Kinetics and Mechanism of Synthesis of Cobalt Telluromolybdate Co$_4$TeMo$_3$O$_{16}$

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The kinetics of synthesis of cobalt telluromolybdate, proceeding according to the equation, Co$_5$TeO$_8$ + 4MoO$_3$ = Co$_4$TeMo$_3$O$_{16}$ + CoMoO$_4$, have been studied in the temperature range from 500 to 650°C. Reaction products were identified by X-ray diffraction, optical microscopy, and X-ray microanalysis. It has been observed that the reaction products form compact, distinctly separated layers on the surface of cobalt tellurate grains. Transport of MoO$_3$ takes place by sublimation of this oxide, which is the rate-determining step of the reaction.

Introduction

In a previous paper physicochemical properties of cobalt telluromolybdate Co$_4$TeMo$_3$O$_{16}$ (I) were described (*1*). Catalytic activity of cobalt telluromolybdate (I) for the oxidation of propylene to acrolein and acrylic acid has also been determined (*2*). In comparing different methods of synthesis of compound (I) it was observed (*3*) that the highest yield of this compound was obtained in the solid state reaction between cobalt tellurate Co$_5$TeO$_8$ (II) and MoO$_3$ which may be described by the equation:

$$Co_5TeO_8 + 4MoO_3 =$$
$$Co_4TeMo_3O_{16} + CoMoO_4. \quad (1)$$
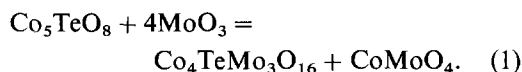
In the present work the kinetics of reaction (1) have been investigated and a mechanism for the process has been proposed. Reaction (1) is an example of numerous and extensively studied processes involving MoO$_3$, many of which are concerned with the synthesis of molybdates (*4*).

Under Discussion the results obtained in the present work will be compared with findings of previous papers on the mechanism of reactions involving MoO$_3$.

Experimental

Cobalt tellurate (II) was obtained by the method described by Kasper (*5*). The specific surface area of this preparation as determined by the BET method (krypton as the adsorbate) was 0.5 m^2/g. Two preparations of MoO$_3$ were used: (a) one which was prepared by thermal decomposition of ammonium paramolybdate with the specific surface area of 2.55 m^2/g, and (b) one prepared from commercial reagent POCH production (pure for analysis) with the specific surface area of 0.06 m^2/g.

The reagents were mixed in stoichiometric ratio and carefully ground. A sample of this mixture was put in a high-temperature chamber of the X-ray diffractometer Rigaku Denki Model D-3F. A Cu lamp and an Ni filter was used. The kinetics of the reaction were determined in the range from 500 to 650°C by registering the intensity of the strongest X-ray lines (3.26 Å in the case of preparation (a) and 3.47 Å for preparation (b)) as a function of time.

Products of reaction were studied by optical microscopy in reflected light using microsections hardened with Canada balsam. Phase identification was based on comparative microscopic observations of standard sub-

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stances, taking into account the shape of crystallites and their optical properties. In selected fragments of the sample chemical composition was determined by X-ray microanalysis. X-ray microanalyzing apparatus SEMQ ARL was employed.

Results

For the reaction mixture containing MoO_3 with relatively well-developed surface area (a), kinetics of the reaction may be described by the Jander equation:

$$[1 - (1 - x)^{1/3}]^2 = k_J t, \qquad (2)$$

where x is the conversion degree. The Jander equation holds for $x < 0.7$; above this value the rate of the reaction rapidly decreases.

The conversion x after time t was calculated as a ratio of intensity of the measured X-ray line at time t to its initial intensity. To check the correctness of this method, in two cases x was calculated also from microscopic observations by planimetric measurements of the surfaces of individual phases. The values calculated by both methods were in good agreement.

Figure 1 shows regression lines determined by the least-squares method for Eq. (2). In all cases the correlation factor was higher than 0.98.

