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The Decomposition of Nitrous Oxide on the Rare-Earth Sesquioxides and Related Oxides

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The decomposition of N_2O, catalyzed by 15 M_2O_3 oxides, including 11 of the rare-earth–*C* crystal structure, is represented with reasonable accuracy at 10–20 cm by the equation $-[d(N_2O)/dt] = K[(N_2O)/(O_2)^{1/2}]$, where the parentheses represent gas pressures.

The desorption of molecular oxygen is an important rate-determining step: this is also the rate-determining step in the isotopic exchange between O_2 gas and the oxide surface, by a dissociative process on the surface, which has recently been measured for this series of oxides. A strong correlation exists between both A_0 and E in the Arrhenius expression for the exchange reaction and the corresponding functions for N_2O decomposition. Since these functions vary in a regular manner with lattice parameter (for instance the molecular volume or the nearest M–O or nearest O–O distances) for the exchange reaction so too do A_0 and E for the decomposition of N_2O. No correlation is found for such properties as the magnetic moment of the M^{3+} ion which do not vary regularly with the lattice parameter.

INTRODUCTION

This paper presents a correlation between the catalytic activity of the stable rare-earth sesquioxides in the N_2O-decomposition and the isotopic exchange reaction between O_2 gas and the oxide surface; the relationship is shown to extend to the sesquioxides of Sc, Y, and In which crystallize in the rare-earth *C*-structure, and La_2O_3.

The observation (*1*) that metallic oxide catalysts of the N_2O decomposition fall into reactivity groups which roughly coincide with the semiconductor type has been widely quoted and a number of attempts have been made to correlate catalytic activity both in this and other reactions with electronic structure. In general for the N_2O decomposition reaction *p*-type oxides are thought to be the best catalysts and *n*-type the worst, but no satisfactory reason why insulator-type oxides occupy roughly an intermediate position has been put forward.

We have shown recently (*2*) that the exchange of ^{18}O between enriched O_2 and the surface of a large number of stable metallic oxides, proceeding by the atomic mechanism:

$$2e^- + 2\square_s^- + {}^{18}O_2\ (\text{gas}) \rightleftharpoons 2({}^{18}O^-|\square_s^-), \tag{1}$$

$$({}^{18}O^-|\square_s^-) + ({}^{16}O^{2-}|\square_s^-) \rightleftharpoons ({}^{18}O^{2-}|\square_s^-) + ({}^{16}O^-|\square_s^-), \tag{2}$$

$$2({}^{16}O^-|\square_s^-) \rightleftharpoons {}^{16}O_2\ (\text{gas}) + 2\square_s^- + 2e^-, \tag{3}$$

is controlled by the desorption step, which is rate-controlling. We have also shown that the activation energy of the exchange reaction, in oxides of the same crystal structure, falls in a linear manner with increasing size of the unit cell. Thus for the MO rock-salt oxides E (kcal mole^{-1}) falls fairly regularly from 45 (NiO) and 38 (MgO) both with M–O distance ca. 2.1 Å to 15 for SrO with M–O distance ca. 2.57 Å: similar relationships hold for the MO_2 (fluorite and tetragonal types) and M_2O_3 (corundum) series. In the case of the rare earths and associated oxides (*3*) considered in the present paper, E falls from 43 (Sc_2O_3) to 12 (Gd_2O_3) and 11 (La_2O_3) in approximately a linear manner with increasing lattice parameters. Since the desorption of the O_2 molecule is rate-determining a critical parameter in the activated state must be the O–O distance: this should be determined by, or at least strongly influenced by, the nearest O–O distance in the oxide surface. In accordance with this it was found that a plot of *E v* the nearest O–O distance grouped the oxides into two sets, the first comprising the rock-salt oxides and the two wurtzite oxides BeO and ZnO, and the other MO_2 and M_2O_3 oxides. Since there was a strong compensation-effect log $[A_0]$ could be substituted for E in all these plots (A_0 is the preexponential term in the rate expression) with no great loss of correlation.

