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# The Joint Application of Flow-System and Micropulse Techniques for a Comparative Study of 2-Propanol Decomposition over MgO, CaO and SrO

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MgO, CaO and SrO were prepared by the same procedure from pure hydroxides. Flow-system catalytic activity measurements of 2-propanol decomposition were carried out at various temperatures and pressures of alcohol. Over each oxide the only reaction to occur was dehydrogenation. The kinetic parameters of the process, determined from the relation $W = A \cdot e^{-E/RT} \cdot p^n$, were:

| | $A$ <br> ($mol_{H_2}\ m^{-2}\ s^{-1}$) | $E$ <br> ($kcal\ mol^{-1}$) |
|---|---|---|
| MgO | 2.69 | $24.7 \pm 1.8$ |
| CaO | $6.17 \times 10^4$ | $37.3 \pm 0.2$ |
| SrO | $8.91 \times 10^3$ | $32.5 \pm 0.2$ |

The order of the reaction was zero in each case.

To supplement the above measurements micropulse experiments were carried out using pulses of the reactant smaller than required for monolayer covering of the BET surface. The main conclusions obtained by this technique were:

a. The lack of dehydration activity is not a consequence of dehydration sites being blocked by water, since there was no detectable amount of propylene, even in the first pulses desorbing from the surface.

b. With MgO it is the alcohol, while with CaO and SrO the acetone that adsorbs strongly, blocking a considerable amount of the originally active surface (which itself is a smaller part of the total BET surface only).

A semiquantitative calculation is performed to explain the results on the basis of a likely mechanism.

## INTRODUCTION

The catalytic decomposition of 2-propanol over alkaline earth oxides and many other surface properties of these catalysts have been thoroughly studied. One can find a summary of the activity data, obtained until 1966, in a handbook edited in the USSR (*1*). There are some later works, as well (*2,3,11*). General trends of catalytic activity on various oxides are outlined in the book by Krylov (4). In the discussion below, some of these studies are discussed in detail. Some common shortcomings of them can be summarized as follows;

i. One cannot use the data of various authors for a reliable comparison of the activity of different oxides, since the origin of the samples has a great influence on catalytic properties (*2*).

ii. In most cases little care was paid to avoid the building-in of traces of foreign ions and that of $CO_2$, though carbonate impurity may cause dehydration activity (*5*), too.

iii. The activity data so far available need to be completed by kinetic analysis, since with CaO and SrO the effect of alcohol pressure has not been studied, and besides, the measurements were carried out at too large conversions.

The present study had been undertaken in order to compare the catalytic activity of very pure MgO, CaO, and SrO prepared by the same procedure, on the basis of a kinetic analysis of activity data, measured in a broader range of temperature and alcohol pressure than hitherto. In addition, the advantages of the joint application of the flow-system and micropulse techniques are demonstrated.

There are a great number of pulse technique results throughout the literature. The method applied in the present work has a special character; the quantity of the substance introduced as a pulse was in each case less than that necessary for monolayer covering of the adsorbent. This method, which takes into account the "stoichiometry" of the reactant–adsorbent interaction, provides more intimate information about the surface and the processes occurring on it than when larger pulses are used.

In this paper we refer to the method as the "submonolayer micropulse technique." Its significance has already been recognized by other authors [see, e.g., Ref. (*12*)].

## EXPERIMENTAL PROCEDURE

### Catalysts

The samples were prepared from pure hydroxides purified by recrystallization from conductivity-water. The hydroxides were decomposed in a stream of purified nitrogen. The phase identity and purity were checked by thermal analysis and emission spectroscopy.

Special attention (dry-box technique) was paid to avoiding the formation of surface carbonate not only during preparation but also during storage and usage of the samples.

BET surface areas were measured by adsorption of nitrogen at the temperature of liquid nitrogen (Table 1).

