Kinetics of Irreversible Chemisorption: Surface Reduction of MnO₂ by Cyclohexane, Cyclohexene, and 1,3- and 1,4-Cyclohexadiene

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The surface reduction of MnO₂ by cyclohexane, cyclohexene, and both 1,3- and 1,4-cyclohexadiene produces benzene and water. A kinetic study and electrical measurements were performed in order to determine the rate-determining step of the reduction. The variations of the rate with temperature are identical to the variations of the number of active oxygen atoms; the apparent activation energy increases in the order cyclohexadienes (7.2 kcal/mole), cyclohexene (8 kcal/mole) and cyclohexane (11 kcal/mole). It has been found that it is the activation of the surface oxygen under the influence of the organic compound—by means of the C–H bond—which determines the rate.

INTRODUCTION

The mechanism of Mars and Van Krevelen (*1*) of successive reduction and oxidation of the surface is now commonly accepted for heterogeneous oxidation using oxides of transition metals as catalysts. For such a mechanism, the adsorptions are real chemical reactions between the surface and the gases and the catalytic process must be considered as two elementary steps:

(a) reduction of the solid by the reactant giving the gaseous product and a new solid;
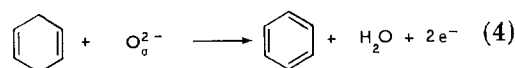
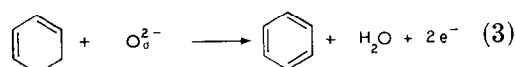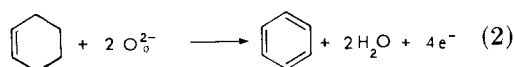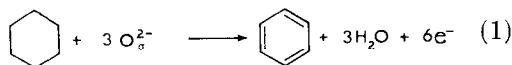(b) oxidation of the reduced solid.

This paper will deal with kinetics of the step (a) which could be identified as an irreversible chemisorption. In a previous work (*2*) we have studied the kinetics of the surface reduction of manganese dioxide by cyclohexene which produces a reduced solid, benzene and water. The variation of the number of active sites with temperature, which followed the same pattern as the rate of reduction, seemed to conform to a concept already advanced by Wolkenstein (*3*) and Taylor and Thon (*4*) concerning nonactivated adsorption. It is the availability of the sites which governs the kinetics of chemisorption and there is no energy barrier for the reacting gas.

In order to check the validity of this concept which could apply to most irreversible gas–solid surface reactions, we undertook a more general study of MnO₂ surface reduction with various compounds. We have chosen cyclohexane, 1,3-cyclohexadiene and 1,4-cyclohexadiene. These three compounds were found to react with

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MnO_2 in the same way as cyclohexene: they produce benzene and water after reaction with the surface oxygen, according to the following reactions:

$$\text{(cyclohexane)} + 3\,O_\sigma^{2-} \longrightarrow \text{(benzene)} + 3H_2O + 6e^- \quad (1)$$

$$\text{(cyclohexene)} + 2\,O_\sigma^{2-} \longrightarrow \text{(benzene)} + 2H_2O + 4e^- \quad (2)$$

$$\text{(cyclohexadiene)} + O_\sigma^{2-} \longrightarrow \text{(benzene)} + H_2O + 2e^- \quad (3)$$

$$\text{(cyclohexadiene)} + O_\sigma^{2-} \longrightarrow \text{(benzene)} + H_2O + 2e^- \quad (4)$$

(O_σ^{2-} is an oxygen ion located at the surface of the oxide).

If there is no energy barrier during the chemisorption of the organic compound, the difference of reactivity of these substrates should not affect the rate of chemisorption and only the number of oxygen atoms involved should determine this rate.

Since the electronic states of the catalyst are changed during a reduction (5), it was also of interest to investigate such a parameter by means of electrical conductivity measurements.

EXPERIMENTAL SECTION

A. Material

A γ pyrolusite previously described (2) was used for this work. After a standard treatment at 400°C under oxygen its specific surface area was found to be equal to 115 m²/g. Cyclohexane (BDH), 1,3-cyclohexadiene (Aldrich) and 1,4-cyclohexadiene (Aldrich) were purified by fractional distillation under nitrogen. The various gases used in a flow system (O_2, N_2) were dried over molecular sieve.

