JOURNAL OF CATALYSIS 1, 103-112 (1962)

Decomposition of Nitrous Oxide on Some Doped Cupric Oxide Catalysts*

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Received October 17, 1961

The decomposition of nitrous oxide on pure and doped cupric oxide with ions of lower and higher valency was studied in detail. The heat treatment of cupric oxide between 550–800°C resulted in about 14 kcal increase of the activation energy. The building-in of ions of higher valency increased to a marked extent the activation energy, whereas the incorporation of lower valency ions decreased the activation energy to a lesser extent. According to the present conductivity measurements, cupric oxide—in contrast with earlier observations—proved to be a defect conductor. The kinetics of the decomposition of N_2O can be interpreted on the basis of this type of conductivity.

INTRODUCTION

From investigations of correlations between the electric structure and catalytic efficiency of semiconductor catalysts, it appeared that the electron and defect electron concentrations, respectively, controlling the rate and the activation energy of the reaction, are only favorable for a process on a determined level. These concentrations may be varied by doping and, in the case of *p*- or *n*-type conductors, the catalytic activity frequently changes unequivocally.

Present investigations aimed to study the correlations between the catalytic activity and the electric properties of the *i*-type (intrinsic) conducting cupric oxide. The decomposition of nitrous oxide was chosen as a model reaction.

Earlier investigations proved that cupric oxide is an effective catalyst for the decomposition of nitrous oxide. The energy of activation of the reaction was determined by Schwab and Staeger (1) who also discussed in detail the retarding effect of oxygen. Amphlett (2) studied the reaction on the surface of cupric oxide previously saturated with oxygen. In contrast to these authors, Schmid and Keller (3) did not observe any retarding effect of oxygen. An interesting result was noticed by Cremer and Marschall (4), when they pointed out that by raising the temperature of the heat treatment of cupric oxide from 450° to 750°C, the energy of activation increases about 30 kcal. Schwab and Schultes (5) have found practically the same value for the energy of activation at catalysts pretreated at 450° and 630°C. Rienäcker and Horn (6) studied the reaction of cupric oxide pellets pressed under various pressures, and they found that both the reaction rate and the energy of activation greatly depend on pressure.

According to Wagner and his co-workers (7), the conductivity of cupric oxide between 800°–1000°C is independent of the oxygen pressure. Thus they classified cupric oxide as an *i*-type conductor. According to later observations (8), at low temperatures (500°C), the conductivity changes with

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* Part of this paper was presented at the Symposium of Hungarian Chemists held in Szeged, October 1959. Preliminary report, in Hungarian, published in *Magyar Kém. Folyóirat* **66,** 278 (1960).

oxygen pressure. Hauffe und Grunewald (9) asserted that the conductivity is increased by doping either with lithium or with chromic oxides, and this seems to support also the *i*-type conductor characteristics.

The scattered investigations performed by Hauffe *et al.* (10) did not result in unequivocal results about the correlations between the electric structure and catalytic activity of cupric oxide, probably owing to the inadequate experimental technique. It seemed, therefore, worthwhile to study the cupric oxide–nitrous oxide system in detail; we also investigated the effect of sintering temperature, the different methods of preparation, the conditions of pretreatment, and the retarding effect of oxygen.

EXPERIMENTAL PROCEDURE

Apparatus

Kinetic measurements were carried out in an apparatus, suggested by several authors and modified by us to some extent. It operates on the thermosyphon principle. The apparatus is shown in Fig. 1.

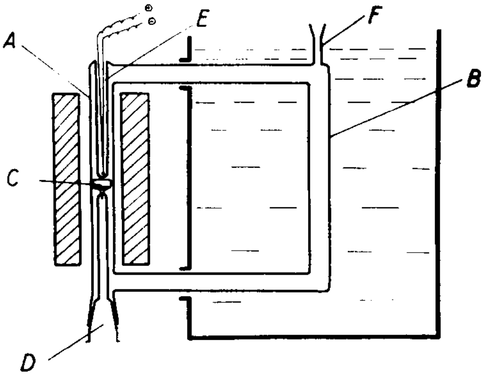

FIG. 1. Experimental apparatus.