For the mixture containing sintered molybdenum oxide (b), the reaction course follows the equation:

$$(1 - x)^{1/3} = 1 - kt \qquad (3)$$

Figure 2 shows regression lines corresponding to Eq. (3). Correlation factors for $x < 0.9$ were higher than 0.98. The values of constants k_J, k, and corresponding activation energies are listed in Table I.

Microscopic observations of samples with different conversion degrees provided more precise data on the mechanism of the process. Figure 3 shows microphotographs of a substrate mixture containing unsintered MoO_3 (a) and microphotographs of selected fragments of samples after the reaction. The microscopic picture of samples with sintered MoO_3 (b) after the reaction is fully analogous to the situation described below.

Cobalt tellurate is present in the mixture of substrates in the form of massive aggregates from 10 to 150 μm in size. The aggregates are composed of crystallites from 10 to 20 μm. Crystallites of MoO_3 smaller than 3 μm form loose and porous agglomerates from 10 to 500 μm. Grains of substrates do not make contact in the mixture.

Observations of samples with different degrees of conversion show that grains of MoO_3 decrease as the reaction proceeds. At
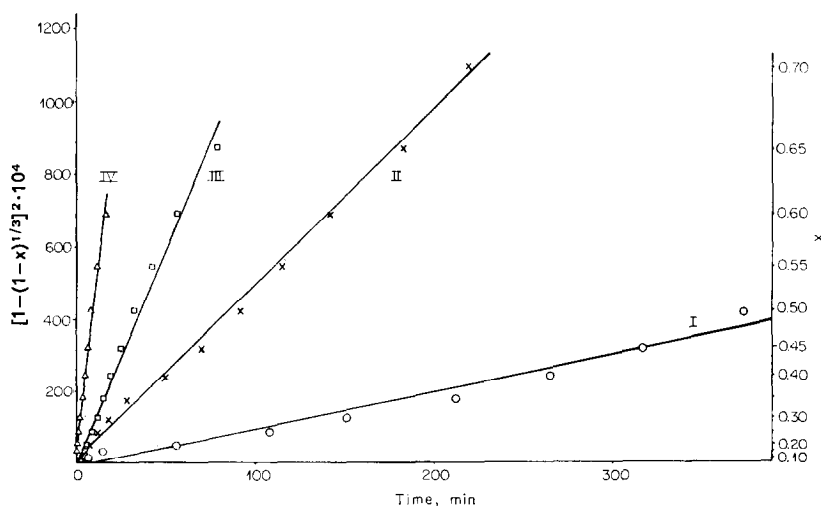

FIG. 1. Kinetic curves for reaction (1) in coordinates of the Jander equation of MoO_3 (a). I–500°C, II–520°C, III–540°C, IV–560°C.
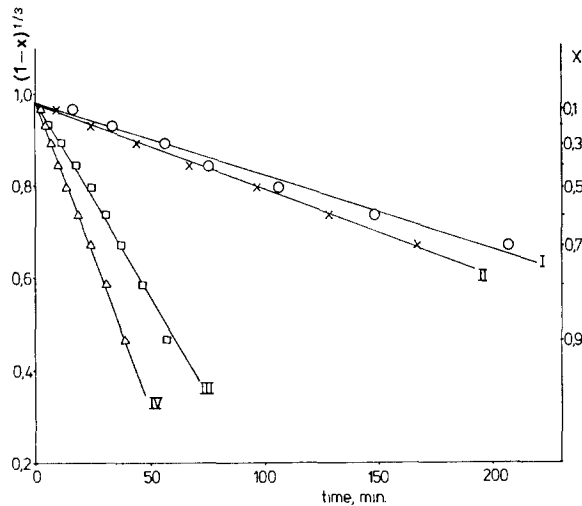
FIG. 2. Kinetic curves for reaction (1) in coordinates of Eq. (3) MoO_3 (b), I–600°C, II–605°C, III–640°C, IV–655°C.

