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Kinetics of the Reaction of Cyclohexene with the Surface of a Manganese Dioxide

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The reaction of cyclohexene with the surface oxygens of MnO_2 produces benzene and water. The kinetics of this irreversible chemisorption has been studied in a flow system. The influence of cyclohexene pressure on the rate of benzene formation, suggests that the surface reaction is rate determining. The number of reactive oxygens has been shown to be increasing with the temperature, reaching a value close to half of the total surface oxygen. The temperature dependency of the number of reactive oxygens, follows the same pattern as the initial rate of reduction (8 kcal/mole). The rate-determining step could thus be the availability of the sites, as was already assumed by Taylor and Thon for the kinetics of chemisorption.

INTRODUCTION

In order to characterize the reactivity of some fourth period metal oxides, two specific test reactions have been studied: the homomolecular exchange of oxygen and the heteromolecular exchange between gaseous oxygen and the surface oxygen of the solid (*1–4*). These first results have indicated the existence, on the best catalysts (MnO_2, Co_3O_4, CuO, and NiO) of mobile oxygen atoms which can be easily reduced by CO (*5*) or H_2 (*5–7*).

Catalytic reactions were performed on these oxides to correlate their catalytic activity with the existence of such active sites. The oxidation of carbon monoxide was the most extensively studied. For manganese dioxide, it now appears (*8*) at least at a sufficiently high temperature, that this reaction proceeds by a simultaneous oxidation and reduction of the catalyst surface probably by means of these mobile oxygens. However, because of the high reductive character of CO, this mechanism cannot be generalized. It was thus worthwhile to study such a redox mechanism over a wider range of catalytic reactions.

We have chosen the oxidative dehydrogenation of cyclohexene to benzene and water. As expected from other systems (*5*), we have found that the reduction of the solid occurred even at very low temperature and have restricted our study to this reduction process (i.e., to the reaction in the absence of oxygen).

EXPERIMENTAL PROCEDURE

A. Materials

The manganese dioxide was supplied by Fisher Scientific. Examination by X-ray diffraction indicated a highly disordered structure. However, a treatment at 400°C under oxygen for 5 hr permitted identification with pyrolusite (*21*). A structural change in Mn_2O_3 was found to occur in the presence of oxygen between 550 and 600°C. The specific surface area determined by the standard BET method varied with the temperature of pretreatment: 200°C, 136 m^2/g; 280°C, 134 m^2/g; 490°C, 92 m^2/g; 630°C (Mn_2O_3), 55 m^2/g.

The cyclohexene (B.D.H.) was purified by fractional distillation. The various gases used (N_2, O_2) were dried over molecular sieves.

The kinetic study was performed in a classical microreactor, differential towards the *gaseous* reactants. Reactants and products (except water) were analyzed by gas phase chromatography, Aerograph 600, with a flame ionization detector. A column of polyethylene glycol (15%) on Chromosorb (5 ft) was used at 105°C.

B. Procedure

A sample of 50 mg of manganese oxide is heated under a stream of dry oxygen during 5 hr at 400°C (unless otherwise indicated). After purging for 10 min with a stream of dry nitrogen at this temperature, it is cooled to the required temperature (between 25 and 350°C). Meanwhile a constant pressure of cyclohexene is established in a flow of nitrogen and checked by gas chromatography. When the pressure and flow rate are stabilized (variations <2%), the flow of cyclohexene and nitrogen is quickly established over the catalyst. We consider the opening of the stopcock as time 0 of the reaction. After 10 sec the dead volume of the reactor is filled with reactant and the quantity of benzene, which is a product of the reaction, is measured by chromatographic injections at various times.

The influence of contact time on the conversion has been studied in the range of 100 to 350°C, Fig. 1. The linear dependency of yield on contact time indicates that diffusion is not rate controlling at high gas velocities. Under the experimental conditions used (50 mg of MnO_2, flow rate of 100 ml/min), the conversion of cyclohexene into benzene ranged between 0.2 and 5%. In the remainder of the paper we shall consider the rate as the number of benzene molecules produced per second and per gram of solid.