One side of a rectangular-shaped reaction vessel (A) containing the catalyst was heated up to the required temperature in an electric oven, at the same time the opposite side (B) was kept at constant room temperature in a thermostat. Tablets of the catalyst were placed in a platinum basket (C) and pushed from below to the middle of the heated side with aid of the ground-glass joint (D). The thermo-element used to regulate and measure temperature was placed in a glass tube (E). With a heat regulator, an accuracy, on the average, of ±1°C was attained. The side of the reaction vessel that was kept at room temperature was connected by the capillary, ground joint (F) to a Hg manometer and to the vacuum equipment.

By this procedure the catalyst could be put in and taken out easier than by earlier methods, and also the cleaning of the reaction vessel was more convenient.

Preparation of Catalysts

To prepare samples of catalysts, cp metal copper was dissolved in nitric acid. Foreign ions were added in form of lithium nitrate, chromic nitrate, aluminum nitrate, zircon nitrate, ferric oxide, and yttrium oxide. The solutions or suspensions, respectively, were first evaporated and then slowly heated in an electric furnace to 450°C and thus transformed to oxides. They were kept at this temperature for another 4 hr. The powdered catalysts thus obtained were pressed into tablets of about 9 mm diameter and 1–2 mm thickness and sintered in air at prescribed temperature

Preparation of Nitrous Oxide

Nitrous oxide was prepared by the thermal decomposition of ammonium nitrate. The product is contaminated by water, nitric oxide, nitrous oxide, and nitric acid. To purify it, oxygen was added to the gaseous mixture and the nitrogen dioxide absorbed in caustic potash solution. Then the product was repeatedly frozen by liquid air and evacuated. Finally the condensate was evaporated into the gas-storing vessel at the temperature of Dry Ice–acetone mixture.

Determination of the Surface Area of the Catalysts

The Brunauer-Emmett-Teller method was applied to the —195.8°C adsorption isotherms of nitrogen. The place requirement of the nitrogen molecule was taken as 16.2 Å.

Conductivity Measurements

These were performed in air by the same procedure as described earlier (11). To study the type of conductivity, the apparatus shown in Fig. 2 was used in which the dependence of cupric oxide conductivity on oxygen pressure could also be followed. Resistance was measured with an electronic voltmeter.

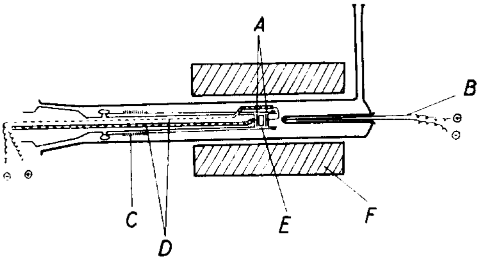

FIG. 2. Device for conductivity measurements.

RESULTS AND DISCUSSION

From the experimental data, we first attempted to ascertain the reaction order; the retarding effect of oxygen can be most easily established from the changes of order. Figures 3 and 4 show the reaction rate as function of the partial pressure of nitrous oxide at different initial concentrations and temperatures, respectively.

These figures show well that experimental data do not lie on a straight line. The higher the initial pressure, the greater is the curvature. The deviation from the first order according to our observations, too, can be attributed to the retarding effect of oxygen formed during the reac-

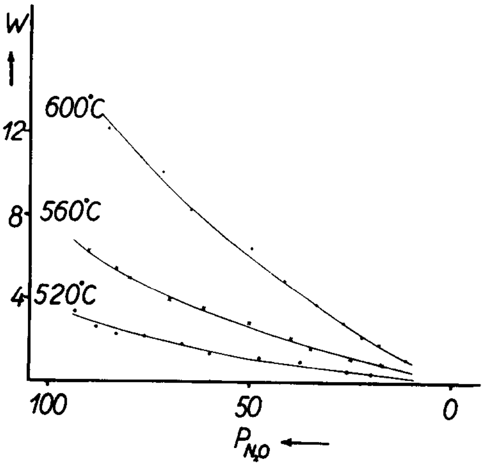

FIG. 4. Rate of decomposition of nitrous oxide as function of its partial pressure. $P_{0(N_2O)} \sim 100$ mm Hg.