TABLE I

RATE CONSTANTS OF REACTION (1)

Temperature (°C)	MoO_3 preparation	$k_J \cdot 10^4 \ min^{-1}$	$k \cdot 10^3 \ min^{-1}$	Activation energy (kcal/mole)
500	(a) $S_0 = 2.55 \ m^2/g$	1.05 ± 0.08		
520		4.80 ± 0.08		
540		11.78 ± 0.55		76 ± 5
560		42.0 ± 2.1		
580	(b) $S_0 = 0.06 \ m^2/g$		0.65 ± 0.05	
600			1.55 ± 0.12	
605			1.86 ± 0.04	65 ± 3
640			8.50 ± 0.80	
655			13.25 ± 0.05	

the same time layers of reaction products concentrically surrounding grains of cobalt tellurate are observed. Figures 3C, 3D, and 3E show grains of cobalt tellurate in which the reaction is not completely finished. Un-reacted cobalt tellurate is seen inside the grain and on its surface two clearly separated layers of products are visible. The internal layer consists of cobalt telluromolybdate (I) and the external one of cobalt molybdate which crystalizes in loose agglomerates in the vicinity of the grains.

A few agglomerates of unreacted MoO_3 among reacted materials can be also seen in Figs. 3E and 3F. Comparison of the last photograph with those of the initial mixture reveals far advanced recrystallization of MoO_3 during the reaction. Presence of iso-lated agglomerates of MoO_3, in sites in which cobalt tellurate has been consumed, causes a rapid inhibition of the reaction observed at high conversions. This effect is particularly distinct at low temperatures (500–560°C). At higher temperatures (600–650°C), owing to the increase in the vapor pressure of MoO_3, its gradient of concentration increases and the range of molybdenum oxide vapor expansion is lengthened. In these conditions MoO_3 can reach more distant places in which unreacted cobalt tellurate is still preserved.

The results of investigations by X-ray microanalysis are in full agreement with
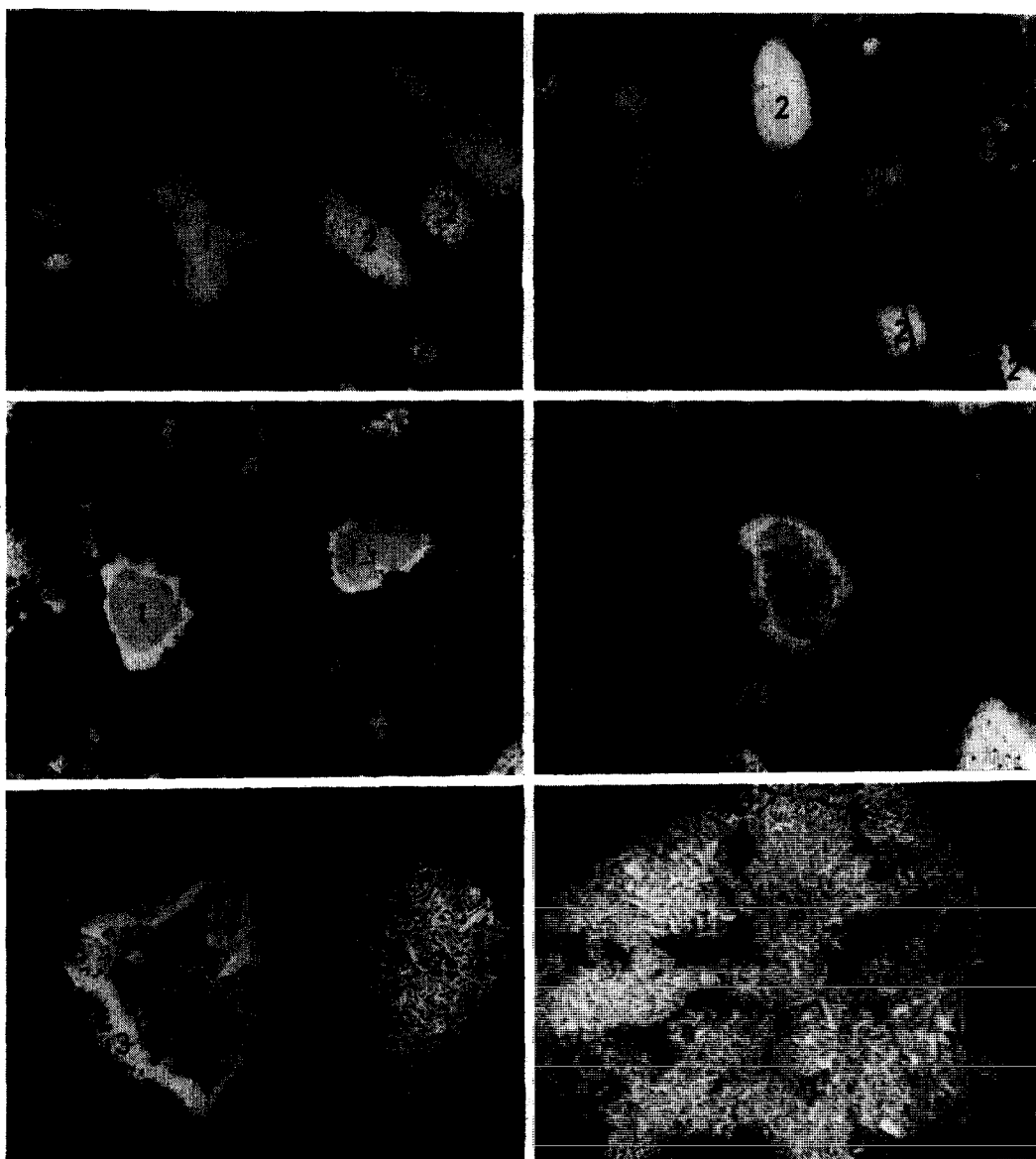
FIG. 3. Microphotographs of the reagent mixture. Magnification, 240×. (1), Co_5TeO_8, (2), MoO_3, (3), $Co_4TeMo_3O_{16}$, (4), $CoMoO_4$. A and B show the mixture of substrates, C, shows the grains of cobalt tellurate (1) in the initial stage of the reaction. A thin, compact layer of cobalt telluromolybdate (3) is surrounded by a dispersed molybdate (4). D shows a grain of the medium conversion. Distinct layers of the reaction products can be seen (3 and 4). In the vicinity of the grain can be seen loose aggregates of $CoMoO_4$ (4). E shows a grain of medium conversion beside recrystallized MoO_3, and F shows an isolated aggregate of recrystallized MoO_3.