### Apparatus

The catalytic activity was measured in a flow microreactor combined with a Carlo-Erba gas chromatograph in a stream of pure nitrogen. The carrier gas passed through the saturator filled with distilled 2-propanol. The saturator was placed in a

TABLE 1
DATA OF CATALYSTS AND ACTIVITY MEASUREMENTS

| | Data of catalysts | | Data of flow-system catalytic activity measurements | | | Pulse to surface ratio in micropulse experiments | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Hydroxide decomp. temp[a] (°C) | BET Surface area ($m^2/g$) | Range of temp (°C) | Range of alcohol pressure (Torr) | Max conversion (%) | Wt of sample (g) | Vol of alcohol pulse ($\mu$l) | % Coverage of surface |
| MgO | 450 | 127 | 270–330 | 25–80 | 0.25 | 0.20 | 1.0 | 8.6 |
| CaO | 500 | 30 | 318–380 | 20–80 | 1.93 | 0.35 | 1.0 | 20.4 |
| SrO | 750 | 4 | 320–380 | 24–80 | 9.70 | 0.50 | 0.5 | 72.4 |

[a] These temperatures were chosen to guarantee a complete decomposition of the hydroxides with approximately the same surface concentration of residual water over the prepared oxides.

thermostat and the pressure of alcohol was controlled by the temperature of the thermostat. For the range of temperature and pressure used, see Table 1.

To standardize the flow conditions the oxides were diluted 1:10 with glass powder. Data for gas chromatographic analysis were as follows:

Carrier gas: $N_2$; rate of flow: 1 ml/s; column: 15% Carbowax 1500 on Chromosorb-P; length: 2 m; diameter: 2 mm; temperature: 120°C; detector: heat conductivity cell.

For the submonolayer micropulse experiments the same apparatus was used with appropriate transformations. The experimental arrangement was similar to that used by Gáti and Knözinger (*6*).

## RESULTS

### Flow-System Measurements

It turned out that only dehydrogenation took place on each of the three oxides and no dehydration or other side reactions (e.g., forming of mesityl oxide or cracking) were detectable.

The activity data, given in Table 2, show a nondependence of activity on the pressure of alcohol, i.e., a zero order kinetics. Thus the reaction rate can be expressed as $W = A \cdot e^{-E/RT}$. The velocities belonging to different alcohol pressures and the same temperature were averaged. The Arrhenius parameters were estimated after linearization by the method of weighted least squares. The rounded values of the ratio "average velocity to range of velocities" served as weighting factors at each temperature. For calculating the limits of Arrhenius constants 0.05 was chosen as the level of significance. The results are given in Table 3.

It is interesting to note that comparison of various catalysts through checking their catalytic activity measured at one selected temperature can be misleading. The preex-

TABLE 2

DATA OF FLOW-SYSTEM ACTIVITY MEASUREMENTS

| Catalyst | $p$ (Torr) | $t$ (°C) | $W$ (mole/m$^2$ s × 10$^9$) |
|---|---|---|---|
| MgO | 25 | 270 | 0.40 |
| | | 290 | 0.70 |
| | | 309 | 1.58 |
| | | 330 | 3.39 |
| | 40 | 270 | 0.35 |
| | | 290 | 0.63 |
| | | 311 | 1.46 |
| | | 330 | 2.82 |
| | 60 | 270 | 0.39 |
| | | 289 | 0.67 |
| | | 310 | 1.59 |
| | | 330 | 3.56 |
| | 80 | 270 | 0.32 |
| | | 290 | 0.62 |
| | | 312 | 1.22 |
| | | 331 | 2.45 |
| CaO | 20 | 318 | 1.33 |
| | | 342 | 3.08 |
| | | 360 | 7.44 |
| | | 378 | 20.60 |
| | 40 | 323 | 1.44 |
| | | 342 | 2.42 |
| | | 361 | 5.03 |
| | | 381 | 21.90 |
| | 60 | 323 | 1.40 |
| | | 340 | 2.86 |
| | | 361 | 7.78 |
| | | 380 | 20.30 |
| | 80 | 318 | 1.12 |
| | | 342 | 2.99 |
| | | 360 | 6.11 |
| | | 380 | 20.36 |
| SrO | 24 | 320 | 9.19 |
| | | 341 | 19.90 |
| | | 360 | 35.90 |
| | | 381 | 124.30 |
| | 40 | 323 | 11.70 |
| | | 340 | 20.60 |
| | | 361 | 36.60 |
| | | 380 | 139.40 |
| | 60 | 320 | 10.41 |
| | | 339 | 23.20 |
| | | 361 | 59.70 |
| | | 380 | 139.40 |
| | 80 | 322 | 11.70 |
| | | 340 | 21.20 |
| | | 360 | 37.10 |
| | | 382 | 135.70 |