Most of the systematic work on the catalytic properties of the rate earths has been Russian: in general no relationship has so far been found between reactivity and any physical, electrical, or chemical property in this series. Thus Minachev and Antoshin (*4*) found no regular relationship between either rate of reaction or the activation energy for isotopic exchange between O_2 and the surface and such properties, although there was some indication that oxides of the cerium subgroup were characterized by a lower value of E than those of the yttrium subgroup: the maximum activity in the oxidation of H_2 by O_2 was associated with the greatest speed of exchange. Bakumenko (*6*), however, found little difference in the reactivity of the oxides when studying the oxidation of hydrogen by oxygen, except that praseodymium and neodymium oxides were distinctly more active than the remainder. Minachev and Khodakov (*7*) noted an anti-batic relationship between the magnetic moment of the M^{3+} ion and activation energy for the conversion of *n*-butane and the dehydrogenation of cyclohexane: similar results were also reported for the dehydrogenation of isopropyl alcohol. However it should be noted that no attempt was made in any of these papers to identify properly the rate-determining steps in the kinetics so that the significance of these observations is uncertain. There appears to have been no systematic examination of the N_2O decomposition upon these oxides so far.

The decomposition of N_2O at a few cm pressure upon oxide surfaces saturated with O_2 has usually been found to be strongly influenced by the rate of desorption of O_2, i.e., O_2 acts as a poison. It seemed therefore desirable to see if the regularities found for the exchange reaction were repeated with the decomposition reaction: the present paper deals mainly with the rare-earth oxides.

METHOD

(a) **Materials.** The oxides were the samples used in the earlier (*3*) work upon ^{18}O-exchange. The N_2O was obtained from a cylinder of medical grade material: it was condensed in liquid N_2 and pumped for some minutes, passed through a trap at −78°C and recondensed and pumped again. The process was repeated and the middle 70% of the product was collected in a storage bulb. O_2 was obtained by heating $KMnO_4$ and collecting and distilling the product *in vacuo*.

(b) **Kinetic measurements.** (1) High pressure: the oxides were first outgassed 18 hrs at ca. 50°C above the highest temperature to be studied, cooled to the first reaction temperature and left in contact with 5 cm of O_2 for ca. 18 hr. The catalyst was pumped for 3 min and the N_2O added: 10 or 20 cm of N_2O were used. Two reaction systems were employed, a static one of ca. 150 ml and one of ca. 300 ml including a circulating pump (*8*). The catalyst was protected by traps at −78°C. Between 5 and 20 m^2 of oxide surface was normally employed. Identical results were obtained in the two systems on several oxides. The reaction was followed by measuring the pressure change. After the first reaction the catalyst was briefly pumped and left in contact with fresh O_2 overnight at the temperature of the next measurement: the temperatures were selected in random order. Some experiments were performed in which a known amount of O_2 was added initially with the N_2O to check the rate expression [Eq. (10)], but only a few oxides were so examined.

(2) At low pressure (ca. 2 mm) the reaction was studied in a system provided with forced circulation (*8*): the catalyst was protected from contamination by traps cooled to −78°C. Samples were withdrawn into evacuated ampoules as required and analyzed for N_2, O_2, and N_2O: pressure changes were followed with a McLeod gauge. The

catalyst was outgassed for ca. 3 hr at 600°C before each experiment, having been exposed to ca. 5 cm normal O_2 for several hours at 550°C before the series of experiments.

It was found that after admission of N_2O the pressure fell during the first 2–5 min owing to the chemisorption of N_2O then remained constant for 5–15 min and finally began to increase until the completion of the decomposition. Analysis showed that until the pressure began to increase the gas phase consisted solely of N_2O and N_2, the proportion of the latter rising in a roughly linear manner with time after the first 2–5 min. All catalysts behaved similarly and reaction temperatures were chosen in accordance with the differing reactivities to give acceptable sampling times roughly within the above limits: generally this meant that the low pressure experiments were performed between 0–150° below the lower temperatures given in the last column of Table 1 of results.

(c) Adsorption of N_2O. The adsorption of N_2O on three oxides was measured by exposing the freshly-outgassed powders to measured amounts of the gas. The pressure was read by McLeod gauge after ca. 10 sec and again at ca. 1 min intervals. The system was calibrated with argon at each pressure. Measurements were performed between 0.2 mm and ca. 4 mm at temperatures at the lower end of the range used in the kinetic studies so as to minimize the effects of the reaction. The quantity of gas adsorbed was obtained by extrapolation to zero time.