B. Kinetics Measurements

1. Apparatus. The kinetic measurements were performed in a classical microreactor, differential with respect to the gaseous reactants. Reactants and products, except water and CO_2, were analyzed by gas phase chromatography (Aerograph 600) with a flame ionization detector. A column of polyethylene glycol (15%) on chromosorb (5 ft), was able to separate at 75°C, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, cyclohexane and benzene. Some experiments were performed with a conductivity cell (Gow-Mac) to check the presence of water and CO_2.

2. Procedure. A sample of 50 mg of manganese dioxide was heated under a stream of oxygen for periods varying from 15 min to 4 hr at 400°C. After a purge with nitrogen during the time necessary to remove the oxygen from the lines, the reactor was cooled to the temperature of the reaction. Meanwhile a measured stream of nitrogen was passed through a carburetor, maintained at a preset temperature, which contained the hydrocarbon reactant. When the flow rate and partial pressure of the hydrocarbon were properly adjusted, the stream of gas was allowed to pass through the reactor and the products of the reaction were analyzed at various times by gas chromatography.

Under the reaction conditions, 50 mg of MnO_2 and a flow rate of 100 ml/min, and temperatures lower than 300°C, the main products detected were benzene and water independent of the initial reactant (cyclohexene, cyclohexane or 1,3- and 1,4-cyclohexadine). Only traces of CO_2 were detected. The linear dependency of the yield (with respect to benzene) on contact time suggested that external diffusion was not rate controlling and that no further oxidation of benzene was occurring to a significant extent. Manganese dioxide samples of various particle sizes reacted with indentical rates, ruling out the possibility of rate-controlling internal diffusion processes.

In order to maintain good reproducibility most of the experiments were made with the same MnO_2 sample, regenerated after each run under oxygen at 400°C for 15 min. The duration and the temperature of the regeneration had a considerable influence on the initial activity of the solid. For example, at 200°C, more than 2 hr under oxygen were required to recover the initial activity. At 400°C, 15 min of treatment

were sufficient for this recovery and regeneration for more than 2 hr produced a slow sintering of the solid. In much the same way, if the reduction by cyclohexane, 1,3- or 1,4-cyclohexadiene lasted more than 10 min, the standard regeneration by oxygen could not reproduce the initial activity. For example, after a reduction at 200°C for 1 hr, a regeneration at 400°C could not restore more than 95% of the preceding initial activity. This suggested that the reduction of the manganese dioxide crystal lattice had already begun.

It must be pointed out that the results concerning the regeneration were the same with the four cyclic compounds: for the early stage of the reduction, only the surface of the solid is involved and the regeneration by oxygen at 400°C is complete. These results are in good qualitative agreement with those obtained by Klier (6) and Brooks (7) who worked on the depletive reduction of MnO_2 by CO or H_2.

C. Electrical Conductivity Measurements

1. **Apparatus.** For measurements of electrical conductivity a conventional cell for powders described by Arghiropoulos (8) was used. The changes of conductivity were followed by means of a DC Lemouzy apparatus. The type of semiconductivity of MnO_2 was estimated by establishing a temperature difference between the two electrodes and detecting the polarity of the ensuing Seebeck voltage.

2. **Procedure.** Two kinds of experiments were performed:

(a) The measurement of the conductivity at various temperatures under oxygen or under vacuum, which allowed us to calculate an activation energy of conduction for a given state of reduction of the solid.

(b) Measurements were made of conductivity at various times in the presence of cyclohexene at various temperatures, followed by regeneration under oxygen as indicated before. All the experimental cycles were done with the same sample. The following procedure was used. The solid was first treated under O_2 (100 Torr) at 400°C during 15 min and then evacuated at the temperature chosen for the reaction. Then

cyclohexene was admitted into the reactor during a 5 min period at a pressure of 24 Torr. The evacuation was then followed by an oxygen treatment at 400°C for 15 min. It was not possible to perform kinetic measurements on the variation of resistance, since the powder was compressed between the two electrodes, and a rate-controlling diffusion process was present.