RESULTS

I. Dependency of the Rate of Dehydrogenation on Time

We have presented in Fig. 2 the variations of the rate of benzene formation with time

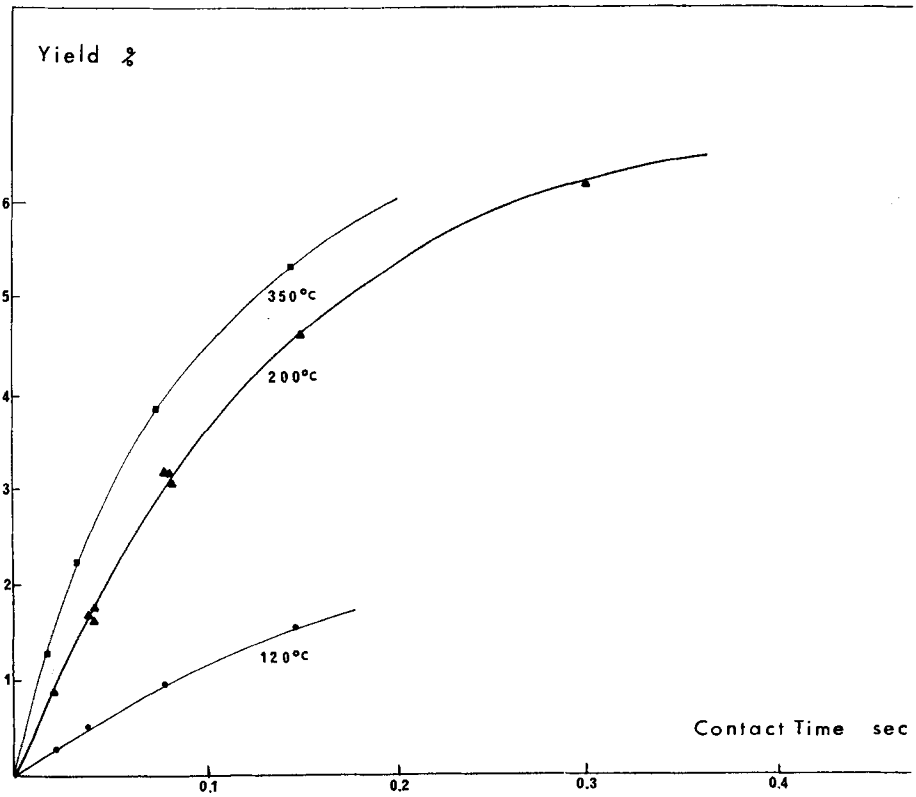

FIG. 1. Influence of the contact time on the yield at three temperatures: ●, 120°C; ▲, 200°C; ■, 350°C

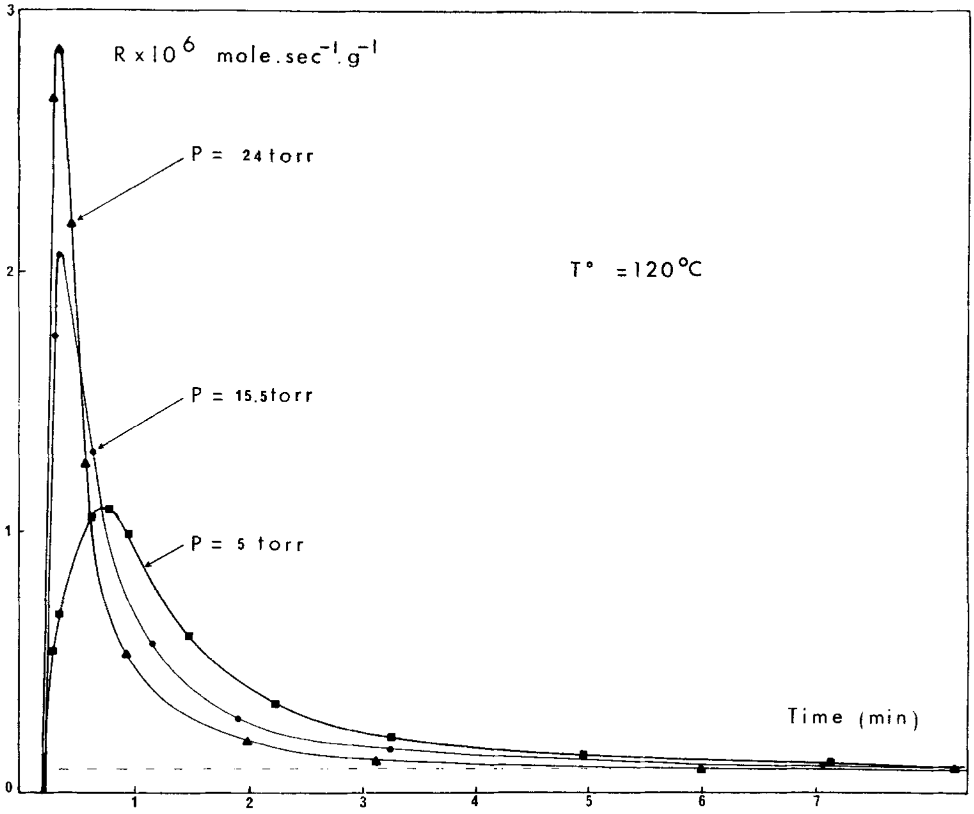

FIG. 2. Evolution of the rate with time at 120°C for various pressures of cyclohexene.

for various pressures of cyclohexene. Each kinetic curve can be divided in three parts:

A first period during which the rate of benzene formation reaches its maximum value; that period ranges between 15 and 30 sec according to the cyclohexene pressure: the higher the cyclohexene pressure the shorter the initiation period.