TABLE 3
RESULTS OF STATISTICAL EVALUATION OF FLOW-SYSTEM ACTIVITY DATA

| Catalyst | Log $A$ | $A$ (mole/m$^2$ s $\times$ 10$^9$) | Range of $A$ | $E$ energy of activation (kcal/mol) | $S_{Y/X}$ variance of regression |
|---|---|---|---|---|---|
| MgO | $9.43 \pm 0.69$ | $2.69 \times 10^9$ | $5.49 \times 10^8$–$1.32 \times 10^{10}$ | $24.7 \pm 1.8$ | $5.09 \times 10^{-2}$ |
| CaO | $13.79 \pm 0.63$ | $6.17 \times 10^{13}$ | $1.45 \times 10^{13}$–$2.63 \times 10^{14}$ | $37.3 \pm 0.2$ | $1.56 \times 10^{-2}$ |
| SrO | $12.95 \pm 0.77$ | $8.91 \times 10^{12}$ | $1.51 \times 10^{12}$–$5.25 \times 10^{13}$ | $32.5 \pm 0.2$ | $5.71 \times 10^{-2}$ |

ponential factor and the energy of activation may compensate each other and the sequence of the activity of the samples may be a function of temperature.

In our case this was the situation with respect to MgO and CaO (Table 4). The reactivity values shown here were calculated from the data of Table 3. SrO is the most active at each temperature but the relative difference between CaO and SrO decreases at elevated temperatures.

This means that the deductions regarding the dependence of catalytic behavior on properties of solid substances, based upon reactivity tests performed at one selected temperature [e.g., in Krylov's book (*4*)] are to be accepted only with some criticism.

## Results of the Micropulse Technique Experiments

### *Dehydration Activity*

The first question to answer by the submonolayer micropulse technique concerned the lack of dehydration activity. It was necessary to establish whether the first portion of alcohol can be dehydrated as well and whether it is one of the products (water) that poisons the surface hindering the further dehydration, or whether this reaction-route of dehydration is impossible from the very beginning. Two sets of experiments were performed.

TABLE 4
ACTIVITY AS A FUNCTION OF TEMPERATURE

| | $W$ (mol/m$^2$ s $\times$ 10$^9$); temp (°C): | | | | | |
|---|---|---|---|---|---|---|
| Sample | 275 | 300 | 325 | 350 | 375 | 400 |
| MgO | 0.26 | 1.02 | 2.52 | 5.79 | 12.53 | 25.45 |
| CaO | 0.08 | 0.36 | 1.43 | 5.05 | 16.16 | 47.12 |
| SrO | 0.98 | 3.60 | 11.76 | 35.20 | 97.05 | 246.59 |

The irreversibly adsorbed quantity of water was measured by our "follow-up" procedure (*7*) over the temperature range of the catalytic measurements. It turned out that at 300°C MgO adsorbs water weakly: less than 5% of its BET surface is covered by water. With CaO and SrO, on the other hand, a complete bulk rehydration of the oxides takes place. These oxides can irreversibly absorb 4–5 monolayers of water without any sign of saturation, and retain it at temperatures below the decomposition temperature of the bulk hydroxide.