RESULTS

A. Kinetics Measurements

1. **Evolution of the rate of dehydrogenation with time.** We have plotted on Fig. 1 the rate of benzene formation versus time for 1,3-cyclohexadiene, cyclohexene and cyclohexane. After 10 sec the rate increases very rapidly to its maximum value and then decreases exponentially with time. As we have already observed with cyclohexene (2) a break has been found in the logarithmic transformation of the rate with time. The time t_0 for which this break is observed is generally between 3 and 5 min. The similarity of behavior among all the compounds suggests the same interpretation (2). The first-order rate must be related to the depletive reduction of surface oxygen of
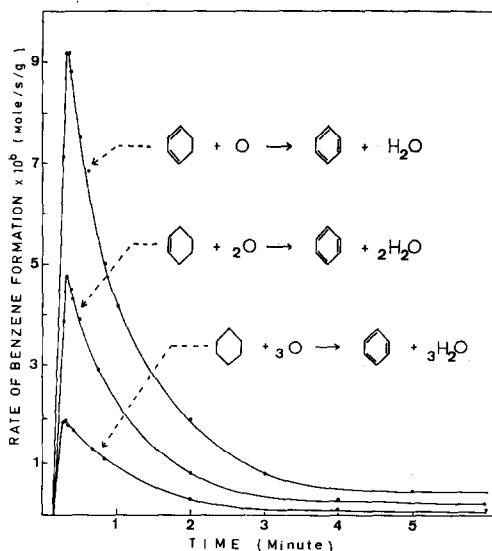
FIG. 1. Evolution of the rates with time for three organic compounds (T° = 200°C; $P_{C_6H_{10}}$ = 8 Torr; $P_{C_6H_8}$ = 8 Torr; $P_{C_6H_{12}}$ = 12 Torr).

the oxide whereas many simultaneous phenomena could occur after the break, especially slow diffusion into the micropores of the solid and bulk reduction of the oxide. We were interested here only in the first very fast reaction which is completed in a few minutes. In the following we will designate as the initial rate, the maximum rate although it might be observed not exactly at time $= 0$, but after several seconds. We have observed that the initial rate as well as the decay of the rate with time were functions of the pressure of the reactant so that the general rate equation could be expressed by the form:

$$R = KS_0 f(P) \exp[-K'g(P)t], \quad (\text{I})$$

where S is the number of oxygen sites able to react at a given temperature and with a given organic compound, $f(P)$ and $g(P)$ are functions of the pressure, K and K' are rate constants.

If we assume that the number of moles of benzene produced up to t_0 is determined by the stoichiometric equations ($1-4$) we have:

$$\int_{t=0}^{t=t_0} R \cdot dt = (1/n) \, S_0 \quad (\text{II})$$

n being the number of oxygen atoms removed by one molecule of reactant, that is 3 for cyclohexane, 2 for cyclohexene and 1 for 1,3- and 1,4-cyclohexadiene. By resolving Eqs. (I) and (II) we get the general time dependence equation:

$$R = KS_0 f(P) \exp[-nkf(P)t], \quad (\text{III})$$

which represents the variation of rate with time for the four organic compounds.

2. Variation of initial rate with pressure. A relevant result concerns the various dependencies of the pressure on the initial rate. For cyclohexadiene (Fig. 2) a first-order law is observed even at very low temperature such as 25°C. For cyclohexene, the compound which has been previously studied (2), a first-order dependency occurred, above 150°C, whereas a fractional order was observed below 120°C. For cyclohexane, (Fig. 3) such a fractional order is obtained at temperatures up to 250°C. These results could not be understood un-
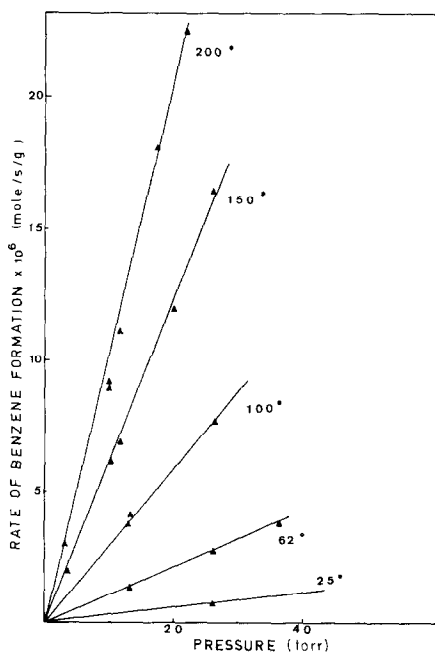

