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Kinetics and Mechanism of Solid-State Reaction between Bismuth(III) Oxide and Molybdenum(VI) Oxide

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The mechanism of the following solid-state reactions between bismuth(III) oxide and molybdenum(VI) oxide was investigated within the temperature range 400–650°C.

(i) $Bi_2O_3 + MoO_3 \rightarrow Bi_2MoO_6$,

(ii) $Bi_2O_3 + 2MoO_3 \rightarrow Bi_2Mo_2O_9$,

(iii) $Bi_2O_3 + 3MoO_3 \rightarrow Bi_2(MoO_4)_3$,

(iv) $Bi_2MoO_6 + MoO_3 \rightarrow Bi_2Mo_2O_9$,

(v) $Bi_2Mo_2O_9 + MoO_3 \rightarrow Bi_2(MoO_4)_3$.

Two types of experiments, capillary and particle size, were performed to ascertain whether MoO_3 diffuses into Bi_2O_3 or vice versa. These show that molybdenum trioxide diffuses into bismuth oxide grains. If α is the fraction of molybdenum trioxide reacted, the kinetics in all five cases are found to be governed by the equation $\alpha^n = kt$ throughout the temperature range, where n and k are constants at a given temperature and t is the time. Both n and k are temperature dependent. The characteristic feature of these reactions is that they proceed to completion. Results are also fitted by the relation $\alpha = k_2t^{1/2} - k_3t$, where k_2 and k_3 are constants, which shows that the reactions occur by bulk diffusion through grain boundary contacts. The number of grain boundary contact points decreases with time in the course of reaction.

Introduction

Bismuth molybdate has been used as a selective catalyst (*1*, *2*) for (i) propylene oxidation to acrolein, (ii) propylene ammoxidation to acrylonitrile, (iii) oxidative dehydrogenation of 1-butene to butadiene, and (iv) oxidation of toluene to benzaldehyde (*3*). All these reactions involve insertion of oxygen without scission of any C–C bond. It has been recognized that the "bismuth molybdate" system is complicated (*4*) since a number of compounds can be formed when Bi_2O_3 reacts with MoO_3, depending on the Bi and Mo ratio. A phase diagram of the Bi_2O_3 and MoO_3 system has recently been studied by X-ray and differential thermal analysis (*5*). The phase diagram is found to be complex and certain phases undergo different solid–solid transformations.

The low-temperature form (K) of $Bi_2O_3 \cdot MoO_3$ is converted (*5*) into the high-temperature form (H) at 600°C. However, Batist *et al.* (*6*) reported that such a conversion occurs in the temperature range 665–690°C. The reaction sequence can be represented by

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$$Bi_2O_3 + MoO_3 \rightarrow Bi_2MoO_6 \xrightarrow{>600°C} Bi_2MoO_6(H).$$

Similarly, the region of the phase diagram in the vicinity of ***AB***$_2$ ($Bi_2Mo_2O_9$) is also complicated. Formation of ***AB***$_2$ has been studied by Batist *et al.* (*6*) from slurry reactions. The stoichiometric mixtures were calcined at different temperatures. X-ray studies showed that the sequence of the reactions can be represented by

$$Bi_2O_3 + 2MoO_3 \xrightarrow[16\text{ hr}]{600°C} Bi_2Mo_2O_9 + Bi_2MoO_6 \text{ (traces)},$$

so that the main reaction involves the formation of $Bi_2Mo_2O_9$ and the side reaction involving formation of Bi_2MoO_6 is insignificant. Further,

$$Bi_2O_3 + 2MoO_3 \xrightarrow[16\text{ hr}]{750°C} Bi_2(MoO_4)_3 + Bi_2MoO_6(H) + Bi_2Mo_2O_9 \text{ (traces)},$$

$$Bi_2O_3 + 2MoO_3 \xrightarrow[15\text{ hr}]{750\text{–}1000°C} Bi_2Mo_2O_9 \text{ (excess)} + Bi_2(MoO_4)_3 + Bi_2MoO_6(H) \text{ (traces)},$$

where (H) denotes the high-temperature form and (K) denotes the low-temperature form of Bi_2MoO_6. Formation of the $Bi_2Mo_2O_9$ phase has also been confirmed by the peritectic reaction (*7–9*)

$$Bi_2MoO_6(H) + MoO_3(l) \xrightarrow{665°C} Bi_2Mo_2O_9.$$

There is controversy regarding the stability of this phase. According to Egashira *et al.* (*5*), the $Bi_2Mo_2O_9$ phase is unstable below 540°C and disproportionates into $Bi_2MoO_6(K)$ and $Bi_2(MoO_4)_3$. However, several workers (*10–12*) have reported its preparation in the temperature range 400–500°C when the coprecipitation reaction was carried out in the pH range 2–5.