The other source of information concerning this question was the measurement of the change of catalytic activity in the course of injecting subsequent micropulses of alcohol. In these experiments no propylene was detectable, not even after the first pulse. Summarizing these facts one can state: the inability of these oxides to dehydrate 2-propanol is an intrinsic property and not a result of being poisoned by products, though this process could readily take place on CaO and SrO.

### *Change of Activity from the Initial to the "Stationary" Value*

The investigations of the change of activity in the course of injecting subsequent pulses of alcohol have shown two interesting phenomena. In each case a continuous change of activity was found from an initial to a "stationary" value, but the trend of this change was different for MgO and for the other two oxides. For MgO there was an increase, while for CaO and SrO a decrease of activity occurred in the course of the first 5–6 pulses (Fig. 1). The initial to stationary state ratio of activity was 0.49 for MgO (at 310°C), while for CaO and SrO (at 350°C) it was 4.20 and 4.25, respectively. Performing these experiments at various temperatures which comprised the range of flow-system activity measurements, these ratios turned out to be nearly constant. The other interesting phenomenon observed was that in the first pulse issuing from MgO there was no alcohol detectable, but in the next pulses its quantity slowly increased (Table 5).

Comparing data of Table 5 with those of Table 1 it turns out that some 16% of the BET surface is blocked by alcohol.

For CaO and SrO there was a similar situation but with respect to acetone. The

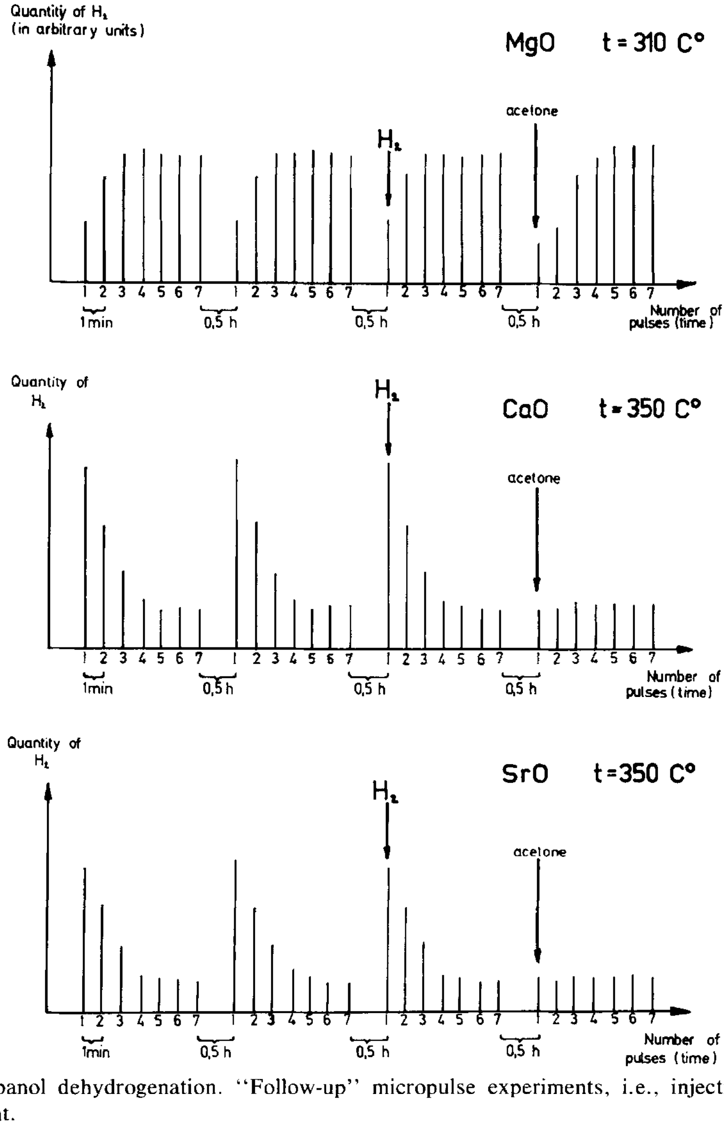

FIG. 1. 2-Propanol dehydrogenation. "Follow-up" micropulse experiments, i.e., injection of successive pulses of reactant.