A second period is characterized by a very fast decay of the rate with time. The dependency of this rate with time obeys an exponential law as shown in Fig. 3. It must be pointed out that the maximum of the rate as well as the observed decay are functions of the pressure of cyclohexene (Fig. 2): the higher the pressure, the higher the initial rate and the faster the decay of the rate with time. So that the end of this period, characterized by a break in the logarithmic transformation (Fig. 3), occurs between 2 and 4 min.

A third period is characterized by a very small rate which decays exponentially with time as well. The reaction is zero order in cyclohexene and the activation energy of this process is equal to 17 kcal/mole. In the rest of the paper we will neglect this phenomenon since it is probably the result of various and simultaneous phenomena: slow surface reaction with other types of sites requiring a higher activation energy; diffusion processes in the pores of the solid; and, for high temperatures, diffusion of oxygen ions from the bulk to the surface.

Subsequently, we will study only the phenomena occurring in the first and second period which seem, a priori, to be restricted to fast surface reactions. We will call "initial rate" the rate corresponding to the maximum of the curve as represented in Fig. 2.

II. Nature of the Surface Reaction

The formation of benzene when cyclohexene is contacted with manganese oxide would, at first, suggest the possibility of a disproportionation reaction of cyclohexene

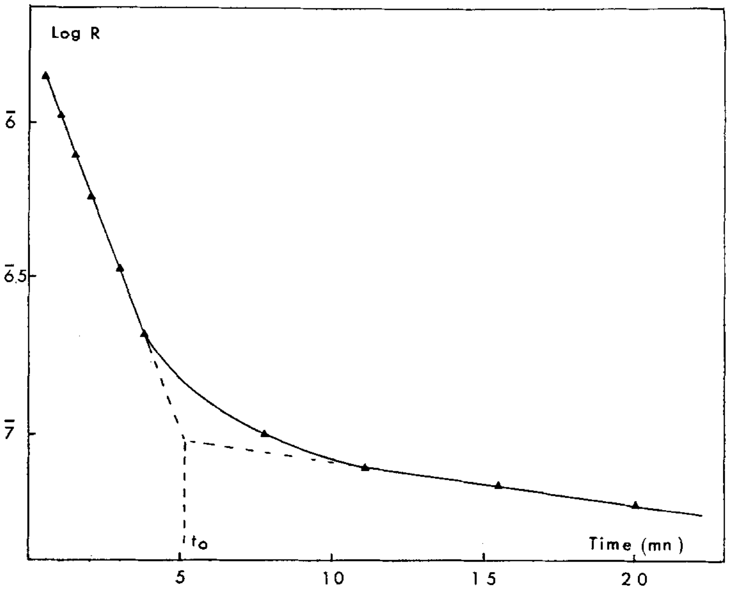

Fig. 3. Logarithm of the rate plotted versus time (t_0 = 150°C, cyclohexene pressure = 5 Torr).

into benzene and cyclohexane first discovered by Zelinskii *et al.* (*9*) on Pd and Pt catalysts and intensively studied further. This reaction of disproportionation was also found to occur over certain oxides of the first series (*10*) of transition elements such as Cr_2O_3, V_2O_5, TiO_2, and Co_3O_4 but not over MnO. For this latter, only oxidative dehydrogenation was observed. On our solid, appreciable amounts of benzene were observed but we have found only traces of cyclohexane, thus only a dehydrogenation reaction occurs.

To determine precisely the nature of the reactive sites over the solids, we studied the influence of the temperature of pretreatment of the catalyst on the initial specific rate: R_0/S_T; S_T being the area of the solid at the temperature of pretreatment T. The results are presented in Fig. 4. The specific activity