The phase ***AB***$_3$ ($Bi_2(MoO_4)_3$) has been prepared by Chen *et al.* (*8*). It has a congruent melting point. Its existence has been supported by a number of workers (*5, 6*). It can even be prepared by the peritectic reaction (*7*)

$$\text{liq.} + Bi_2Mo_2O_9 \xrightarrow{640°C} Bi_2(MoO_4)_3.$$

Egashira and co-workers (*5*) have found evidence of the formation of other compounds, like $7Bi_2O_3 \cdot MoO_3$ and $3Bi_2O_3 \cdot MoO_3$. However, the range of composition $Bi/Mo = \frac{2}{1} \sim \frac{2}{3}$ is of much greater interest from the viewpoint of high catalytic activity. Trifiro *et al.* (*12*) have made extensive ir studies of different phases and mixtures of MoO_3 and Bi_2O_3 in different compositions. Some of the results are at variance with the results of Grzybowska *et al.* (*11*). Conclusions based on ir studies alone cannot be definitive and greater reliance has to be placed on X-ray diffraction results.

Bismuth molybdate catalysts for the selective oxidation of olefines are usually prepared by precipitation from solutions of ammonium molybdate and bismuth nitrate (*10*). The resulting precipitate is heated at about 500°C. Batist *et al.* (*10*) have pointed out that solid-state reactions occur in this process.

Since it is desirable to study the scientific aspects of catalyst preparation, it was planned to investigate the kinetics and mechanisms of solid-state formation of ***AB***, ***AB***$_2$, and ***AB***$_3$ phases. Hence the present investigation was undertaken.

Experimental

Materials

Bi_2O_3 (LR, Thomas Baker & Co., London), MoO_3 (AR, BDH, England), and $(NH_4)_6 \cdot Mo_7O_{24} \cdot 4H_2O$ (AR Judex) were used as such without purification. Bismuth carbonate was prepared (*13*) by adding an excess of solid ammonium carbonate (AR, BDH) to a solution of bismuth nitrate (AR, BDH). The precipitate was filtered and washed with water to remove carbonate and nitrate ions and dried at 100°C in a desiccator. It was analyzed for bismuth as bismuth oxyiodide (*14*) (percentage of Bi obsd., 81.54; calculated for $(BiO)_2CO_3$, 81.96).

Preparation of Bismuth-Molybdenum Mixed Oxides

These were prepared by solid-state reaction between (a) bismuth oxide and molybdenum oxide and (b) bismuth carbonate and ammonium molybdate. For this purpose molar ratios of (a) 1 : 1, 1 : 2, 1 : 3, 2 : 1, and 3 : 1 for bismuth oxide and molybdenum trioxide and (b) 7 : 1, 7 : 2, 7 : 3, 14 : 1, and 21 : 1 for bismuth carbonate and ammonium molybdate were taken. The mixtures were homogenized in an agate mortar using acetone (AR). The mixtures were dried and heated in a platinum crucible at 580 ± 10°C initially for 2 hr, cooled, crushed in the mortar with acetone, and reheated at the same temperature for another 3 hr.

Results

Characterization

The different reaction products have been characterized by (i) chemical analysis, (ii) powder X-ray diffraction pattern, and (iii) thermal analysis.

(*i*) *Chemical Analysis*

The reaction products were analyzed for bismuth and molybdenum qualitatively and quantitatively. Weighed amounts of products obtained from reaction mixtures (a) and (b) were boiled with concentrated HCl (AR). Bismuth was analyzed as bismuth oxyiodide and molybdenum as lead molybdate (*14*). The results are recorded in Table I.

(*ii*) *X-ray Diffraction Studies*

Powder X-ray diffraction patterns of products obtained from reaction mixtures of 1 : 1, 1 : 2, 1 : 3, 2 : 1, and 3 : 1 of bismuth oxide and molybdenum trioxide were done at BARC, Bombay, using Cu$K\alpha$ radiation. The results are given in Table II.