TABLE 1

SUMMARY OF EXPERIMENTAL RESULTS[a]

Element	High pressure		Low pressure		Temp range (°C)
	$\log_{10}(A_1)$	E_1	E_L	$E_L + \frac{1}{2}E_B$	
Sc	5.72	46	21	42.5	500–650
Y	1.60	27.5	19	28	450–550
In	3.32	35	10	28	500–600
La	0.47	20	14	19.5	350–550
Nd	2.06	28	24	30	350–450
Sm	2.65	29.5	23	32.5	390–550
Eu	1.49	27.5	17	25	400–530
Gd	1.18	26.5	22	28	380–550
Tb	5.21	41	26	38	500–600
Dy	4.21	36	27	36	450–600
Ho	5.42	40	25	43.5	430–550
Er	4.26	39.5	21	39	530–630
Tm	1.95	32	18	35	370–550
Yb	1.57	32	21	36	370–550
Lu	4.00	35	16.5	31	400–550

[a] Activation energies, E_1, E_L, and E_B in kcal mole^{-1}; units of A_1: (dynes cm^{-2})$^{1/2}$ sec^{-1}/cm^2 of catalyst surface in a reaction volume of 320 ml.

Kinetics

The following equations have been proposed for this reaction:

$$N_2O_{(g)} \rightleftharpoons N_2O_{(ads)}, \tag{4}$$

$$N_2O_{(ads)} + e^- \text{ (from catalyst)} \rightarrow N_2O^-_{(ads)}, \tag{5}$$

$$N_2O^-_{(ads)} \rightarrow O^-_{(ads)} + N_2, \tag{6}$$

$$O^-_{(ads)} + N_2O_{(g)} \rightarrow O_2 + N_2 + e^- \text{ (to catalyst)}, \tag{7}$$

$$O^-_{(ads)} + O^-_{(ads)} \rightleftharpoons O_2 + 2e^- \text{ (to catalyst)}, \tag{8}$$

It is evident that Eq. (8) is the same as Eq. (3) above—the rate-determining step in the ^{18}O-exchange reaction.

(1) Reactions at 10–20 cm pressure. We find that the reaction can be adequately described on all our catalysts by:

$$\frac{-dP_{N_2O}}{dt} = K\frac{P_{N_2O}}{(P_{O_2})^{1/2}}, \tag{9}$$

where P_{N_2O} is the pressure of N_2O at time t: P_{O_2} being the O_2 pressure at time t. The integrated form of this expression, neglecting the integration constant is

$$Kt = (P_1 + P_2)^{1/2} \times \left\{ ln\left[\frac{(P_1 + P_2)^{1/2} + (P_1 + P)^{1/2}}{(P_1 + P_2)^{1/2} - (P_1 + P)^{1/2}}\right] - 2\frac{(P_1 + P)^{1/2}}{(P_1 + P_2)^{1/2}}\right\}, \tag{10}$$

where $2P_2$ = initial pressure of N_2O; $2P$ = pressure of N_2O decomposed at time t; P_1 = initial pressure of O_2.

K was obtained from a plot of the R.H.S. of Eq. (10) against time: the reaction was followed for, usually, 50–80% of its course and fair to good straight lines were obtained for all oxides.

As we have shown elsewhere (*9*), the above kinetics result from the assumption that the three important reactions are those represented by Eqs. (5), (6), and (8) above, when O_2 is strongly adsorbed compared with N_2O. Thus, writing n_1 for the surface concentration of $N_2O^-_{(ads)}$, n_2 for that of $O^-_{(ads)}$, and n for the number of empty active sites at the steady state, we have

$$N = n_1 + n_2 + n, \tag{11}$$

and we may put

$$K_1 = \frac{n_1}{nP_{N_2O}}, \tag{12}$$

$$K_3 = \frac{n_2^2}{n^2P_{O_2}}, \tag{13}$$

from Eqs. (4) + (5) and Eq. (8), respectively.

The observed rate of reaction

$$\frac{-dP_{N_2O}}{dt} = kn_1, \tag{14}$$

where k is the rate constant of reaction (*6*).