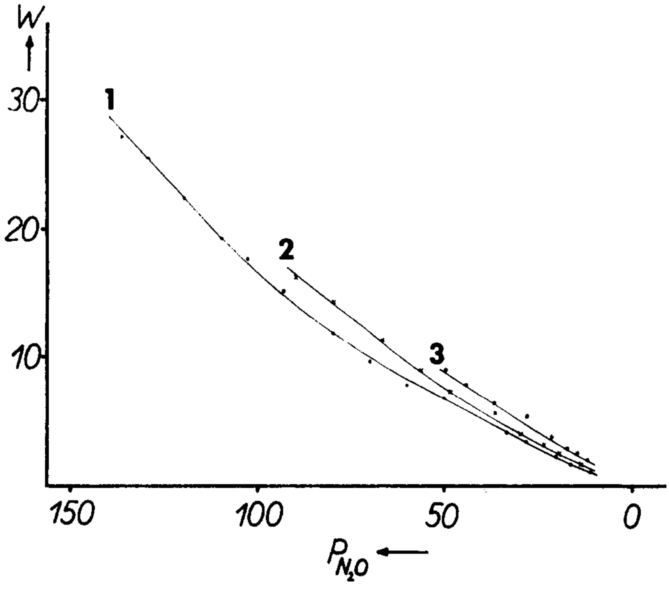

FIG. 3. Rate of decomposition of nitrous oxide as function of its partial pressure. $P_{0(N_2O)}$—(1) 146 mm Hg; (2) 100 mm Hg; (3) 57 mm Hg. Temperature—600°C.

tion. This will be discussed in detail later in the present paper.

To compare the efficiency of variously doped and pretreated cupric oxides, we first calculated only the over-all rate constants and from the dependence of these on temperature the apparent activation energy. The reaction rate can be suitably described by the Langmuir-Hinshelwood equation,

$$-dp/dt = kp/[1 + b(p_0 - p)]$$

where p_0 is the initial pressure of nitrous oxide in mm Hg, p is the actual pressure of nitrous oxide, and b and k are constants. The reciprocal was plotted as function of the reciprocal of the partial pressure of nitrous oxide,

$$-\frac{dt}{dp} = \frac{1}{w} = \frac{1 + bp_0 - bp}{kp}$$

$$= \frac{1 + bp_0}{k} \cdot \frac{1}{p} - \frac{b}{k}$$

Figure 5 shows that the reciprocal function is always a linear one. From the slope, the value of k_{overall} can be calculated. Of course, the value of the rate constant thus obtained still depends on the initial pressure of nitrous oxide. Therefore each experiment was carried out to make comparisons at almost the same initial pressure (~100 mm). Over-all rate constants contain also the adsorption coefficient of oxygen. As we shall see later, the consideration of oxygen adsorption causes only a slight change in the activation energies.

Effect of Sintering Temperature

In view of the contradictions mentioned in the Introduction and also of results obtained by Cremer and Marschall and by Schwab and Schultes, already referred to, it appeared necessary to investigate the effect of sintering temperature. The sintering was carried out with special care. Experimental results are given in Table 1.

Table 1 gives the specific activity referred to $\ln^2$ $[k/A]$, the logarithm of the pre-exponential factor and the energy of activation. As it appears, the rate constants and the specific activity depend reversely on sintering temperature. With increasing temperature, the former decreases and the latter slightly increases (see Fig. 6).

A similar increase can be observed in the values of the activation energy and of log k_0. However, it must be noted that the

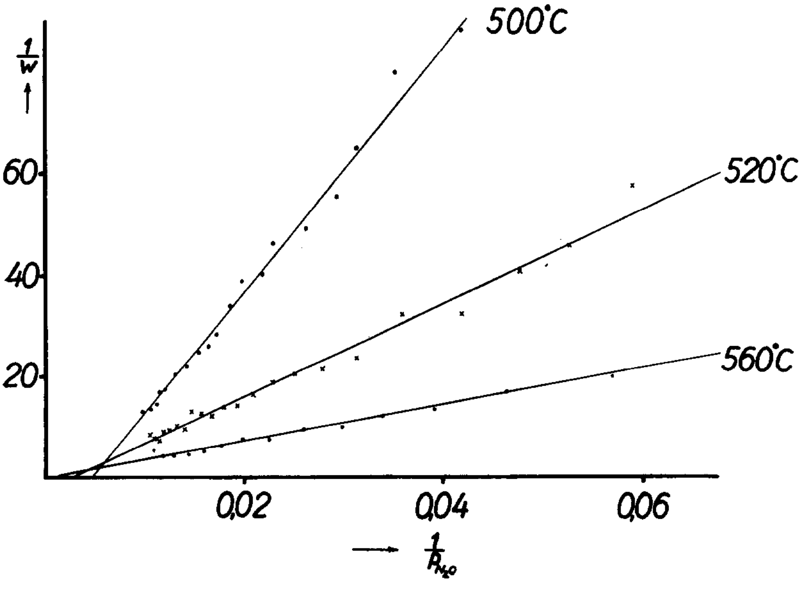

FIG. 5. Reciprocal rate of decomposition of nitrous oxide as function of its reciprocal pressure.

