271 (1966) and later papers.