These equations give

$$\frac{-dP_{N_2O}}{dt} = \frac{kK_1NP_{N_2O}}{1 + K_1P_{N_2O} + (K_3P_{O_2})^{1/2}}, \tag{15}$$

which, with O_2 strongly chemisorbed, reduces to

$$\frac{-dP_{N_2O}}{dt} = \frac{kK_1NP_{N_2O}}{(K_3P_{O_2})^{1/2}}, \tag{16}$$

so that from Eqs. (9) and (16)

$$K = \frac{kK_1N}{(K_3)^{1/2}}. \tag{17}$$

Since O_2 is dissociatively adsorbed at these temperatures we have, if $n_2 > n_1$,

$$\frac{n_2^2}{n^2} = K_3P_{O_2} = \frac{\alpha P_{O_2}}{\mu\beta}, \tag{18}$$

where α is the accommodation coefficient for the adsorption of O_2 molecules, $\mu = (2\pi mkT)^{1/2}$ and B is the rate of desorption of O_2 molecules, both per unit area of the surface (*10*). B is thus the rate constant for the ^{18}O-exchange reaction between O_2 and the oxide surface which we have evaluated elsewhere (*2*, *3*).

Thus

$$K = kK_1N\left(\frac{\mu\beta}{\alpha}\right)^{1/2}. \tag{19}$$

(2) Reactions at 2 mm pressure. The measurements at low pressure (which determined the initial rate of appearance of N_2, before the production of significant amounts of O_2) refer to the product (kK_1N) as may be seen from a consideration of reactions (4), (5), and (6). Thus we may write for this reaction

$$k_e = kK_1N. \tag{20}$$

(3) General. Since

$$K = k_e\left(\frac{\mu\beta}{\alpha}\right)^{1/2}. \tag{21}$$

Writing

$$K = A_1 \exp(-E_1/RT), \tag{22}$$

with similar expressions for k_e and B we have:

$$\log A_1 = \log(A_e) + \tfrac{1}{2}\log(A_B), \tag{23}$$

and

$$E_1 = E_e + \tfrac{1}{2}E_B, \tag{24}$$

which assume that $(\mu/\alpha)^{1/2}$ is effectively independent of temperature.

Also from Eq. (21), at any temperature, we have

$$\log(K) = \log(k_e) + \tfrac{1}{2}\log(B) + \tfrac{1}{2}\log\left(\frac{\mu}{\alpha}\right). \tag{25}$$

The above analysis assumes that the low pressure (2 mm) value of k_e (and the associated A_e and E_e) will be unchanged at 10–20 cm. There is evidence (*11*) that on NiO made from $NiCO_3$ and on certain rare-earth oxides this reaction is complex and that its velocity and activation energy depend on the initial pressure of N_2O. However, we found satisfactory agreement upon a series of doped NiO preparations made from the nitrates at around 1 cm of N_2O (*9*).

Thus if the desorption of O_2 is a dominant term in the rate expression, and particularly when it varies widely from oxide to oxide, it might be expected that, provided the product $k_e\ (\mu/\alpha)^{1/2}$ does not vary much from one oxide to another, a plot of log (K) against log (B) [cf. Eq. (25)] should have a slope of $\frac{1}{2}$. Even if there are appreciable errors in the arguments and assumptions above, and also in the experimental observations, provided the approach is substantially correct we would expect a reasonable correlation between log (K) and log (B) over a temperature range in the vicinity of that used for the experimental work. Thus Eqs. (23), (24), and (25) may be used to assess the applicability of these arguments and approximations over a series of oxides.

RESULTS

It must first of all be emphasized that a detailed examination of the kinetics has not been attempted. Although most oxides appeared to obey Eq. (10) at high pressure there were slight curvatures in some experiments in what should be a linear plot: these were confined to the initial stages of the reaction and in some cases were obviously due to a lag in setting up a steady state on the surface. In other cases it is probable that the approximations made in arriving at Eq. (16) from Eq. (15) were not valid, i.e., that the chemisorption of O_2 was not sufficient to justify the assumption that

$$[K_3P_{O_2}]^{1/2} \gg 1 + K_1P_{N_2O}$$

[cf. the case of Mn_2O_3 (*12*)].

Nevertheless the general relationships which are discussed below seem to leave no doubt as to the basic correctness of the arguments presented and justify the somewhat drastic approximations which have been made. X-Ray examination has shown (*3*) that the oxides of La and Nd used here had the rare-earth A-structure, Sm_2O_3 was 10% C + 90% B, and the remainder were C-type. For this reason the oxides are considered below in two groups—the first including all 15, and the other excluding the oxides of Nd and La, and also "Tb_2O_3" since this is unstable and nonstoichiometric under the experimental conditions used here and also shows abnormal oxygen exchange kinetics (*3*). It is shown that although "Tb_2O_3" appears somewhat anomalous the remaining 14 oxides all fall closely into one pattern.