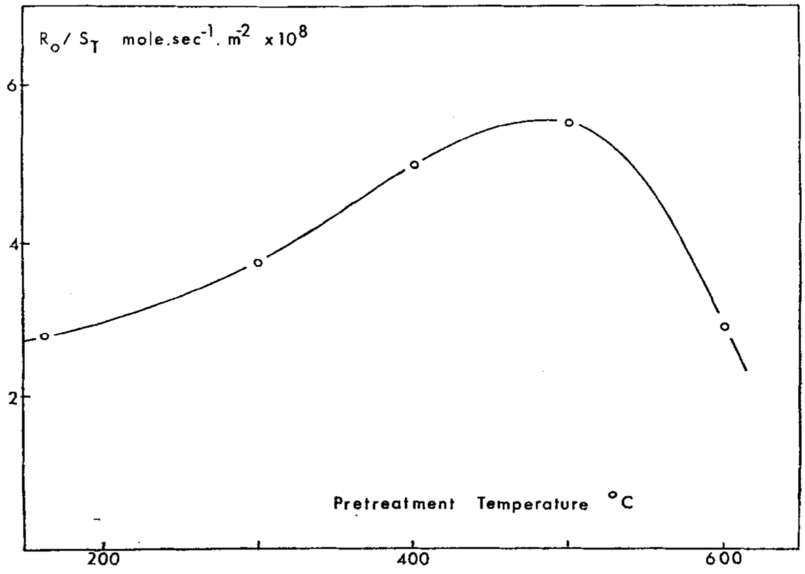

Fig. 4. Influence of the pretreatment temperature of the catalyst on the initial rate.

of the solid increases slightly with the temperature of pretreatment under O_2, as far as the structure remains close to pyrolusite. The decay observed after 500°C must be related to the formation of Mn_2O_3 which is detected by X-ray. Since the highest activity is observed for the highest temperature of calcination of the solid, corresponding to the lowest water content *(11)*, we can obviously assume that the reaction does not proceed through the elimination of hydroxyl groups of the solid. It is therefore likely that surface oxygen of the solid is involved as we have proved in the regeneration experiments: after an initial run under cyclohexene at 200°C, the catalyst was treated under oxygen at 400°C for 15 min. After a purge with nitrogen, a new run was performed and the same initial activity was obtained. After 20 similar runs, the solid presented the same activity as initially. If the regeneration was performed at 200°C during 1 hr only 95% of the initial activity was recovered. In another set of experiments the reaction and the regeneration were performed at 150°C. In this experiment we could not recover more than 15% of the initial activity even after a regenerating treatment of 24 hr. These experiments show that the reactive species are the oxygen atoms of the solid and we can assume that the overall reaction is:

$$C_6H_{10} + {}_2O_{(surface)} \rightarrow C_6H_6 + {}_2H_2O.$$

Kinetics of this reaction have been studied to get further information about its mechanism as well as the reactivity of the solid.

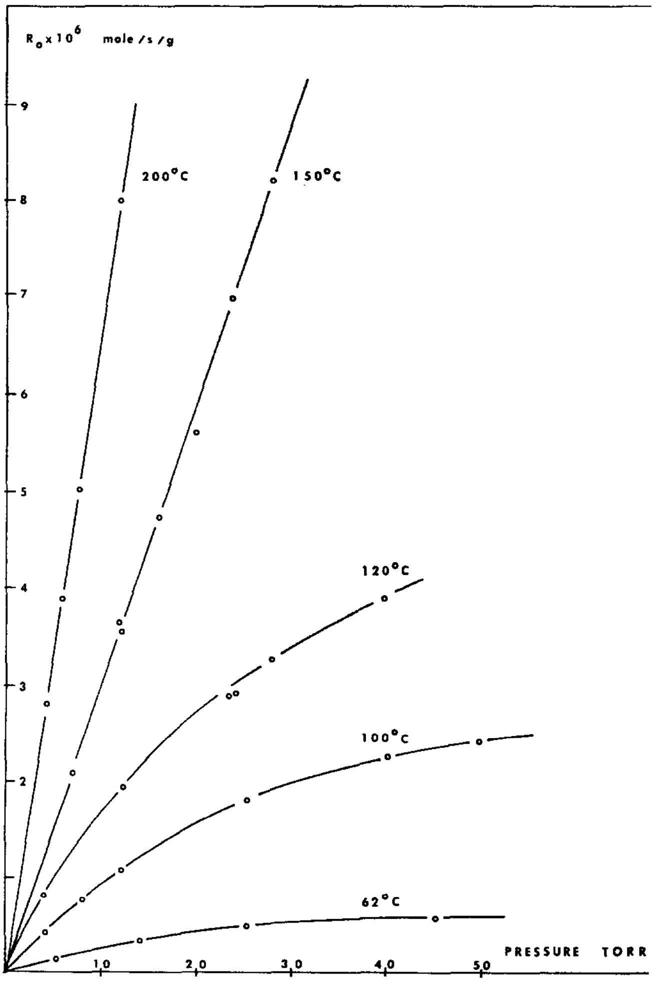

FIG. 5. Dependence of initial rate R_0 on cyclohexene partial pressure at several different temperatures

III. Influence of the Pressure of Cyclohexene on the Initial Rate

The study has been performed in a wide range of temperatures (62–200°C) and pressures (5–50 mm). The plots of the initial rate versus the partial pressure of cyclohexene indicate two different sets of results (Fig. 5).