TABLE 5
MATERIAL BALANCE OF ACTIVITY MEASUREMENT OVER MgO AT 310°C USING THE "FOLLOW-UP" PROCEDURE

| No. of pulse | Quantity of alcohol ($\mu$mol)<br>Desorbed unchanged | Transformed into acetone | Remained at the surface[a] |
|---|---|---|---|
| 1 | 0.0 | 1.60 | 11.48 |
| 2 | 2.56 | 2.80 | 7.72 |
| 3 | 6.32 | 3.33 | 3.43 |
| 4 | 8.16 | 3.36 | 1.56 |
| 5 | 9.76 | 3.28 | 0.04 |
| 6 | 9.80 | 3.28 | 0.00 |
| 7 | 9.80 | 3.28 | 0.00 |
| Sum | | | 24.23 |

[a] Calculated, considering that the injected pulse contained 13.08 $\mu$mol of 2-propanol.

irreversibly adsorbed quantity of acetone calculated from material balance was, respectively, 8.9 and 0.41 $\mu$mol, that is some 13.5 and 3.4% of the quantity necessary for monolayer covering.

These experiments were repeated after preadsorption of $H_2$ and acetone. It was found that hydrogen had no effect, and acetone had a slight decreasing effect for MgO and a very marked effect for CaO and SrO. After preadsorption of acetone on these latter oxides the earlier measured stationary activities were obtained at once (Fig. 1).

These observations can be explained by strong adsorption of alcohol on MgO and strong adsorption of acetone on CaO and SrO.

At the surface of MgO there may be sites that adsorb 2-propanol without decomposing it. Injecting alcohol to the pure surface we obtain a small activity since a considerable part of the alcohol is retained to saturate these sites. As these are more and more saturated, more and more alcohol occupies reactive sites and can decompose (the activity increases). At the same time, more and more alcohol is detectable in the exit pulses coming from the sample.

At the surface of CaO and SrO there are sites which are able to decompose 2-propanol but they adsorb acetone very tightly. When a pulse of alcohol is introduced to the clear surface the activity is high but decreases as a greater and greater fraction of the surface is poisoned by acetone. In the course of this process more and more acetone can desorb from the oxide.

Comparing the quantities of irreversibly bonded alcohol on MgO, and acetone on CaO and SrO, with the initial to stationary ratio of activities, we can conclude on the bases of the above interpretation:

With MgO not more than 84% of the BET surface operates in the steady state;

With CaO 17.7% of the BET surface is originally active but in the steady state only 4.2% of it operates;

With SrO some 4.4% of the BET surface is active at the beginning and only 1% of it works in the steady state.

The method of calculating the above values for CaO and SrO was as follows. Let $S_{\mathrm{BET}}$ stand for the whole BET area of the adsorbent and $S_0^*$ and $S_\infty^*$ stand for the active surfaces working originally and in the steady state, respectively. Let $\theta_{\mathrm{Ac}}$ denote the surface area covered with acetone in the steady state, as a percentage of the whole BET area. Let $W_0$ and $W_\infty$ denote the activities measured over clean surfaces and surfaces in equilibrium, respectively, and let their ratio $W_0/W_\infty$ be $r$. Then,

$$S_0^* = k\, S_{\mathrm{BET}},$$

where $k$ is a constant, and

$$S_\infty^* = S_0^* - \text{(area covered with acetone)}$$
$$= S_0^* - 10^{-2}\,\theta_{\mathrm{Ac}}\, S_{\mathrm{BET}}.$$

Also

$$W_0 = \text{const. } S_0^*$$

and

$$W_\infty = \text{const. } S_\infty^*.$$

Thus

$$r = S_0^*/S_\infty^*$$

whence

$$k = 10^{-2}\,\theta_{\mathrm{Ac}}/\left(1 - \frac{1}{r}\right).$$

The originally active part of the surface as a percentage of the whole BET area is $10^2 \cdot k$. Thus the fraction of the surface working in the steady state, expressed as a percentage of the whole BET area, is $10^2(k - 10^{-2}\,\theta_{\mathrm{Ac}})$.