The main results are summarized in Table 1: the preexponential terms, A, for the low pressure reaction are not given as the measurements were of poor reproducibility: the estimated uncertainty in the activation energy, based upon duplicate series of experiments carried out on several of the oxides after intervals of 6–12 months is ±4 kcal: at the high pressure the estimated uncertainty is ±2 kcal. By determining the initial rates of the high pressure experiments it was found that in general the initial rate at 10 cm initial pressure of N_2O (upon an oxygenated surface) was between 1 and about 10 × that at 2 mm on the freshly outgassed oxides at the same temperature: extrapolation was usually necessary.

The adsorption experiments, summarized in Fig. 1, show the amount of rapid chemisorption of N_2O which was detectable before reaction began to obscure the position: the adsorption is clearly activated in nature. It is evident that all three oxides behave very similarly, the adsorption reaching saturation at about 1m around 300°C, but continuing to increase up to ca. 4mm 320°C and upward. (Unfortunately measurements at higher temperatures and pressures were not

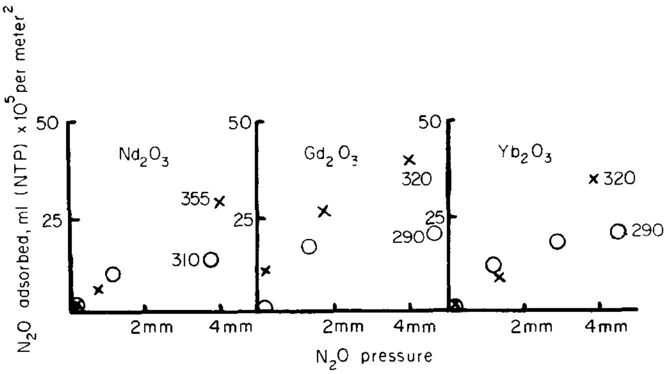

FIG. 1. Adsorption of N_2O.

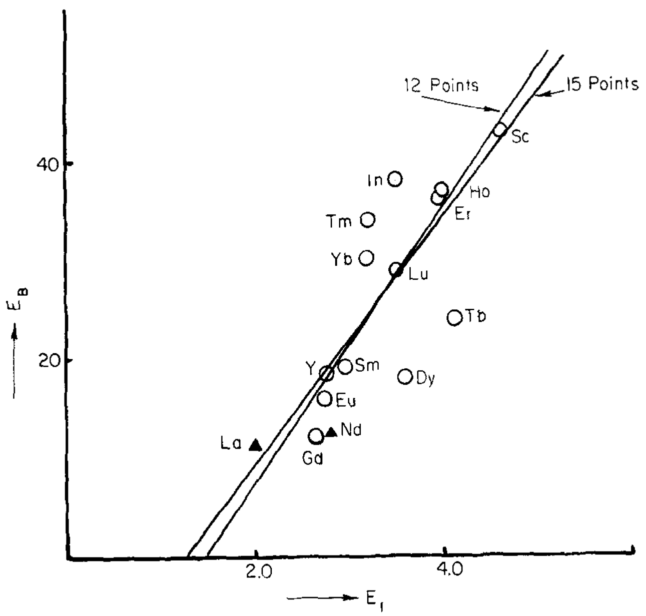

FIG. 2. Relationship between the activation energies for O_2-exchange and for N_2O-decomposition.

possible.) This means that K_1 and probably k increase with pressure and this is probably the reason for the scatter of the experimental points in Figs. 2–6 and for the fact that the observed slopes are not always those predicted by the kinetic analysis.

It is of interest to note that since there are very roughly 10^{19} surface oxygen ions per square meter of surface, and since 1 ml of gas at STP contains about 2.7×10^{19} molecules, the coverage is small, even assuming a roughly linear increase from 4 mm to ca. 20 cm.