At 120°C and below the initial rate obeys the Langmuir isotherm,

$$R_0 = k \cdot \frac{aP}{1 + aP}, \qquad (1)$$

which indicates that a nondissociative adsorption occurs before the surface reaction, the desorption of the products not being rate controlling. The linear form of the equation,

$$R_0 = k - \frac{1}{a} \cdot \frac{R_0}{P}, \qquad (2)$$

allows the calculation of the adsorption coefficient a from the slope. The enthalpy of adsorption preceding the reaction may be evaluated by expressing this adsorption coefficient in the form:

$$\log a = -\frac{\Delta H}{kT} + \frac{\Delta S}{k}. \qquad (3)$$

(ΔH and ΔS corresponding to the transfer of 1 mole of cyclohexene from the gas phase to the adsorbed layer.) Since no siginficant and coherent change in the slope can be detected at various temperatures (Fig. 6), we must admit that a is temperature independent, which means according to Eq. (3) that the heat of adsorption has a very low value ($\Delta H < 3$ kcal/mole).

At 150°C and above we observe first order with respect to the cyclohexene. This result could be assumed to be logical in a typical concept of activated reaction following an exothermic chemisorption. An increase of the temperature would be expected to decrease the amount of chemisorbed cyclohexene and give thus first order, the higher rate being produced by the increase of the rate constant with temperature. However, this explanation is no more valid, if we consider the very low heat of adsorption found, and if we assume, as we shall prove later, that the surface reaction has a zero activation energy. The explanation of the increase in order and in rate constant, with temperature must be then correlated with an increase of the number of active sites and probably with a change of the reaction mechanism (the Langmuir-Hinshelwood scheme could be

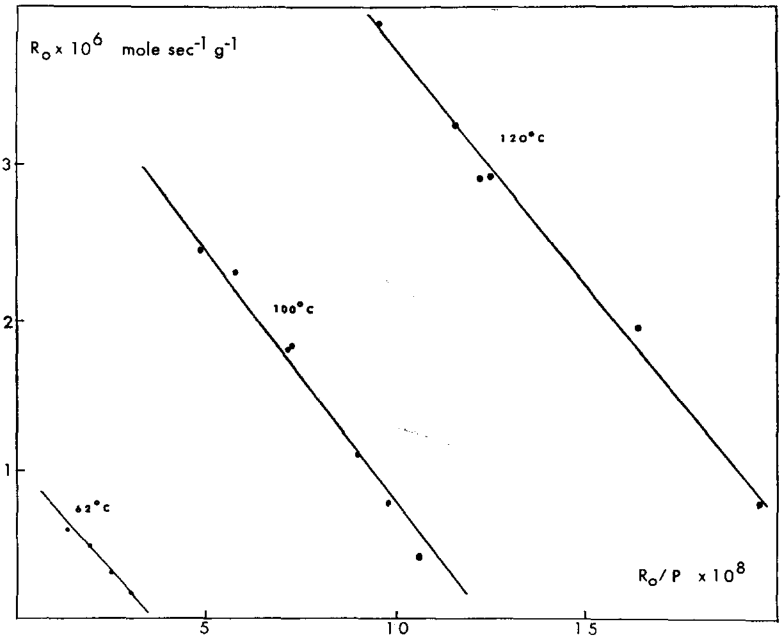

FIG. 6. Linear transformation of the Langmuir isotherm applied to the results of Fig. 5.

changed to a Rideal-Eley one at temperatures higher than 120°C).

The influence of the products on the initial rate has not been intensively studied since we worked in a range of flow rate where the conversion was proportional to the contact time, so that no inhibiting effect of the products could occur. Nevertheless, some experiments were performed with water and benzene supplied with cyclohexene. For water no inhibiting effect was found at 100 and 150°C for a partial pressure of 2.4 mm of mercury. Presence of benzene did not change the initial rate either, proving that this compound was not strongly adsorbed on the oxide, as was already shown by Dixon *et al.* (*10*).

IV. Temperature Dependence on the Initial Rate

Results are given in Fig. 7 for 3 pressures of cyclohexene in a range of temperature varying from 25 to 350°C. The Arrhenius plots fit two straight lines, one between 25 and 200°C which gives an apparent activation energy of 8 kcal/mole and one between 200 and 350°C which corresponds to a very small activation energy ($E \leqslant 1$ kcal). Since a rate controlling diffusion could be claimed to explain the break in the Arrhenius plot, we have studied carefully the influence of the contact time on the rate at 350°C and we did not find any significant rate controlling diffusion at the low contact time we have used. Besides this first anomaly it is of relevant interest to point out that for temperatures lower than 200°C no change in the slope was observed for the wide range of pressure used (4, 12, 24 mm Hg) for which the order varies considerably. A significant change between an apparent ($\Delta E - \Delta H$) and true activation energy (ΔE) would have been expected when the order decreases from 1 to 0, unless the heat of the initial adsorption is very low as already supposed.