Fig. 2. 1,3-Cyclohexadiene pressure dependency on the initial rate of benzene formation at various temperatures.
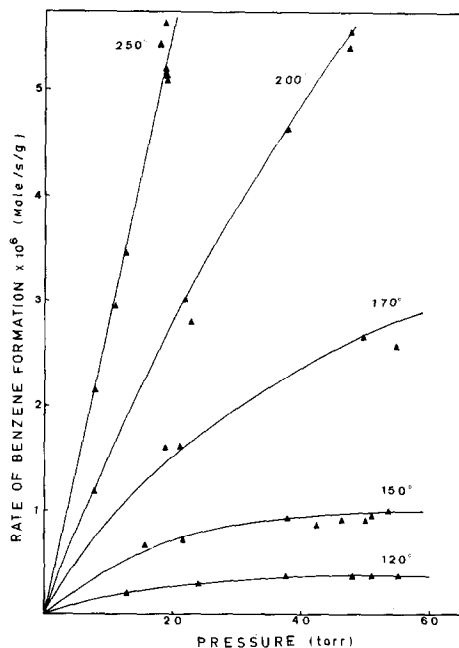

Fig. 3. Cyclohexane pressure dependency on the initial rate of benzene formation at various temperatures.
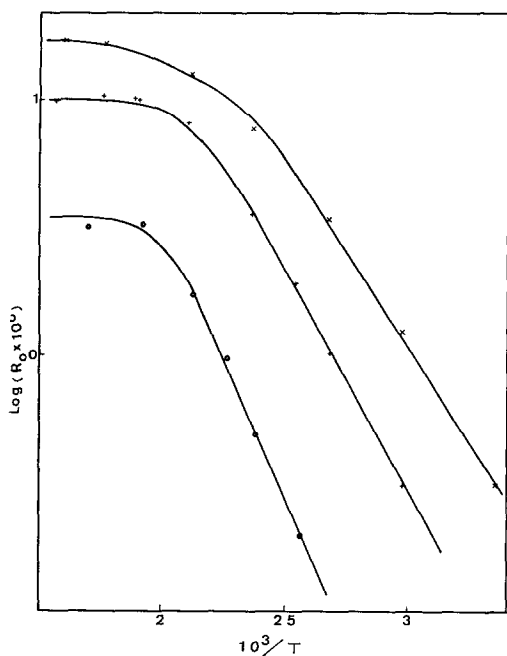
FIG. 4. Arrhenius plot of the initial rate for the order one: $\bigcirc$: cyclohexane; $+$: cyclohexene; $\times$: 1,3-cyclohexadiene.

FIG. 5. Dependency of the reaction temperature on the number of oxygen sites S_0 reacting with: $\times$: cyclohexane; or $\blacktriangle$: cyclohexene.

less the assumption is made that the number of active sites is dependent on the organic compound.

3. Variation of initial rate with temperature. In Fig. 4 the temperature dependency for a first-order process is plotted. For all the compounds a break is observed in the Arrhenius plot above 200°C. At high temperatures the initial rate is almost independent of the temperature and the apparent activation energy is close to 0 kcal/mole. Below 200°C the apparent activation energy decreases in the order:

cyclohexane,	cyclohexene,	1,3- or 1,4-cyclohexadiene
(11 kcal/mole)	(8 kcal/mole)	(7.3 kcal/mole)