microscopic observations. Figure 4 shows an electronic picture of topography for a selected grain and photographs illustrating distributions of concentration of cobalt, molybdenum, and tellurium. For easier identification a contour of the examined grain has been marked in the last photographs. As shown in Fig. 4 the distribution of particular elements is in qualitative agreement with the microscopic description given above. Results of a quantita-

tive analysis which have been performed for the points marked on the photograph of Fig. 4A are listed in Table II. To facilitate interpretation, the contents of particular elements in pure phases of reagents are also presented in the table. The results of analysis indicate that the inside of grain (point I) contains unreacted cobalt tellurate; the internal layer (point II) is composed of cobalt telluromolybdate with a small amount of $CoMoO_4$, whereas the external layer (point III) consists of practically only pure cobalt molybdate.

On the basis of the results of microscopic investigation some conclusions about transport of reagents during the reaction can be drawn. Observations of many samples of the substrate mixture indicate that the aggregates of both components form a system of isolated grains. The situation does not change during the reaction. No joints between the grains are observed after the reaction.

Products of the reaction are formed only on the surface of cobalt tellurate. The above facts indicate that the reaction proceeds due to the transport of MoO_3 through the gas phase to the surface of cobalt tellurate.

In order to determine whether other transport processes of MoO_3, such as wetting and surface diffusion, participate in the overall reaction, special experiments have been performed for the samples in which contacts between grains of substrates were generated by pressing them under pressure at 2500 kG/cm^2. Microscopic observations of the samples with different conversions show that

the initial contacts between the grains do not extend during the reaction; in particular, no characteristic necks connected with the creep of MoO_3 are formed. At the same time kinetic measurements show that the rate of reaction decreases about 20 times as a result of the pressing of the initial mixture. This effect can be explained by diminution of the effective evaporation surface of MoO_3. The above experiments clearly indicate that the generation of intergrain contacts does not activate additional processes of the transport of MoO_3.