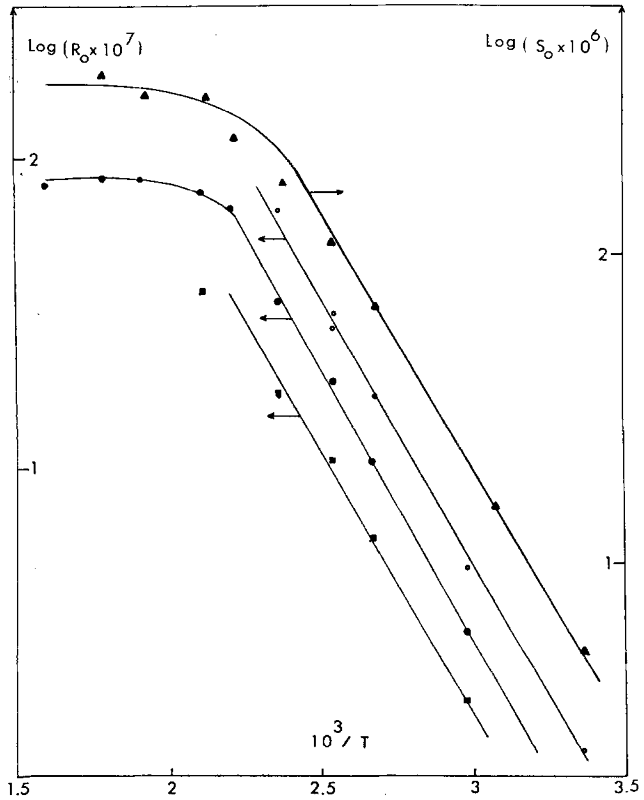

FIG. 7. Arrhenius plots for the initial rate R_0 at three pressures (■, 6 Torr; ○, 12 Torr; ●, 24 Torr) and for the number of sites S_0 ▲.

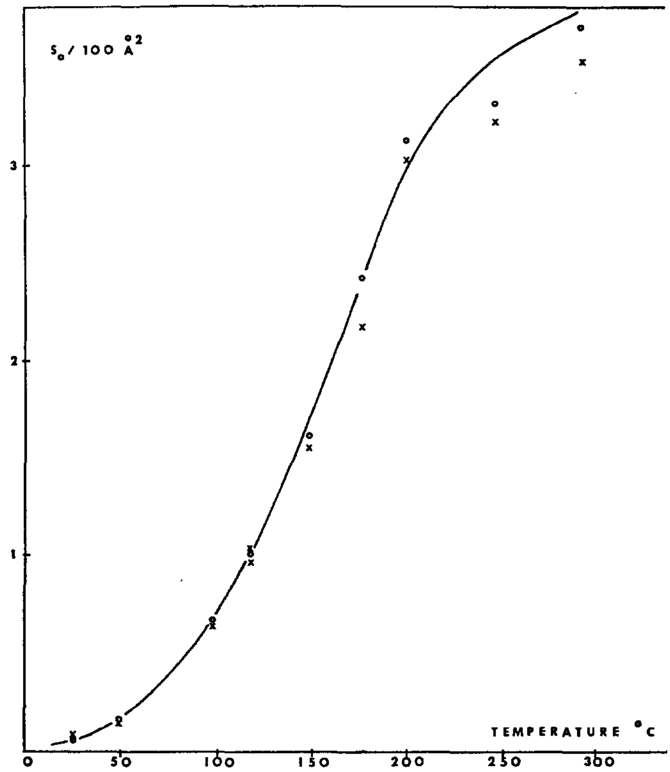

FIG. 8. Dependency of the reaction temperature on the number of oxygen sites S_0 (O, integral method; ×, analytical method).

V. *Temperature Dependence on the Number of Active Sites*

Since the reaction we were studying was a depletive reduction of manganese oxide surface, it seemed worthwhile to deduce the number of active oxygens of the solid from our kinetical data. Two different methods were used that we call integral and analytical methods.

a. Integral method. The number of oxygen sites can be determined by the integration of the rate of benzene formation with time, owing to the fact that the transformation of one molecule of cyclohexene into benzene requires two oxygen atoms:

$$S_0 = 2 \int_0^{t_0} R \cdot dt, \qquad (4)$$

t_0 corresponding to the break in the logarithmic first order transformation (Fig. 3). In order to know if the preceding assumption was valid we calculated this number by integration for 3 various pressures of cyclohexene. As shown in Table 1, the integral method allows the calculation of the number of sites with an accuracy of 10%. We have presented in Fig. 8 the variation of this number with the temperature of reaction.