4. Number of oxygen sites S_0. The number of moles of oxygen removed during the fast surface reduction can be easily calculated from our kinetic data (2). This number S_0 varies with the temperature of reaction and with the organic compound (Fig. 5). For cyclohexane, S_0 increases from 100 to 200°C and then stabilizes at a value of 1.8 $O^{2-}/100 \text{ Å}^2$. This value corresponds
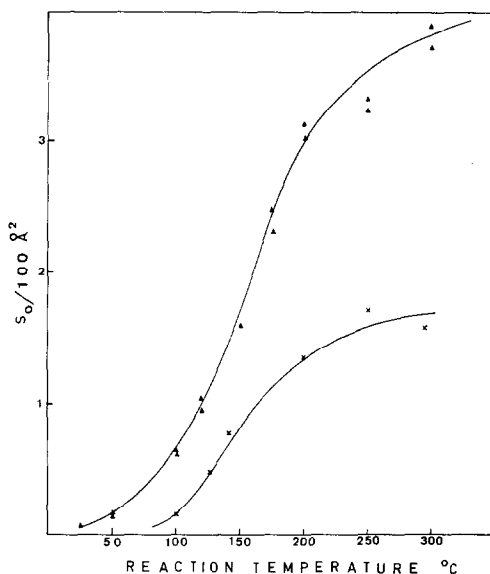
roughly to $\frac{1}{4}$ of the total surface oxygen available on a γ pyrolusite (9). With cyclohexene S_0 maximum is equal to 4 $O^{2-}/100 \text{ Å}^2$. It is interesting to point out that an Arrhenius plot of S_0 follows the same pattern as that of the initial rate. This fact already observed for cyclohexene is general: the specific activity R_0/S_0, that is the activity per site, seems to be completely temperature independent.

5. Variation of initial rate with hydrocarbon structure. The influence of the structure of the organic compound on the rate is illustrated in Table 1. We have represented the ratios of the rate of benzene formation from the various compounds, at a given pressure and for various temperatures. Many conclusions may be drawn from this table.

The same rates obtained with 1,3- and 1,4-cyclohexadiene show that the position of the double bond has no effect on the rate of oxidative dehydrogenation. A second very significant result concerns the ratios R_3/R_2 and R_4/R_2 which tend to a value of

TABLE 1

RATIOS OF THE RATES OF BENZENE FORMATION[a]

Temperature (°C)	R_1/R_2	R_3/R_4	R_4/R_2	R_3/R_4
62	—	4	4.3	0.91
100	—	3.7	—	—
120	0.09	—	—	—
150	0.14	2.04	2.0	0.99
200	0.26	1.81	—	—
300	0.42	1.95	2.03	0.96

[a] Starting from cyclohexane (R_1), cyclohexene (R_2), 1,3-cyclohexadiene (R_3), 1,4-cyclohexadiene (R_4). Pressure of the reactants: 10 Torr.

2 for temperatures higher than 200°C. This value is the inverse of the ratio of the oxygens involved in reaction (3) and (2) or (4) and (2). This would indicate, as we already supposed (2), that the availability or the activation of the oxygen sites is the rate-determining step. If we suppose that the solid can release X atoms of oxygen per second, $1 X$ or $2 X$ sec will be required to produce one molecule of benzene starting, respectively, from cyclohexadiene or from cyclohexene.

Numerous experiments were performed in order to detect the presence in the gaseous phase of intermediate compounds such as cyclohexene and cyclohexadiene when the reactant was cyclohexane. A drastic decrease of the contact time did not bring about any change of the products of the reaction. Intermediate unsaturated compounds, if produced, did not appear in appreciable amount in the gaseous phase and exist only in the adsorbed state.

Some experiments were done with a constant partial pressure of water in the stream to investigate the possible inhibition of the reaction by water (7). A slight increase of the rate (lower than 5%) was observed, however this did not appear to be significant.

B. Electrical Conductivity Measurements

Our powder was shown to be an n-type semiconductor by the polarity of the Seebeck effect. This kind of conductivity is usually related with a surface oxygen deficiency (10).