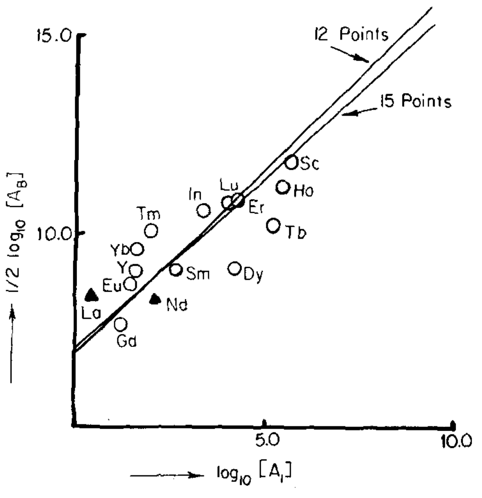

FIG. 3. Correlation between the preexponential terms for O_2-exchange and for N_2O-decomposition.

Column 5 of the Table provides a test of Eq. (24), where E_B, the apparent activation energy for ^{18}O-exchange by Eqs. (1)–(3) has been taken from an earlier paper (*3*). It is evident that, allowing for the uncertainty in the various energy terms, the agreement is good: thus the variation in k_e from oxide to oxide is less important than the variation in B. We should therefore expect, from Eq. (24) if E_e is roughly constant across the series of oxides, that $E_1 \alpha$ E_B. Figure 2 shows that this is so, although the slope is greater than 0.5 showing that in fact E_e increases somewhat with increasing E_B. The equation for the regression of E_B (or y) on E_1 (or x) is

$$y = 1.25x - 16.02,$$

for all 15 oxides and

$$y = 1.41x - 20.9,$$

for the 12 C-type oxides, excluding "Tb_2O_3" and the two A-type structures La_2O_3 and Nd_2O_3. The correlation coefficients for these two lines are 0.79 and 0.82 so that the relationship is highly significant.

Figure 3 similarly shows a test of Eq. (23)

by plotting $\log_{10}(A_1)$ against $\frac{1}{2}\log_{10}(A_B)$: the resulting lines of regression are

$$y = 1.137x - 8.019 \quad \text{(15 points)},$$
$$y = 1.065x - 7.409 \quad \text{(12 points)},$$

where $y = \log_{10}(A_1)$ and $x = \frac{1}{2}\log_{10}(A_B)$: the corresponding correlation coefficients are 0.82 and 0.70, which are again highly significant. The slopes are very close to the value of unity predicted by our approximations.

Figures 2 and 3 lead us to expect that, at least over a temperature range where the N_2O decomposition and the isotopic exchange between O_2 and the surface are of comparable speed, log (K) should vary as $\frac{1}{2}$ log (B), as predicted by Eq. (25): Fig. 4 shows that the relationship is linear at 450°C although, as in Fig. 2, the slope is not the required value, which here should be -0.5. The two regression lines are

$$x = -0.70y + 10.76 \quad \text{(15 points)},$$
$$x = -0.77y + 11.25 \quad \text{(12 points)},$$

where $y = -\log_{10}(K)$ and $x = \frac{1}{2}\log_{10}(B)$.

The correlation coefficients are 0.97 and 0.98—indicating a highly significant relationship. A temperature of 450°C was chosen as this is the only temperature common to the temperature ranges given in Table 1, but tests show the relationship is also of high significance at 350°C and at 500°C at least: judging from Figs. 2 and 3 we would expect the correlation between log (K) and log (B) to hold over a very wide temperature range.

Figure 5 shows a strong compensation-effect correlation between log A_1 and E_1 with a correlation coefficient of 0.61 for the 15 catalysts and 0.93 for the 12.

The results presented here show a remarkably strong correlation between the rate of desorption (from an initially dissociated state) of molecular oxygen and the rate of decomposition of nitrous oxide; the relationship is valid over a very wide temperature interval. Since the oxygen desorption reaction is dependent on the lattice parameter of the oxide catalyst, so too will be the decomposition reaction, and this is confirmed by Fig. 6 which shows a plot of E_1 (or y) against [Molecular Volume]$^{1/3}$ (or x): the two regression lines are

$$x = -41.8x + 208 \quad \text{(15 points)},$$
$$x = -39.9x + 200 \quad \text{(12 points)},$$

with correlation coefficients 0.825 and 0.70, respectively. This may be compared with the corresponding plot of E_B (*3*) which gave correlation coefficients of 0.84 for the same 12 catalysts and 0.86 for all 15.