TABLE 1

EFFECT OF SINTERING TEMPERATURE ON THE DECOMPOSITION

Pretreatment temperature (°C)	Surface of catalyst A (m²/g)	k_{overall} (min^{-1}) at 574°C[a]	k_{overall}/A (min^{-1}/m^{-2}) at 574°C	E (kcal/mole)	log k_0
550	2.23	0.136	0.061	23.0	4.7
550		0.104	0.047	24.9	5.1
600	2.00	0.124	0.062	27.4	5.8
650	1.65	0.116	0.070	28.3	6.1
700	0.84	0.078	0.093	28.0	6.2
750	0.52	0.055	0.106	30.0	6.8
800	0.59	0.070	0.119	38.4	9.0

[a] Values of k_{overall} (574°C) were extrapolated and interpolated, respectively, from the straight line, showing the dependence of rate constants on temperature.

increase of the energy of activation is considerably smaller than that described by Cremer and Marschall. The energy of activation and the logarithm of the pre-exponential factor are linearly related, log $k_0 = E/a + \text{const}$; i.e., theta-rule is valid (see Fig. 7). The value $a = 3.5 \times 10^3$, calculated from our data agrees well with 3.2×10^3 calculated from results of Cremer and Marschall, in spite of the considerably great changes of activation energies as function of sintering temperature. In our case the characteristic temperature $\theta = a/2.3R$ was 780°K, as compared with 710°K given by Cremer and Marschall. In view of the agreement of these data it is hard to interpret the great differences in the energies of activation. It seems probable that the deviation must be attributed to the different procedures of preparation of cupric oxide. Cremer and Marschall precipitated cupric oxide with potassium hydroxide, pretreated *in vacuo* for only 1 hr. Literature data suggest that cupric oxide thus precipitated is not free of alkali ions even after a long process of purification. It can be assumed that potassium ions concentrated on the surface layer of cupric oxide diffuse into it when the temperature is raised, thus decreasing the electron-hole concentration of the surface layer and this results in the increase of the activation energy.

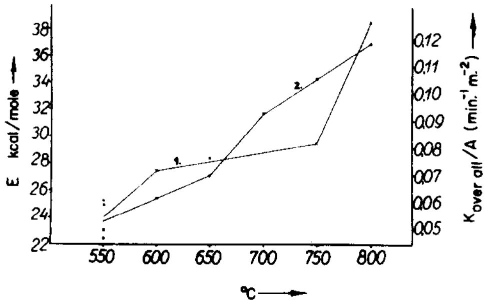

FIG. 6. Dependence of (1) activation energy and (2) specific activity on the sintering temperature of cupric oxide.

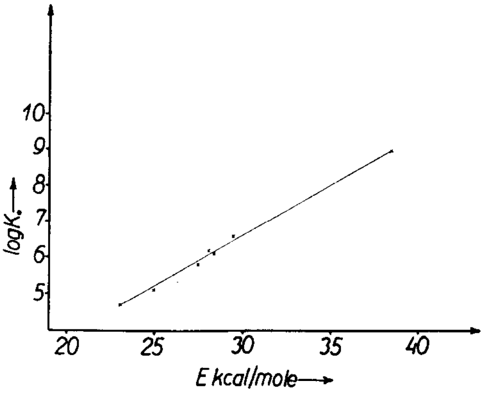

FIG. 7. Pre-exponential factor as function of energy of activation.