## DISCUSSION

### *1. Comparison of the Present Data with Some Earlier Results*

On MgO Slinkin and co-workers (*8*) have observed a 93.3% selectivity in favor of dehydrogenation and the rest of the products were unsaturated substances (5.6%) and products of cracking ($CO_2$ and CO). They worked in the temperature range 320–360°C so this small extent of a side reaction is not in contradiction with the 100% dehydrogenation found by us at some 40°C lower. The energy of activation measured by them (22.8 kcal/mol) seems to be identical with 24.7 ± 1.8 kcal/mol given in the present work. They did not publish the dimension of their activity data. Thus their preexponential factors cannot be compared with those presented here.

De Vleesschauwer (*11*) investigated a series of MgO samples prepared by thermal decomposition of $MgCO_3$ at various temperatures. He observed parallel dehydrogenation and dehydration of 2-propanol over these substances. It turned out that the higher the temperature of preparation the higher is the selectivity in favor of dehydrogenation. This suggests—in accordance with differential-isotope data of Krylov and Fokina (*5*) concerning the same reaction over CaO—that the dehydration is caused by surface carbonate centers. It is understandable on this basis that the reaction order measured by de Vleesschauwer (between 0 and 1) differs from that obtained here (constantly zero order). As De Vleesschauwer concludes, the variable order of reaction can be explained by the assumption of variable adsorption of 2-propanol on the active sites of the catalyst surface, probably in competition with the oxygen-containing reaction products. Our samples being quite free of carbonate they did not catalyse dehydration and the lack of strongly adsorbed water ruled out the competition of alcohol for the active sites.

The absolute values of the rate constant agree within an order of magnitude. There is a greater difference between the values of the energy of activation (De Vleesschauwer obtained 34.9 kcal/mol).

Krylov and his co-workers (*10*) have studied the decomposition of 2-propanol over CaO, SrO, BaO, $Ca(OH)_2$, $CaCO_3$ and $BaCO_3$. The catalytic activity was measured in a stream of air in the temperature range 310–450°C. Their results are in contradiction with the present data at two points: they found a significant dehydration, especially at elevated temperatures, and they measured a much smaller energy of activation for the dehydrogenation (12.0 kcal/mol for CaO and 11.0 kcal/mol for SrO). The dimension of the activity being not given the preexponential factor is thus again not calculable. The low energy of activation suggests that some transport process might control the activity at these measurements.

### *2. Conclusions Derived from the Results of the Joint Application of Flow-System and Submonolayer Micropulse Technique*

The results of the micropulse technique experiments show that in the steady state a part of the surface is blocked; thus the flow-system data have to be corrected. This correction involves only the preexponential factor. For MgO where the active surface

$$F' \leqslant 0.84\, F_{\mathrm{BET}},$$

$$A' \geqslant \frac{1}{0.84} A \geqslant 3.20 \text{ mole/m}^2 \text{ s},$$

where $A'$ is the corrected value of $A$. For CaO

$$F' = 0.042\, F_{\mathrm{BET}},$$
$$A' = 1.469 \times 10^6 \text{ mol/m}^2 \text{ s};$$

for SrO

$$F' = 0.01\, F_{\mathrm{BET}},$$
$$A' = 8.91 \times 10^5 \text{ mol/m}^2 \text{ s}.$$

In the general case these corrections are a function of temperature and not $A$ itself but the reaction rates, measured at each temperature, are to be corrected. This correction can be taken now as a constant, since pulse experiments performed at various temperatures showed little variance of the initial to stationary ratio of the activities.