TABLE 2

ACTIVATION ENERGY OF CONDUCTION OF MnO_2 AFTER VARIOUS TREATMENTS

| Treatment	E_C (eV)
400°C under O_2 (100 Torr)	0.25
400°C under vacuum (10^{-5} Torr)	0.30
100°C under cyclohexene 5'	0.335
290°C under cyclohexene 5'	0.455
Regeneration under O_2 at 400°C	0.265

Most of the experiments are summarized in Table 2.

1. After treatment at 400°C under 100 Torr O_2, the activation energy for electrical conduction was found to be 0.25 eV. After evacuation at 400°C we observed a slight increase of E_C (0.30 eV) and the initial value of 0.25 eV was easily restored by treatment under oxygen. If we assume that the evacuation only removes a few oxygen atoms from the surface, E_C should decrease, which was not observed. To explain such an increase of E_C on an n-type semiconductor we must therefore admit that the removal of these oxygens brings about the formation of a new crystalline oxide which is likely Mn_2O_3 (7).
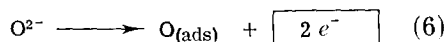
The relationship $R = R_0 \exp (E_C/KT)$ characterizes the transfer of electrons from the donor level to the conduction band (energetic gap $\epsilon = 2 E_C$):

$$\boxed{2\,e^-} \longrightarrow \boxed{} + 2\,e^- \quad (5)$$

In fact this relationship is valid for a given number of vacancies

$$\boxed{2\,e^-}$$
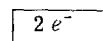
that is, for a given state of reduction. The number of vacancies corresponding to the reaction:

$$O^{2-} \longrightarrow O_{(ads)} + \boxed{2\,e^-} \quad (6)$$

is a function of the temperature and of the partial pressure of O_2, and is involved in the expression of R_0.

2. In the reaction of cyclohexene with MnO_2, the following results were obtained:
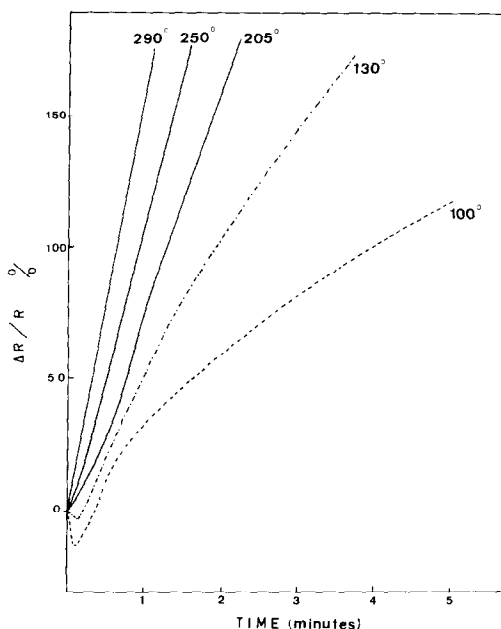(a) With the exception of the first cycle

FIG. 6. Variation of the resistance of MnO_2 with time after treatment with cyclohexene (24 Torr) at various temperatures.

of reduction and oxidation, a catalyst reduced by cyclohexene at temperatures lower than 300°C recovers its initial conductivity and its activation energy of conduction in a few minutes by a treatment at 400°C under oxygen. The standard value of E_C which was obtained (0.265 eV) is slightly higher than that of the initial solid (0.25 eV). This is in agreement with our kinetic results: except for the first run, a treatment at 400°C under oxygen restores completely the initial activity of the solid.

(b) As indicated on Fig. 6. during the reaction of cyclohexene with MnO_2, the resistance first decreases, passes through a minimum after 8 sec and then increases. On an n-type semiconductor, the decay of the resistance means that electrons are released to the solid according to the scheme:

$$2\,O^{2-} + \bigcirc \longrightarrow \bigcirc + 2H_2O + 4e^- \quad (7)$$
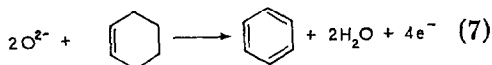
The later increase of the resistance must be due to the change of the energy level scheme following the transformation of the surface into a new crystalline form. For temperatures higher than 200°C this allotropic transformation is so fast that we could not observe the first decay.