Discussion

It has been shown above that molybdenum oxide sublimes under the reaction conditions described and is transported through the gas phase to the surface of cobalt tellurate where it forms a compact layer of cobalt telluromolybdate (I). To study the further progress of the reaction diffusion the transport of cobalt, tellurium, and molybdenum ions through this layer is required. Analysis of kinetic data permits one to decide whether the rate-determining step of the reaction is solid state diffusion or sublimation of MoO_3.

It has been found that in the mixture containing well-sintered molybdenum oxide, (b), the reaction follows Eq. (3). This can be readily accounted for by assuming that sublimation of MoO_3 is the rate-determining step whereas surface reaction and solid state diffusion are fast processes.

Further considerations were based on the following model of the sublimation process:

1. Crystallites of MoO_3 have the shape of a sphere of mean radius r_0. They are surrounded uniformly by grains of the second substrate, the average distance of a MoO_3 crystallite from its closest neighbors being R_0.

2. In the vicinity of the surface, pressure p corresponds to the equilibrium pressure of evaporation. It drops to zero at the distance R_0 at which MoO_3 reacts forming nonvolatile product.

3. Expansion of MoO_3 is uniform in all directions and takes place due to the gradient p/R_0.

TABLE II

RESULTS OF X-RAY MICROANALYSIS

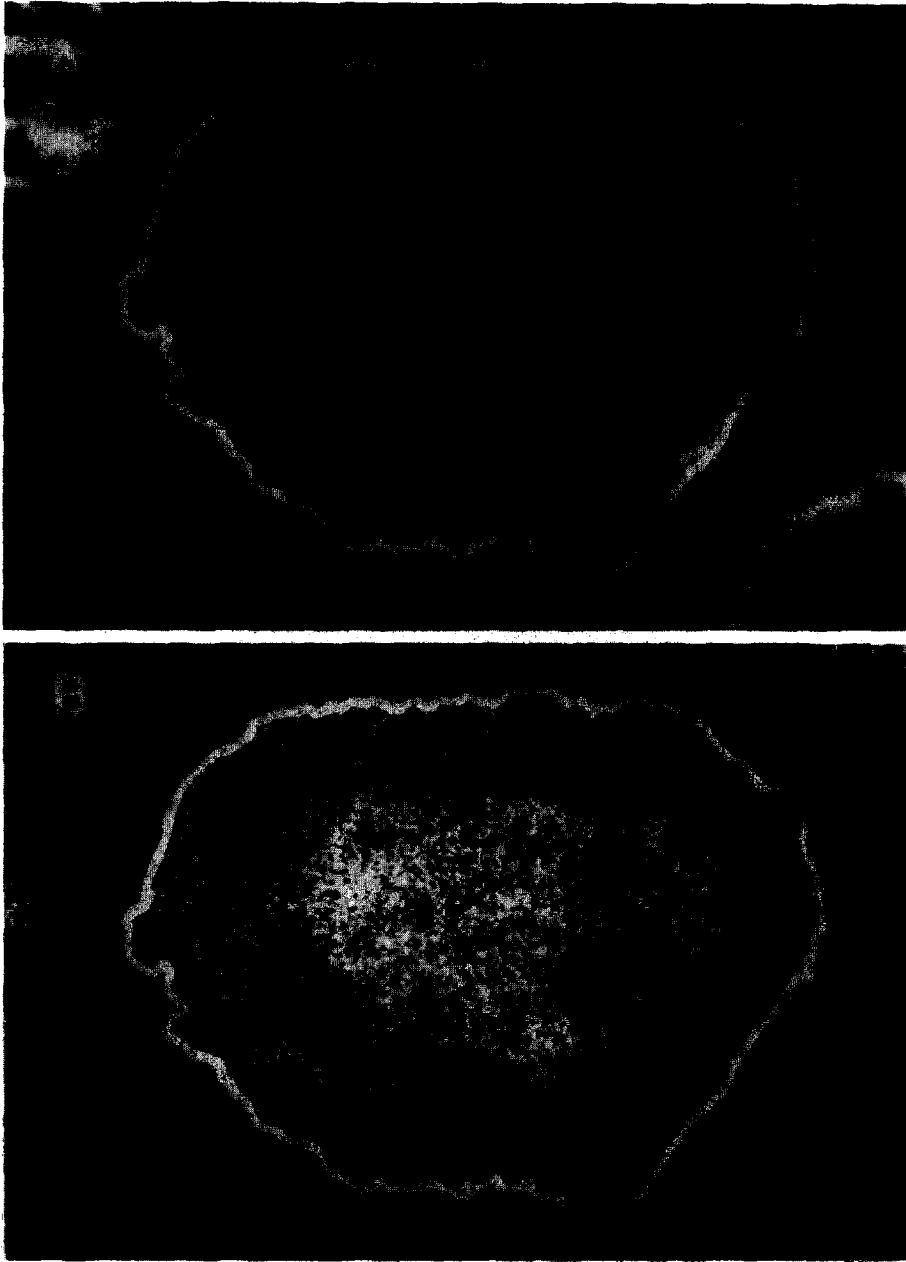| Sample	wt%		
	CoO	TeO$_3$	MoO$_3$
Co$_5$TeO$_8$	68.1	32.0	0
Point I	66.6	32.0	0.3
Co$_4$TeMo$_3$O$_{16}$	33.0	19.4	47.6
Point II	34.1	15.5	50.0
CoMoO$_4$	34.2	0	65.8
Point III	32.6	2.1	64.6