It is evident that as is the case for the oxygen exchange reaction (*3*), there is no correlation between either A_1 or E_1 for the present reaction and physical or chemical properties of these oxides which do not vary in a regular manner with lattice parameter: for example there is no resemblance between the reactivity pattern found here and the variation of the magnetic moments of the M^{3+} ion in this series. The relationships presented in the present paper may not appear surprising in view of the fairly similar chemical and physical properties of this series of catalysts: of more interest is an examination of the same reactions on a range of metallic oxides from other groups

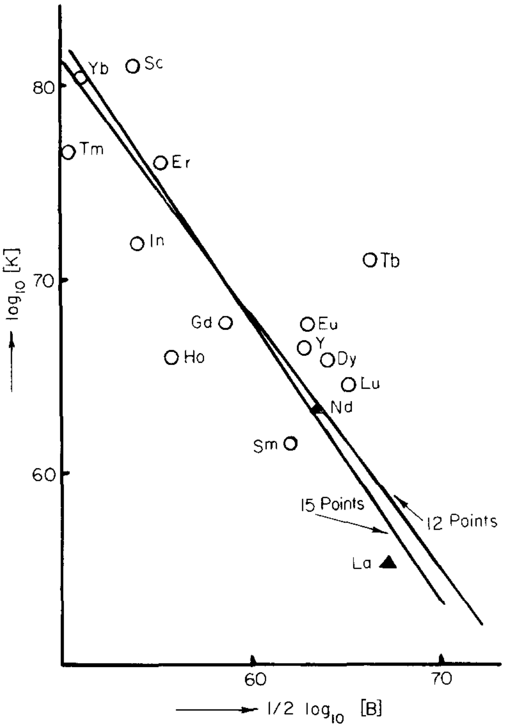

FIG. 4. Correlation between the rate of O_2-exchange and the rate of N_2O-decomposition at 450°C.

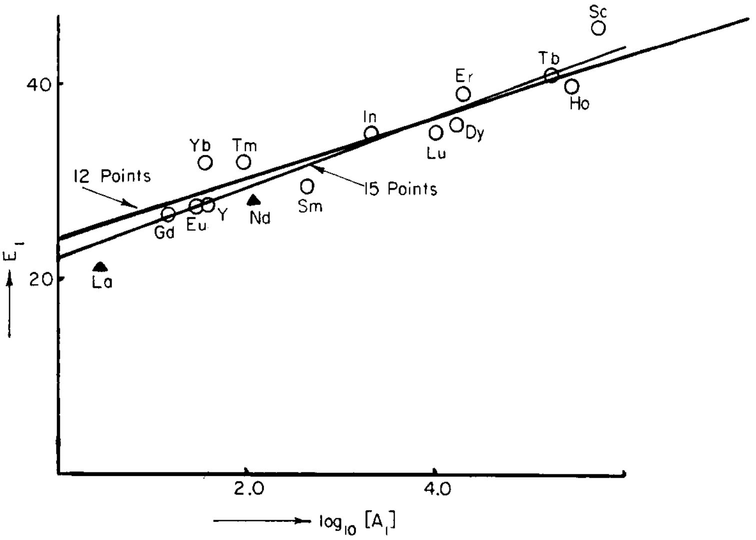

FIG. 5. Compensation-effect correlation between the activation energy and the preexponential term for the N_2O–decomposition.

in the periodic table: this is at present in progress.

Reaction Mechanism

Table 1 and Table 2 in Ref. *3* show that the N_2O decomposition has been studied at temperatures similar to, but usually a little higher than, those used in the exchange work. Thus it is reasonable to assume that the reactions between O_2 gas and the surface which we have proposed in discussions of the mechanism of exchange will be occurring while the N_2O decomposition is proceeding. We therefore suggest that the decomposition occurs by the chemisorption of N_2O molecules onto single anion vacancies on the oxide surface: these vacancies are assumed to contain trapped electrons (surface *F*-centers) or else the adsorbed molecule acquires one electron by surface migration:

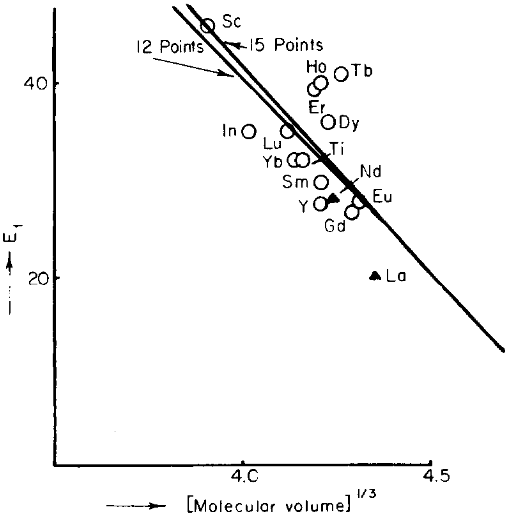

FIG. 6. Dependence of the activation energy of the N_2O-decomposition upon crystal lattice parameter.

$$(e^-|\square_s^-) + N_2O \rightleftharpoons (N_2O^-|\square_s^-), \tag{26}$$

or:

$$\square_s^- + N_2O \rightleftharpoons (N_2O|\square_s^-), \tag{27}$$

followed by, for example:

$$(O^{2-}|\square_s^-) + (N_2O|\square_s^-) \rightleftharpoons (O^-|\square_s^-) + (N_2O^-|\square_s^-) \tag{28}$$

although the election could equally well arise from altervalent impurity ions (*2*). Then follows the decomposition of the charged adsorption complex.

$$(N_2O^-|\square_s^-) \rightarrow N_2 + (O^-|\square_s^-). \tag{29}$$

The O^- migrate across the surface by charge-exchange.

$$(O^-|\square_s^-)_1 + (O^{2-}|\square_s^-)_2 \rightleftharpoons (O^{2-}|\square_s^-)_1 + (O^-|\square_s^-)_2 \tag{30}$$

where the subscripts refer to different sites. This migration continues (at a speed controlled by the normal lattice jump frequency which is of the order of 10^{11} $\sec^{-1}$ and upwards—compare the lattice frequency of ca. 10^{13} $\sec^{-1}$) until two singly-charged oxygen species "collide" in the surface by appearing on adjacent sites. When this occurs there is a finite probability of desorption of gaseous O_2, leaving a surface R_2-center:

$$2(O^-|\square_s^-) \rightleftharpoons O_2\ (\text{gas}) + (e^-|\square_s^-)(e^-|\square_s^-). \quad (31)$$

Equations (30) and (31) are the same as Eqs. (2) and (1) and (3) above. Detailed arguments proposing Eqs. (30) and (31) for the mechanism of O_2 adsorption and isotopic exchange have been presented elsewhere (*2*). It is suggested (*2*) that the R_2-centers are relatively stable: they would be most readily destroyed by chemisorption of molecular oxygen (i.e., the reversal of Eq. (31) but, particularly at higher temperatures, will be destroyed also by the migration of neighboring O^{2-} ions:

$$(e^-|\square_s^-)_1\,(e^-|\square_s^-)_2 + (O^{2-}|\square_s^-)_3 \rightleftharpoons (e^-|\square_s^-)_1 + (e^-|\square_s^-)_3 + (O^{2-}|\square_s^-)_2. \quad (32)$$

Where as before the subscripts serve to identify the sites. We consider that chemisorption of N_2O onto R_2-centers in the surface is unlikely to occur: the dependence of the rate of N_2O decomposition upon $[P_{O_2}]^{1/2}$ [Eq. (9)] is determined by competition between Eqs. (28)–(32), generally according to the manner indicated in the kinetic derivation of Eq. (15). [Note that if we are correct in assuming the participation of R_2-centers, and if these are not available for N_2O-adsorption, the continuance of the decomposition reaction requires the regeneration of single anion vacancies, or of single F-centers in the surface, e.g., by reaction (32).]

It is thus evident that, since at these temperatures isotopic exchange occurs rapidly between gaseous oxygen and the whole oxide surface (*3*), the N_2O-decomposition, which the N_2O-adsorption measurements show is occurring under conditions of low total surface coverage, is also likely to occur randomly all over the surface, accordinogti the random appearance of uncharged anon vacancies or of $(e^-|\square_s^-)$, e.g., by reaction (32). There would appear to be no localized (immobile) areas of catalytic activity in the present case.

Praseodymium oxides were not examined in detail in this work [nor in the parallel study of O_2-exchange (*3*)] because the complex phase changes suffered by this system (*13*) caused much irreproducibility. Terbium oxide, which we have found to be somewhat anomalous in both reactions experiences similar phase changes (*14*).

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