Effect of Doping with Foreign Ions

Doped catalysts were always sintered at 750°C. Over-all rate constants, calculated as already described, were referred to 1 g of substance and are given in Table 2. The specific activity practically does not change by doping with lithium oxide; however, it markedly decreases when chromic and ferric oxides, respectively, are built-in. The energy of activation slightly decreases

TABLE 2

EFFECT OF DOPING ON THE DECOMPOSITION

Catalyst	Surface of catalyst A (m²/g)	k_{overall} (min⁻¹) at 574°C	k_{overall}/A (min⁻¹/m⁻²) at 574°C	E (kcal/mole)	log k_0
$CuO + 1$ mole % Li_2O	0.92	0.114	0.125	28.4	6.4
$CuO + 0.2$ mole Li_2O	0.99	0.112	0.113	27.8	6.2
CuO	0.52	0.055	0.106	30.0	6.8
$CuO + 0.1$ mole % Cr_2O_3	0.72	0.0066	0.0091	38.0	7.7
$CuO + 1$ mole % Cr_2O_3	0.70	0.0039	0.0056	39.0	7.8
$CuO + 0.1$ mole % Fe_2O_3	—	0.092	—	29.8	—
$CuO + 1$ mole % Fe_2O_3	—	0.0065[a]	—	—	—
$CuO + 0.1$ mole % Al_2O_3	—	0.094	—	30.1	—
$CuO + 1$ mole % Al_2O_3	—	0.044	—	36.2	—
$CuO + 1$ mole % Y_2O_3	—	0.175	—	31.2	—

[a] At 650°C.

when lithium oxide is doped, whereas in presence of chromic oxide it increases by about 10 kcal. Small amounts of ferric and aluminum oxides do not change the energy of activation, but a doping of 1 mole % does already increase it considerably.† It is interesting that yttrium oxide does not increase markedly the energy of activation.

The Retarding Effect of Oxygen

Previously we mentioned that activation energy values independent of the gas composition and the initial pressure could only be obtained if these factors are taken into account in the complex, over-all rate constant. To this end, in the nominator of Langmuir-Hinshelwood's equation, also the actual oxygen concentration must be considered. Thus the real rate constant (k) can be calculated by equation

$$1/k_{\text{overall}} = 1/k + b/k(p_0 + p')$$

where p' is the initial partial pressure of oxygen measured in mm Hg of nitrous oxide from which it formed previously. Figure 8 shows that the reciprocal of the over-all rate constant as function of $p_0 + p'$ gives a straight line with good approximation.

Results of experiments performed with pure cupric oxide sintered at 750°C are values for k and b calculated from them given in Table 3.

These calculations make possible first of all the determination of k. From the dependence of k on temperature, the activation energy is found to be 28 kcal/mole, that is, 2 kcal smaller than that calculated from k_{overall}, but exactly in agreement with that obtained by Schwab and Staeger.

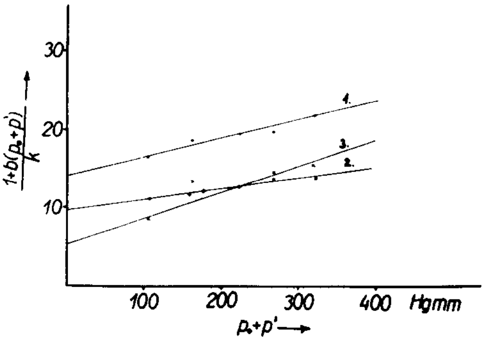

FIG. 8. Dependence of reciprocal over-all rate constant on the initial pressure. (1) CuO at 559°C; (2) CuO at 573°C; (3) CuO + 1 mole of Li_2O at 574°C.

It is true that these authors determined the value of b only at 589° and 569°C and that they applied cupric oxide sintered at 610°C. In view of the small oxygen retardation, a greater error occurs in the determination of b. From the dependence of b on temperature, we calculated for the heat of adsorption 28 and 30 kcal/mole, respectively—a surprisingly high value—

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† Nearly the same increase of the energy of activation was found by Rienäcker and Latka (12) when building-in 1% of aluminum oxide.