FIG. 4. Microphotographs of the sample after the reaction obtained with X-ray microanalysis technique. Magnification, 500×. A is the topography of a grain of high conversion, B, C, and D show the distribution of Co, Mo, and Te concentration within a grain, respectively.
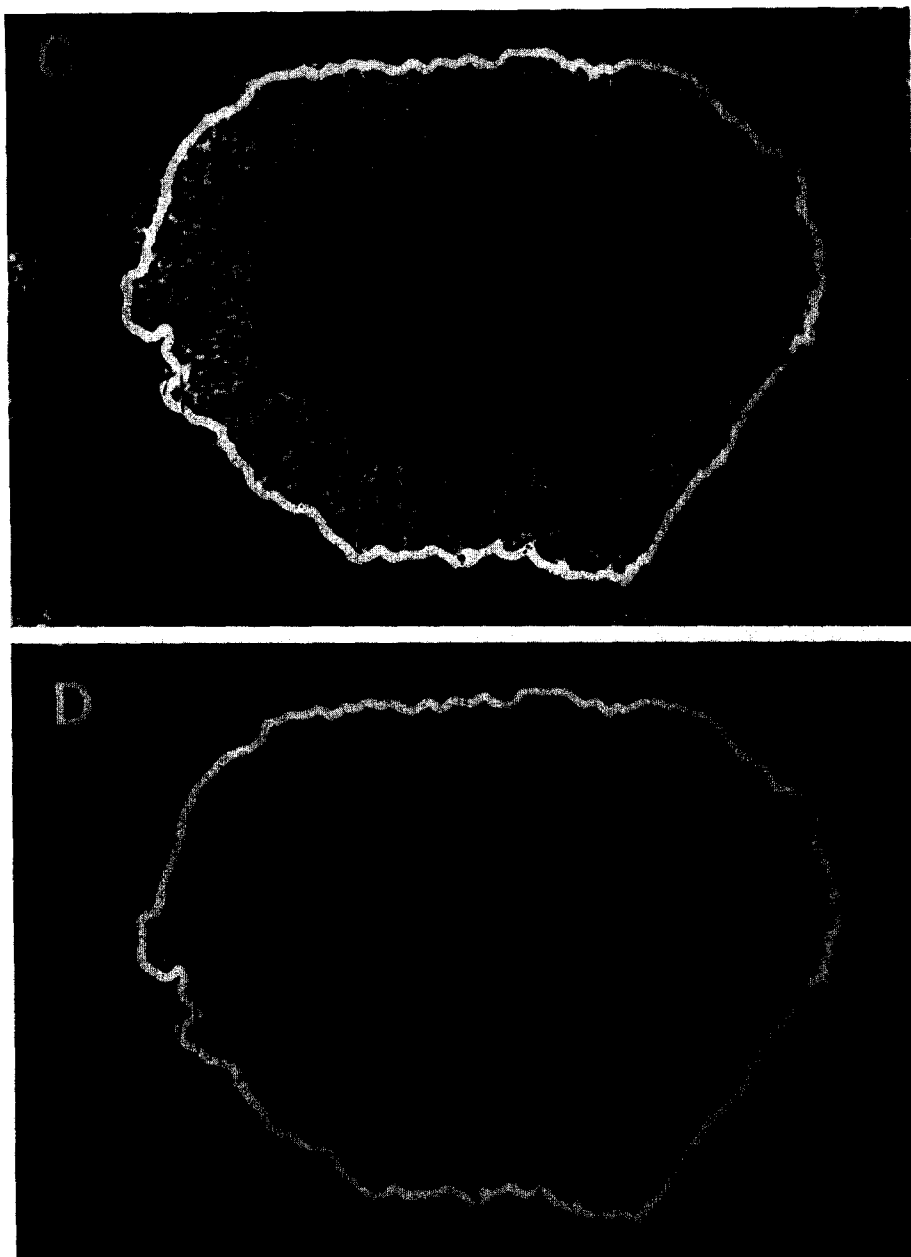
FIG. 4. *Continued.*