The joint application of the two techniques show furthermore that the Arrhenius parameters obtained for MgO and for the other two oxides refer to different steps of the surface process. On MgO it is probably the surface reaction and on CaO and SrO the desorption of acetone which controls the reaction rate.

### 3. *The Interpretation of the Arrhenius Parameters on the Basis of a Mechanism Suggested for a Similar Case*

Kibly and Hall (9) have studied the dehydrogenation of alcohol over hydroxyapatite catalysts and on the basis of a very rich experimental material they propose a mechanism which is acceptable in our case, too. According to this idea the active ensemble consists of two adjacent metal ions and a basic $O^{2-}$ ion of the surface. The surface steps are as follows:

1. The alcohol chemisorbs over one of the metal ions, the alcoholic hydrogen dissociates as $H^+$ to the $O^{2-}$ transforming it into $OH^-$ and the alcohol transforms into an alkoxide carbanion.
2. The alkoxide carbanion gives a $H^-$ ion from its $\alpha$-carbon to an adjacent metal ion and transforms into an adsorbed acetone molecule.
3. Surface $H^+$ and $H^-$ ions unite yielding $H_2$ which easily desorbs.
4. The adsorbed acetone desorbs.

Let us suppose that this mechanism is valid for all the three oxides, but with different rate controlling steps. For MgO step 2, while for CaO and SrO step 4, may be the rate controlling one. Besides the pulse technique data this idea is supported by the energy of activation on MgO, since with hydroxyapatite Kibly and Hall (9) found step 2 to be rate controlling with an energy of activation 22 ± 2 kcal/mol, which is identical with the value obtained in the present investigations. This identity is understandable since the only difference between the two cases is that over hydroxyapatite it is a surface $Ca^{2+}$ while at MgO a $Mg^{2+}$ that accepts the $H^-$ ion. The identity of energies of activation means that not this bond formation but the breaking of the C–H bond in the surface carbanion is determining the energy profile of this step and this idea is readily acceptable.

How can the preexponential factor of CaO and SrO be explained on this basis? The corrected values for these oxides have been calculated and let us consider that these constants involve two quantities: the surface concentration of acetone ($C_{\mathrm{Ac}}$) and frequency factor ($k_0$). $A' = C_{\mathrm{Ac}} \cdot k_0$. The value of $k_0$ can be taken as the frequency of the valence vibration of the oxygen–metal bond of the adsorbed acetone. In the lack of exact ir data we can fix only a range for $k_0$:

$$5 \times 10^{12} \leqslant k_0 \leqslant 10^{14} \text{ s}^{-1}.$$

A knowledge of the exact value could not help much more, since we have seen (Table 3) that $A$ itself is rather uncertain.

One can thus calculate a lower and an upper limit for the surface concentration of acetone:

$$C_{\mathrm{Ac(min)}} = \frac{A'_{\mathrm{min}}}{k_{0(\mathrm{max})}} \text{ and } C_{\mathrm{Ac(max)}} \frac{A'_{\mathrm{max}}}{k_{0(\mathrm{min})}}.$$

Therefore, for CaO,

$$8.20 \times 10^{-9} \text{ mol/m}^2 \leqslant C_{\mathrm{Ac(CaO)}}$$
(0.13% of monolayer)
$$\leqslant 1.34 \times 10^{-6} \text{ mol/m}^2$$
(21.68% of monolayer)

and for SrO,

$$1.51 \times 10^{-9} \text{ mol/m}^2 \leqslant C_{\mathrm{Ac(SrO)}}$$
(0.24% of monolayer)
$$\leqslant 1.05 \times 10^{-6} \text{ mol/m}^2$$
(16.99% of monolayer).