(c) During the evacuation, following the treatment by cyclohexene, the resistance slightly increased. It is likely that some cyclohexene was adsorbed on the surface without formation of benzene and that this adsorption was reversible.

(d) The reduction of the solid produced a marked increase of the activation energy of conduction. When the temperature and the reduction time do not exceed 290°C and 5 min respectively, the limiting value of E_C is 0.455 eV, much higher than that obtained after evacuation of the initial βMnO_2 at 400°C (0.30 eV). The number of oxygen atoms released is therefore much higher after a treatment with cyclohexene than with vacuum. It is mainly the organic compound which removes the surface oxygen of the solid, and it is impossible to distinguish between the following two equations:

$$O^{2-} \longrightarrow O_{(ads)} + \boxed{2\,e^-} \quad (6)$$

$$2O_{(ads)}^+ \quad \bigcirc \longrightarrow \bigcirc + 2H_2O \quad (8)$$
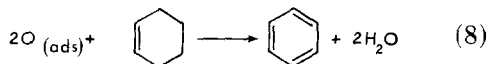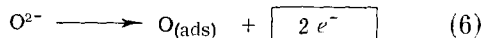
DISCUSSION

The purpose of this work was to determine the rate-determining step of the surface reduction of MnO_2 by various cyclic compounds.

The first significant result concerns the variation of order with respect to the hydrocarbon. At a given temperature and for a given pressure (e.g. at 120°C and for a pressure of 50 Torr) this order increases from 0 for cyclohexane to a fractional power for cyclohexene and to unity for cyclohexadiene. A possible explanation for this variation would be that a physical adsorption is the precursor to the surface reduction and the P/P_0 could vary from one compound to the other, even though the four organic compounds used are very similar, and their vapor pressures, P_0, are

almost identical in a large range of temperatures.

It must be pointed out, too, that for a given compound the order increases from a fractional value (Langmuir type) to unity (Rideal type) when temperature increases. This phenomenon is quite pronounced for cyclohexene—in the temperature range 120–150°C—and for cyclohexane—in the temperature range 200–250°C.

In conclusion, a Langmuir model is valid either for low temperature and fairly reactive compounds or for rather high temperatures and weakly reactive compounds. A Rideal–Eley model predominates at any temperature for highly reactive compounds and at high temperature for weakly reactive compounds. For a highly reactive compound such as cyclohexadiene, the energy gap to the activated complex with surface oxygen ions will be small, so that a large amount of this oxygen will be activated, and the probability of a gaseous molecule striking such an oxygen will be high and a Rideal mechanism will be likely. For a weakly reactive compound, the energy gap being very high, this probability is small so that an adsorption equilibrium is more likely to be observed.

A second interesting point, although already considered in the preceding paragraph, concerns the temperature dependency of the number of reactive oxygens S_0, so that the activation energy deduced from R_0/S_0 is zero for all these organic compounds. The question is: Are the oxygens activated by the temperature, or are they activated under the influence of the organic compound? The first hypothesis would be to assume that a given amount of adsorbed oxygen would exist at a given temperature, the number of which would be determined by the enthalpy variation of the reaction:

$$O^{2-} \longrightarrow O_{(ads)} + \boxed{2\,e^-} \qquad (6)$$
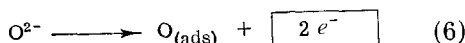
The rate-determining step would then be the surface diffusion of this adsorbed oxygen to the adsorbed reactant. Our electrical conductivity measurements, however,

indicate that it is the organic compound itself which activates the surface oxygen and this reaction involves an electron transfer. This hypothesis finds corroboration in the fact that the surface concentration of reactive oxygen depends on the nature of the organic compound.