4. $R_0 \gg r_0$ which means that the pressure gradient practically does not change with decrease in the crystallite radius due to evaporation.

Under these conditions the reaction rate will be equal to the diffusion flux of MoO_3 through the total surface area of this component. It will be decreased with the increase in conversion by the factor $[(1 - x)^2]^{1/3}$ which accounts for the effect of the decrease of the sublimating component surface area with the extent of the reaction. Taking into account the assumptions given above we may write the following equation describing kinetics of the reaction at constant temperature:

$$dx/dt = k_1 S_0[(1 - x)^2]^{1/3} \qquad (4a)$$

where $k_1 = p^D/R_0$ is a rate constant of sublimation, $D =$ diffusion coefficient of MoO_3, $p =$ equilibrium vapor pressure, and S_0 is the initial surface area of MoO_3. At constant D and R_0, k_1 depends exponentially on temperature; $k_1 = \text{const} \exp(-E_1/RT)$ where E_1 is the heat of vaporization of MoO_3. After integration and simple transformations we obtain:

$$\sqrt{(1 - x)^{1/3}} = 1 - \tfrac{1}{3}k_1 S_0 t \qquad (4b)$$

i.e., an equation identical with (3), k being equal to $\tfrac{1}{3}k_1 S_0$.

In the case of nonsintered MoO_3 (a) kinetics of the reaction will be more complex owing to the decrease of the MoO_3 surface in the course of the process. Assuming that sublimation is still the slowest step we obtain the following kinetic equation:

$$dx/dt = k_1 S_0[(1 - x)^2]^{1/3} \, 1/k_2 f(t) \qquad (5)$$

where k_2 is the rate constant of sintering and $f(t)$ is the function describing the kinetics of the decrease of the surface area during heating. The form of the function $f(t)$ may be determined bearing in mind the fact that the reaction follows Eq. (2). After differentiating Eq. (2), we obtain

$$\frac{dx}{dt} = 1.5k_J \frac{[(1 - x)^2]^{1/3}}{1 - (1 - x)^{1/3}} =$$

$$1.5k_J[(1 - x)^2]^{1/3} \cdot \frac{1}{t^{1/2}} \qquad (6)$$

Comparison of Eqs. (5) and (6) yields:

$$f(t) = 1/t^{1/2} \quad \text{and} \quad 1.5k_2(k_J)^{1/2} = k_1 S_0 \qquad (7)$$