TABLE 3
REACTION RATES ON PURE CuO

°C	p_0	p'	$[1 + b(p_0 + p')]/k$ found	k	b	b/k	$[1 + b(p_0 + p')]/k$ calculated	Δ%
560	104.2	0	16.5	0.072	0.00182	0.0253	16.5	0
559	107.7	53.3	18.6	0.072	0.00182	0.0253	18.0	−3
559	108.3	104.3	19.5	0.072	0.00182	0.0253	19.3	−1
560	107.8	158.8	19.8	0.072	0.00182	0.0253	20.7	+5
559	107.3	212.7	21.9	0.072	0.00182	0.0253	22.1	+1
573	106.8	0	11.1	0.104	0.00145	0.014	11.1	0
573	124.0	53.4	12.1	0.104	0.00145	0.014	12.1	0
573	105.3	54.0	11.7	0.104	0.00145	0.014	11.8	+1
573	115.3	106.8	12.7	0.104	0.00145	0.014	12.7	0
573	105.2	162.8	13.7	0.104	0.00145	0.014	13.3	−3
573	100.1	222.0	13.8	0.104	0.00145	0.014	14.1	+2
594	107.0	0	8.8	0.155	0.00087	0.00561	7.1	−19
594	106.0	53.0	7.5	0.155	0.00087	0.00561	7.4	−1
595	110.5	100.0	7.9	0.155	0.00087	0.00561	7.7	−3
594	108.3	159.0	7.6	0.155	0.00087	0.00561	8.0	+5
594	116.0	218.0	8.5	0.155	0.00087	0.00561	8.4	−1
611	104.0	0	5.9	0.184	0.00058	0.00313	5.8	−2
613	103.7	0	5.6	0.184	0.00058	0.00313	6.8	+2
613	104.7	55.0	5.0	0.184	0.00058	0.00313	6.0	+20
612	111.0	104.0	7.1	0.184	0.00058	0.00313	6.1	−13
613	106.3	160.0	6.2	0.184	0.00058	0.00313	6.3	+2
613	105.2	215.0	6.6	0.184	0.00058	0.00313	6.5	−1

whereas Schwab and Staeger obtained 21 kcal/mole only.

As it can be seen from Table 3, the value of b/k decreases with the increase of temperature. This indicates that k increases more rapidly than b decreases with temperature.

It is to be mentioned that the value of b/k can be calculated also from the axial intercept of the linearized equation. Since the value of the intercept is mostly somewhat greater than its own limit of error, values thus obtained are highly uncertain. Table 4 contains data calculated in this manner.

The oxygen dependence was also investigated of samples doped with lithium and chromic oxide, respectively. Data for cupric oxide containing 1 mole % of Li_2O are shown in Table 5.

Accordingly, the kinetic correction lowered the energy of activation of the catalyst doped with lithium oxide to 27 kcal and that of the sample doped with chromic oxide, from 39 kcal to 38 kcal/mole, that is, not decisively.

TABLE 4
REACTION RATES ON PURE CuO

°C	$1/k_{overall}$	b/k	p_0	k	b
560	16.50	0.0545	99.0	0.087	0.0047
571	9.78	0.0171	98.0	0.123	0.0021
573	11.10	0.0398	100.0	0.123	0.0049
594	10.50	0.0315	110.0	0.142	0.0045
594	8.82	0.0241	103.0	0.158	0.0038
611	5.89	0.0221	98.0	0.269	0.0069

TABLE 5
REACTION RATES ON DOPED CuO

°C	p_0	p'	$[1 + b(p_0 + p')]/k$ found	k	b	b/k	$[1 + b(p_0 + p')]/k$ calculated	Δ%
557	104.3	0	13.2	0.133	0.0068	0.051	12.8	−3
557	108.2	52.6	26.2	0.133	0.0068	0.051	15.6	−40
557	107.7	104.3	17.8	0.133	0.0068	0.051	18.3	+3
557	107.0	212.0	24.2	0.133	0.0068	0.051	23.8	−2
574	105.3	0	8.5	0.193	0.0065	0.034	8.8	+3
574	110.7	51.3	13.4	0.193	0.0065	0.034	10.6	−20
574	104.7	105.3	12.4	0.193	0.0065	0.034	12.3	−2
575	109.4	158.7	14.5	0.193	0.0065	0.034	14.2	−2
574	108.6	210.0	15.5	0.193	0.0065	0.034	15.9	+2

Measurements of Electric Conductivity

Data on the conductivity of pure and doped cupric oxides are shown in Fig. 9. Since experimental data are rather scattered, values in the figure represent average results of at least 5–6 series of measurements. Energies of activation calculated from the dependence of conductivity on temperature are also summarized in Fig. 9. Doping with lithium increases the conductivity and decreases the activation energy, whereas doping with chromic ion slightly decreases the conductivity but markedly increases the energy of activation.