It is possible to visualize the reactivity of the oxygen ion towards the organic compound, and the variations of S_0 with temperature in the following way. Let us assume a heterogeneous surface of manganese dioxide (12) corresponding to a Gaussian distribution of energy with a rather high standard deviation for the surface oxygen ions (Fig. 7). When the temperature increases the number of O^{2-} ions having a high energetic state increases. The same phenomenon occurs for the energetic state E_1 of the C–H bond of the organic compound, although the standard deviation is smaller. If E_A is the heat of formation of the activated complex (e.g., C – – – H – – – O – – –), we can easily observe on Fig. 7 that all the O^{2-} ions having an energetic state higher than E_A–E_1 will react so that the number of reacting sites will be S_0 as indicated on the dotted area of the graph. When the temperature increases E_A–E_1 will decrease so that S_0 will reach a plateau for a temperature T_3. There-
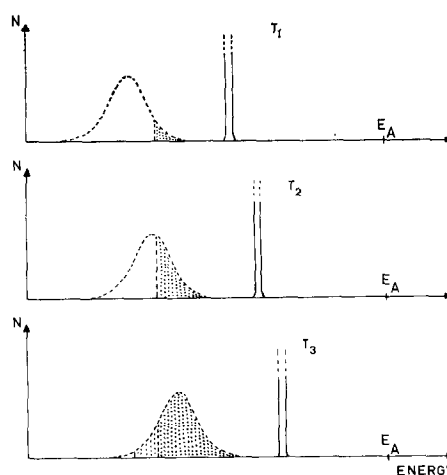

FIG. 7. Number of O^{2-}–solid bond or C–H bond having the energetic state E. E_A is the heat of formation of the activated complex between C–H– –O. The dotted area represents the O^{2-} ions able to react at a temperature T $(T_1 < T_2 < T_3)$.

fore, there will be a temperature for which all surface oxygen atoms will react and the apparent activation energy will be zero. However, it does not mean that there is no energy barrier for the organic compound, as previously supposed $(3, 4)$.

In conclusion, the rate-determining step is the formation of an activated complex, which is in fact the activation of the surface oxygen under the influence of the organic molecule. We can assume the following mechanism:
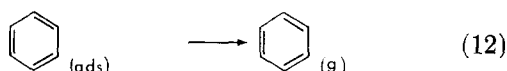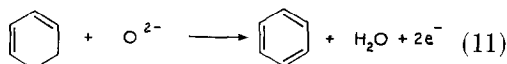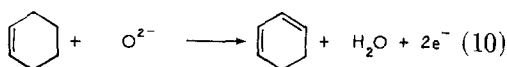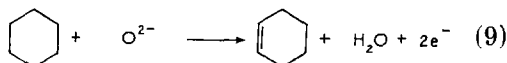
Reactions (9–11) would be rate determining, and the slow step of each one would be the activation of O^{2-} under the influence of a C–H group.

REFERENCES

1. MARS, P., AND VAN KREVELEN, D., *Chem. Eng. Sci.* 3, 41 (1954).
2. BASSET, J. M., AND GRAYDON, W. F., *J. Catal.* 20, 383 (1971).
3. WOLKENSTEIN, F. F., *Z. Fiz. Khim.* 23, 917 (1949).
4. TAYLOR, H. A., AND THON, N., *J. Amer. Chem. Soc.* 74, 4169 (1952).
5. GARNER, W. E., *in* "Advances in Catalysis" (W. G. Frankenberg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 9, p. 169. Academic Press, New York, 1957; PEACOCK, J. M., PARKER, A. J., ASHMORE, P. G., AND HOLKEY, J. A., *J. Catal.* 15, 387 (1969).
6. KLIER, K., *J. Catal.* 8, 272 (1967).
7. BROOKS, C. S., *J. Catal.* 8, 272 (1967); *J. Catal.* 4, 535 (1965).
8. ARGHIROPOULOS, B. M., AND TEICHNER, S. J., *J. Catal.* 3, 477 (1964).
9. PRALIAUD, H., Thèse, Lyon (1970).
10. BREDY, G., Thèse, Lyon (1967); CLARK, H., AND BERETS, D. J., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 9, p. 294. Academic Press, New York, 1957; WELLER, W., AND VOLTZ, S. E., *ibid.*, p. 215.
11. CHARACHORIN, F., AND ELOVITCH, S. T., *Acta Fiz. Khim. SSR* 5, 326 (1936).
12. PEACOCK, J. M., PARKER, A. J., ASHMORE, P. G., AND HOLKEY, J. A., *J. Catal.* 15, 398 (1969).