From the values of k and k_J derived experimentally we may calculate the rate constants of the respective partial reactions. For the determination of constants k_2 in the low temperature region from 500 to 560°C, extrapolated values of k_1 were used. The results of the calculations are given in Table III. In order to check the correctness of the method applied, some experiments of sintering of MoO_3 (a) were performed. The values of sintering rate constants obtained in these experiments are also given in Table III. The differences between the calculated and experimental values are within the limits of experimental error. The form of the function $f(t)$ describing the process of the surface decrease most probably has no physical sense in that it is only a formal mathematical expression.

In keeping with the proposed mechanism in the case of the reaction mixture containing sintered MoO_3 (b) the activation energy of the reaction should be close to the heat of evaporation of this oxide. The values of the heat of sublimation for MoO_3 reported in the literature do not agree with each other. Earlier works (6) report 80.5 kcal/mole for trimer MoO_3 and 93.6 kcal/mole for tetramer, whereas recent works give these values as 68.5 and 79.2 kcal/mole, respectively (7). The value of the activation energy of 76 kcal/mole found for the reaction with nonsintered MoO_3 (a) depends on two parameters: the heat of sublimation of MoO_3 and the activation energy of the sintering process. According to Eq. (7), $E_1 - E_2 = \tfrac{1}{2}E_J$. From this latter dependence the value of $E_2 = 27$ kcal/mole close to experimental value given in Table III was derived.

In conclusion we may state that all the facts described in the present work may be satisfactorily explained in terms of the model according to which the rate-determining step of the reaction is sublimation of molybdenum trioxide. It is at the same time the sole transport process supplying MoO_3 to the reaction zone. In the case under discussion one may exclude the transport by intergrain contacts

TABLE III

RATE CONSTANTS OF SUBLIMATION (k_1) AND SINTERING (k_2) OF MOLYBDENUM OXIDE

Temperature (°C)	$k_1 \cdot 10^3$ g/m²min	Activation energy (kcal/mole)	k_2 min$^{-1/2}$ Determined from Eq. (7)	Experimental	Activation energy (experimental) (kcal/mole)
500	0.62^a		0.10	—	
520	1.80^a		0.14	—	
540	4.95^a		0.25	0.29	
560	12.9^a	65 ± 3	0.34	0.38	26 ± 5
580	32.5		0.48	0.66	
600	77.5		—		
605	93.0		—		
640	425.0		—		
655	662.5		—		

^{a} Extrapolated values.

observed in the synthesis of cobalt molybdate from Co_3O_4 and MoO_3 (8) or the mechanism of wetting of the surface by MoO_3 described for the reaction between Mn_2O_3 and MoO_3 (9).

It is interesting that in the case of MoO_3, which undergoes sintering during the reaction, the kinetics of the synthesis can be described by the Jander equation whose applicability usually is related to diffusion processes in solids. The simultaneous action of inhibiting factors such as decreasing the crystallite surface area with reaction progress and sintering of the sample results in the simulation of limitation by solid diffusion.

The role of MoO_3 sublimation in reactions of synthesis of molybdates has been studied by Pozin, Ginstling and Pechkovskii (10). Performing experiments with systems of isolated tablets of MoO_3–MeO where $Me =$ Ca, Mg, Pb, Cu, Fe they have shown that formation of the molybdates proceeds at a considerable rate at temperatures as low as 500°C. The activation energy of MoO_3 sublimation they determined to be about 55 kcal/mol. It was observed at the same time that the presence of another metal oxide in the vicinity of MoO_3 tablets considerably enhances its sublimation. This latter effect may be easily explained in terms of the mechanism proposed in the present work as being due to the increase in gradient of the

MoO_3 vapor concentration in the presence of the component reacting with molybdenum trioxide with the formation of nonvolatile product. Unfortunately quantitative comparison of the results of the present work with those reported by Pozin et al., is not possible since it is not clear whether the sublimation rate given by these authors is related to the real surface area of MoO_3 or to the geometrical surface area of the tablet.

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