b. Analytical method. A simple kinetic law can be derived from our kinetic data. In effect, since the rate is exponentially decreasing with time (first order law versus the

TABLE 1

DETERMINATION OF THE NUMBER OF SITES AT 120°C FOR VARIOUS PRESSURES AND BY TWO DIFFERENT METHODS

Pressure of cyclohexene (Torr):	5	15	25	Av
No. of sites determined by the integral method (O‡/100 Å^2)	1.1	1.08	0.94	1.04
No. of sites determined by the analytical method (O‡/100 Å^2)	1.04	0.96	0.83	0.94

number of sites) and since the initial rate as well as the decrease of the rate with time are functions of the pressure, we can write the general equation,

$$R = k \cdot f(P) \cdot S_0 \cdot \exp(-g(P) \cdot t), \quad (5)$$

$f(P)$ and $g(P)$ being functions of the pressure. (We have obviously $f(P) = \theta = aP/(1 + aP)$ for a Langmuir-Hinshelwood mechanism and $f(P) = bP$ for a Rideal-Eley mechanism.) To determine $g(P)$, let us solve analytically Eqs. (4) and (5):

$$\int_{t=0}^{t=t_0} k \cdot f(P) \cdot S_0 \cdot \exp(-g(P) \cdot t) = \cdot dt \frac{S_0}{2}. \quad (6)$$

We deduce from this integration assuming t_0 is high enough to neglect $\exp(-t_0 g(P))$ compared to 1,

$$g(P) = 2k \cdot f(P). \quad (7)$$

So that the general rate equation is:

$$R = k \cdot S_0 \cdot f(P) \cdot \exp - (2k \cdot f(P) \cdot t). \quad (8)$$

This is a classical first order rate equation applied to our reaction. From this equation we can deduce S_0 since the initial rate is equal to $k \cdot S_0 \cdot f(P)$ and the slope of the linear logarithmic transformation is equal to $2\,k \cdot f(P)$. The ratio of the initial rate to this slope is equal to $S_0/2$. The results are represented on Fig. 8, and they are in good agreement with those obtained by the analytical method. It is interesting to point out here that the fact that we get the same results by both methods gives a strong support to the hypothesis we have given at the beginning, that is, the phenomena observed during the first and second periods, until time t_0, concern a single type of sites of the surface.

The results of Fig. 8 show that the number of active sites increases considerably with the temperature of the reaction and at 250°C stabilizes at a value of 3.5 $O^{\ddagger}/100$ Å^2, which represents approximately half of the maximum oxygen available on the surface layer of a manganese oxide (*8*). The logarithm of the number of the sites plotted versus the reciprocal value of the absolute temperature, Fig. 7, gives exactly the same two slopes as those obtained for the determination of the activation energy. This result proves that the variations of rate with temperature cannot be attributed to an activation energy of the gaseous reactant but to an increase in the number of the surface sites S_0. As a proof, the Arrhenius plots of the "true" specific rate R_0/S_0 gives an activation energy of 0.7 ± 0.5 kcal/mole, Fig. 9.

DISCUSSION

The most relevant data of this work concern the experimental proof of the temperature dependency of the number S_0 of reactive oxygens of the surface. Up to a value close to half of the oxygens available on the surface, the free energy of formation of these surface oxygens is equal to the "apparent" activation energy of the depletive oxidation of cyclohexene, whereas no

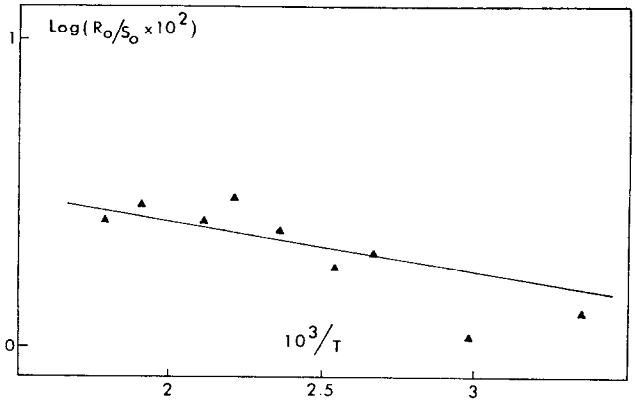

FIG. 9. Arrhenius plot for the "true specific rate": R_0/S_0.

change in the rate occurs when this number of sites is stabilized.

Similar data were obtained by Winter (*3, 4*) studying the isotopic exchange between $^{18}O_{2(g)}$ and the surface oxygen of various oxides. A plateau in the Arrhenius plot of the rate was found at a certain temperature but not further explained, and an increase in the number of surface reactive oxygen with temperature of the exchange reaction was observed. However, no accurate value of the activation energy of this process was obtained. Winter compared the values of this number of oxygen atoms for many oxides with the value of monolayer capacity expressed as nitrogen atoms adsorbed per gram (calculated from BET isotherm). For most of the oxides a very close value was obtained between both methods, indicating that when he was working at high temperatures (300–500°C) the isotopic exchange reaction involved the whole surface, i.e., the total surface oxygens were activated.