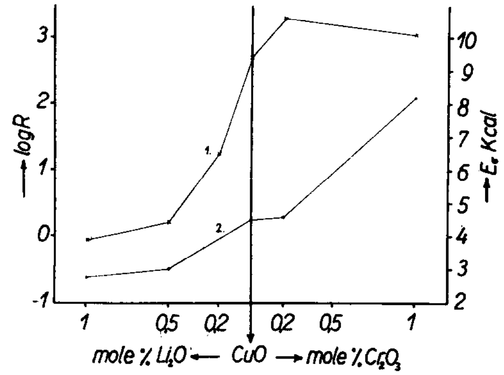

FIG. 9. Resistance of cupric oxide (1) at 200°C and activation energy of conductivity; (2) in air as function of concentration of added lithium and chromic oxides, respectively.

Therefore our results contradict those of Hauffe and Grunewald. It is rather hard to interpret the deviation, since these latter authors publish nothing about the preparation of cupric oxide and the manner of doping it with foreign ions. However, Le Blanc *et al.* (13) pointed out as early as 1933 that the conductivity and the electric properties of cupric oxide are sensitive to the methods used in preparing it.

If cupric oxide is prepared from cupric nitrate, cupric carbonate, or cupric hydroxide by heating, the values of resistance are different, although the qualitative behavior is the same. Doping with chromic oxide decreases the conductivity. This decrease is even greater when aluminum or yttrium oxide is built-in.

Dependence of Conductivity on Oxygen Pressure

Hauffe and Grunewald describe the effect of doping with chromic oxide (i.e., the increase of electron concentration) by the following equation:

$$Cr_2O_3 \rightleftharpoons 2Cr^{\bullet\cdot}(Cu) + 2\ominus + \tfrac{1}{2}O_2 + 2CuO$$

Therefore according to the equation

$$x_{\ominus} \cdot x_{\oplus} = K \qquad p_{O_2} = \text{const}$$

the defect electron concentration decreases. However, doping with lithium oxide causes, according to equation

$$Li_2O + \tfrac{1}{2}O_2 \rightleftharpoons 2Li^{\bullet\prime}(Cu) + 2\oplus + 2CuO$$

an increase in the defect electron concentration. Consequently, if cupric oxide would be an i-type conductor, for building-in of chromic oxide, we would have an n-type conductor, and a p-type conductor when lithium is doped. If this is true, the conductivity of cupric oxide doped with chromic oxide must decrease when the oxygen pressure is raised, while the conductivity of the sample doped with lithium oxide must increase. Our measurements of these variables are shown in Fig. 10.

As it can be seen, the conductivity of pure cupric oxide slightly increases with the increase of oxygen pressure and the conductivity of cupric oxide doped with lithium oxide does not change at all. It can also be observed that the conductivity of samples doped with ions of higher valency increases more markedly with the increase of oxygen pressure than in the case of pure cupric oxide. Thus the doping with Cr_2O_3 does not convert CuO into an electron conducting oxide.

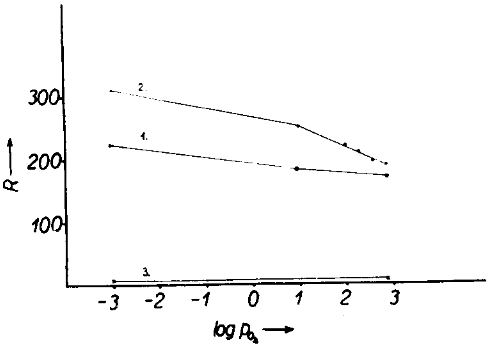

FIG. 10. Resistance of pure cupric oxide and cupric oxide doped with lithium and chromic oxide, respectively, as function of oxygen pressure. (1) CuO at 501°C; (2) CuO + 1 mole % Cr_2O_3 at 498°C; (3) CuO + 1 mole % Li_2O at 530°C.

The fact that the conductivity of cupric oxide—in agreement with earlier data—increases only to a small extent, or not at all, with the oxygen pressure does not necessarily mean that pure cupric oxide is an *i*-type conductor. It may be supposed that the defect electron excess originated during the chemisorption of oxygen,

$$\tfrac{1}{2}O_2 \rightarrow O_{(chem)}^- + \oplus$$

is negligibly small as compared to the otherwise great electron-hole concentration of the catalyst. Therefore the chemisorption of oxygen does not cause any further change in the conductivity. This is also indicated by the initial conductivity of cupric oxide doped with lithium oxide *in vacuo* and in 1 atm oxygen, since the CuO + 1% Li_2O mixed oxide cannot be regarded in any way as an *i*-type conductor. Even in this case, the defect electron concentration is originally so great that the chemisorption of oxygen cannot modify it considerably. This conception is supported by the results of dopings with tervalent ions. Namely, as a result of these dopings, the defect electron concentration decreases, and, thus, the excess of defect electrons formed during the chemisorption of oxygen is manifest in the proportional increase of conductivity to the oxygen concentration.