It was seen for MgO that $A' \geqslant 3.2$ mol/m$^2$ s. If this inequality is taken as equality (assuming that the unpoisoned surface takes part in the reaction) and if the range of $C_{\mathrm{Ac}}$ is taken as identical with the average of that for CaO and SrO, i.e.,

$$4.86 \times 10^{-9} \leqslant C_{\mathrm{Ac}} \leqslant 1.20 \times 10^{-6} \text{ mol/m}^2,$$

then taking the range of $A$ from Table 3 we obtain:

$$k_{0(\mathrm{min})} = 5.0 \times 10^5 \text{ s}^{-1} \text{ and } k_{0(\mathrm{max})} = 3.23 \times 10^9 \text{ s}^{-1}.$$

A rough calculation interprets this value. Unlike CaO and SrO, over MgO it is a bimolecular elementary step that controls the rate. Two particles, namely, a hydrogen atom of an adsorbed carbanion and a surface Mg$^{2+}$ must approach near to each other for an elementary act. $k_0$ can be taken as the frequency of formation of such "successful" conformations. Figure 2 shows that 7 stretching vibrations, one rotating and one bending motion of the involved chemical bondings are taking part in the formation of a successful conformation. At first approximation these motions can be considered as independent of each other. A successful conformation is a proper phase-coincidence of these motions. Let us assume that the probability of being in proper phase is for stretching vibrations and bending 1/3 and 1/8 for rotation. If all the frequencies of these motions are taken as $10^{13}$ s$^{-1}$, then the frequency of occurrence of a successful conformation:

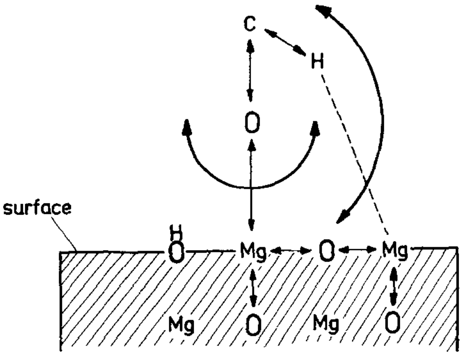

FIG. 2. Schematic representation of a "successful" arrangement for hydride ion elimination in 2-propanol dehydrogenation over MgO.

$$k_0 = \frac{1}{3^8} \cdot \frac{1}{8} \times 10^{13} = 1.91 \times 10^8 \text{ s}^{-1},$$

i.e., within the range derived earlier for $k_0$.

## REFERENCES

1. "Catalytic Properties of Substances." Akad. Nauk SSSR, Kiev, 1968.
2. Schachtler, A., and Pines, H., *J. Catal.* **11**, 147 (1968).
3. Krylov, O. V., and Fokina, E. A., *Proc. Int. Congr., 4th, Catal. 1968.* Pap. No. 64, p. 229 (1971).
4. Krylov, O. V., "Catalysis by Non-metals," Izd. Khim., Leningrad, 1967.
5. Krylov, O. V., and Fokina, E. A., *Kinet. Katal.* **1**, 421, (1960).
6. Gáti, G., and Knözinger, H., *Proc. Int. Congr. Catal., 5th, 1972* p. 819 (1973).
7. Szabó, Z. G., and Jóvér, B., *React. Kinet. Catal. Lett.* **1**, 25 (1974).
8. Slinkin, A. A., Yakerson, V. I., and Rubinstein, A. M., *Izv. Akad. Nauk SSSR* **3**, 435 (1960).
9. Kibly, C. L., and Hall, W. K., *J. Catal.* **31**, 65 (1973).
10. Krylov, O. V., Roginskii, S. Z., and Fokina, E. A., *Izv. Akad. Nauk SSSR* **6**, 668 (1965).
11. De Vleesschauwer, W. F. N. M., *in* "Physical and Chemical Aspects of Adsorbents and Catalysts" (B. G. Linsen, Ed.), pp. 265–314. Academic Press, London, 1970.
12. Stone, F. S., Agudo, A. L., *Z. Phys. Chem. NF* **64**, 161 (1969).