Studying the same exchange reaction over NiO, Bailly and Teichner (*19*) have also observed a variation of active oxygen with temperature of reaction. At 200°C only a fraction of surface oxygen participates in the exchange whereas at 250°C the complete surface is reacting. They attribute this fact to the heterogeneity of the surface. The activation energy that they observe (8 kcal/mole) for this process would represent a phenomenon of migration of surface ions; this migration could occur at temperature higher than $\frac{1}{4}$ of the tamman temperature of the oxide.

Studying the reaction between CCl_4 and the surface oxygen of TiO_2 (*22*), one of the authors has also observed an increase of the reactive oxygen with temperature, till the complete exchange of available surface oxygen.

No general theory has been proposed about the activation of sites. However, many authors starting from various experimental facts adopted this concept. First Volkenstein (*12*) studying the energetical changes between active and inactive defects on a surface arrived at the conclusion that a temperature increase may augment the number of active sites and thus stimulate an activated adsorption. He supposes that the energy of activation in this case is that of active sites rather than active gas molecules. Thus there would not be energy barrier for oncoming gas moles. Taylor and Thon (*13*) studying the range of applicability of the Elovitch and Zhabrova equation (*14*) to many kinetics of chemisorption, criticized the meaning of the activation energy of chemisorption since new kind of active sites come into operation in a certain range of temperature. Besides this fact they assume that the rate of chemisorption is governed by the availability of the sites. Finally Barnad and Mitchell (*15*), in order to explain the very fast adsorption of benzene over palladium, accompanied by a positive change in entropy, proposed the existence of an activationless adsorption on active centers the number and freedom of which increases with the temperature.

If we assume that the first fast decaying reaction studied, concerns a single type of surface oxygen, then our results support the hypothesis of activationless adsorption on activated centers. However, since the reaction studied can be more assimilated to an irreversible chemisorption process than to a catalytic reaction the validity of the activation of sites seems to be restricted to chemisorption processes. Obviously further measurements in other systems are required to demonstrate the degree of generality of the present result.

The meaning of the activation of the sites may be easily explained in a typical concept of surface reactivity of semiconductors. On this kind of solid many forms of chemisorbed oxygen may be present (*3, 23*). It is possible to classify them in order of increasing reactivity: O^{2-}, O^-, $O_{(ads)}$, $O^-_{2(ads)}$; O^{2-} is simply the ionic form of the oxygen in the lattice. From the reactive species $O^-_{(ads)}$, $O_{(ads)}$, and $O^-_{2(ads)}$, the most frequently involved in oxidation reactions are $O^-_{(ads)}$ and $O_{(ads)}$ (*17, 19*), since many authors (*3, 16*) seem to reject $O^-_{2(ads)}$ as nonstable. Consequently, we can assume that $O_{(ads)}$ or $O^-_{(ads)}$ are two possible reactive forms of oxygen reacting easily with cyclohexene. These "adsorbed" oxygen ions would not be supplied in our case by an exothermic chemisorption of oxygen since this compound is not present in the gaseous phase but from one of the two following endothermic reactions:

$$O^{2-} \rightarrow O_{ads}{}^{-} + e^{-} + 6.5 \text{ eV } (3)$$

or

$$_2MnO_{2(surface)} \rightarrow Mn_2O_{3(surface)} + O_{(ads)}{}^{\ddagger 0}\Delta G_{300} = +11,7 \text{ kcal/mole } (20)$$

Since both these reactions are endothermic, it is logical to observe an increase in the number of O^{-} or $O_{(ads)}{}^{\ddagger}$ when temperature increases, followed by a plateau when the whole surface is concerned (or the fraction of the surface corresponding to the stoichiometry Mn_2O_3). As a proof of this hypothesis, we can mention that Winter (*3*) has shown it was impossible to distinguish between chemisorbed oxygen and the oxygen coming from the lattice of semiconductor oxides.

CONCLUSION

The oxidative dehydrogenation of cyclohexene by means of surface oxygen of manganese dioxide provides an interesting approach to the study of the reactivity of the surface oxygen of the solid. Consideration of the variations of the number of sites with temperature following the same pattern as the rate constant, seem to supply evidence for a theory given by Volkenstein (*12*) concerning the activation of the sites. For such a case, after Taylor and Thon (*13*), it is the availability of the sites which governs the kinetics of chemisorption, and there is no energy barrier for the reacting gas.

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