Reaction Mechanism

The electron mechanism of the decomposition of nitrous oxide on defect conducting oxides may consist of the following steps:

$$N_2O = N_2O_{(chem)}^- + \oplus \qquad (1)$$

$$N_2O_{(chem)}^- = O_{(chem)}^- + N_2 \qquad (2)$$

$$O_{(chem)}^- + \oplus = \tfrac{1}{2}O_2 \qquad (3)$$

$$O_{(chem)}^- + N_2O = N_2 + O_2 + \ominus \qquad (4)$$

However, more recent measurements do not prove the last step. From experimental data, we must suppose that the rate-determining step is the desorption of chemisorbed oxygen, just as in the case of nickel oxide, i.e., the elementary reaction (3). As our measurements on conductivity show, the building-in of lithium oxide increases the defect electron concentration, presumably according to the following equation:

$$Li_2O + \tfrac{1}{2}O_2 \rightleftharpoons 2Li^{\bullet\prime}(Cu) + 2\oplus + 2CuO$$

thus, making it easier for the elementary reaction (3) to take place. That ions of higher valency raise the activation energy is also in accordance with the foregoing reaction scheme and supports the elementary step (3) as a rate-determining one. Namely, when doping with chromic oxide and other ions of higher valency, it is likely that, by the equation,

$$Cr_2O_3 + 2\oplus \rightleftharpoons Cr^{\bullet\cdot}(Cu) + \tfrac{1}{2}O_2 + 2CuO$$

the defect electron concentration decreases. Therefore the elementary reaction (3) gets on the second place. The supposition of Hauffe and Grunewald on an *i*-type conductor character would interpret the mechanism of the catalysis in a similar manner. From the investigation of the catalyzed reaction, it is, thus, impossible to formulate unequivocal deductions about the mechanism and the electron structure, respectively.

It remains to interpret the slight effect exerted by doping with lithium oxide on the energy of activation and on the specific rate constant. The building-in of lithium oxide should bring about an increase in the defect electron concentration. The reason why a more marked effect does not take place is, again, that the most proper electron hole concentration for the reaction is already set in the pure cupric oxide. Also, a further increase of the electron hole concentration, owing to doping with lithium oxide, does not render an advantage for the catalyzed reaction.

The above interpretation of the effect of doping of cupric oxide seems plausible. However, the behavior of the catalyst contaminated simultaneously with lithium and chromic ions, shows that the building-in of foreign ions changes not only the electric structure but also influences the catalytic properties in some way not yet considered.

REFERENCES

1. SCHWAB, G. M., AND STAEGER, R., *Z. phys. Chem.* **B25,** 418 (1934).
2. AMPHLETT, G. B., *Trans. Faraday Soc.* **50,** 273 (1954).
3. SCHMID, G., AND KELLER, N., *Naturwissenschaften* **37,** 42 (1950).
4. CREMER, E., AND MARSCHALL, E., *Monatsh. Chem.* **82,** 840 (1951).
5. SCHWAB, G. M., AND SCHULTES, H., *Z. phys. Chem.* **B9,** 265 (1930).
6. RIENÄCKER, G., AND HORN, G., *Z. Elektrochem.* **60,** 828 (1956).
7. BAUMBACH, H. H., DÜNWALD, H., AND WAGNER, C., *Z. phys. Chem.* **B22,** 226 (1933).
8. GUNDERMAN, J., WAGNER, C., *Z. phys. Chem.* **B37,** 157 (1937).
9. HAUFFE, K., AND GRUNEWALD, H., *Z. phys. Chem.* **198,** 248 (1951).
10. HAUFFE, K., GLANG, R., AND ENGELL, H. J., *Z. phys. Chem.* **201,** 223 (1952).
11. SZABÓ, Z. G., AND SOLYMOSI, F., *Z. Elektrochem.* **63,** 1177 (1959).
12. RIENÄCKER, G., private communication (1961).
13. LE BLANC, M., SACHSE, H., AND SCHÖPEL, H., *Ann. Physik* **17,** 334 (1933).