(*iii*) *Thermal Analysis*

Thermogravimetry (*TG*). Thermogravimetric analysis of Bi_2O_3 and MoO_3 was carried out using a manual thermogravimetric analyzer at a heating rate of 4°C min^{-1}. The heating rate was controlled manually with the help of a dimmerstat fitted with the analyzer. Measurements were made up to

TABLE I

MELTING POINTS AND CHEMICAL ANALYSIS OF REACTION RRODUCTS

Molybdate[a]	mp (°C)	Wt% of Bi		Wt% of Mo	
		Calcd	Exptl	Calcd	Exptl
Bi_2MoO_6 (1 : 1)	—	68	68	—	—
$Bi_2Mo_2O_9$ (1 : 2)	680 ± 10[b]	55	54	—	—
$Bi_2(MoO_4)_3$ (1 : 3)	640 ± 10[c]	47	46	48	47
Bi_4MoO_9 (2 : 1)	—	78	76	—	—
Bi_6MoO_{12} (3 : 1)	—	81	80	—	—

[a] These compounds had been prepared earlier by coprecipitation from solution and subsequent calcination (*6*).

[b] The value obtained by Batist *et al.* (*6*) is 690°C.

[c] The values reported by Dean (*19*), Bleijenberg *et al.* (*20*), and Belyaev and Smolyaninov (*21*), respectively, are 643, 676, and 648°C.

TABLE II

Comparison of X-Ray Diffraction Data of Bismuth Molybdates and Component Oxides

Bi_2MoO_6				$Bi_2Mo_2O_9$				$Bi_2(MoO_4)_3$											
This work		Literature (*10*)		This work		Literature (*10*)		This work		Literature (*10*)		Bi_4MoO_9 This work		Bi_6MoO_{12} This work		Bi_2O_3 ASTM		MoO_3 ASTM	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
3.278	97.5	5.68	w	4.9	11.5	5.95	m	6.969	73.6	6.90	m	3.291	54.4	3.278	100	3.51	35	6.93	34
3.267	100	3.26	s	3.209	100	4.90	m	6.326	35.9	4.89	ms	3.243	100	2.858	18.5	3.17	100	3.81	82
2.885	30.7	3.245	s	2.814	40.8	4.74	m	5.096	12.4	3.57	m	2.903	16.9	2.797	43.6	2.90	35	3.463	61
2.814	28.1	2.87	m	2.706	18.9	3.195	vs	4.928	34.8	3.26	m	2.831	32.8	2.006	27.3	2.71	100	3.260	100
2.797	31.7	2.79	m	2.002	14.6	3.145	m	3.754	14.6	3.18	vs	2.772	11.1	2.002	28.6	2.53	10	3.006	13
2.014	34.4	2.005	m	1.989	14.3	2.80	s	3.466	14.0	3.05	s	2.730	17.2	1.985	15.5	2.39	35	2.702	19
2.002	14.1	1.975	w	1.957	37.9	2.70	m	3.414	24.2	2.87	s	2.027	12.5	1.722	17.3	2.27	20	2.655	35
1.985	22.4	1.725	w	1.692	27.5	1.99	m	3.326	14.0	2.79	m	2.018	16.0	1.7	23.0	2.16	45		
1.734	13.8	1.720	w	1.689	28.3	1.978	m	3.267	12.4	2.47	m	1.981	18.9	1.695	16.6	2.06	45		
1.728	16.6	1.690	w	1.645	17.6	1.94	s	3.187	54.2	2.005	m	1.965	20.9	1.689	19.8	1.99	45	2.527	12
1.698	27.6	1.635	vw	1.607	10.5	1.682	vs	3.058	28.9	1.915	m	1.731	12.9			1.84	35	2.332	12
1.639	10.3	1.630	vw	1.603	15.8	1.638	m	2.885	100	1.690	m	1.716	12.7			1.75	100	2.309	31
1.629	10.6			1.266	10.5	1.598	m	2.276	14.0			1.704	15.6			1.670	65	2.271	18
								1.892	18.0							1.65	100	1.982	13
								1.838	16.3							1.50	100	1.96	17
								1.623	44.4							1.44	65	1.849	21
								1.618	30.3							1.39	35	1.821	11
								1.597	44.9							1.35	35	1.733	17
								1.556	30.9							1.30	35	1.26	20
								1.554	21.9							1.26	20		
								1.528	25.8							1.22	90		
								1.509	12.4										
								1.384	10.7										
								1.281	30.6										
								1.278	19.7										
								1.245	20.8										

700°C. A loss in weight of the order of 2.3% was recorded, which was also obtained in the case of a parallel study with an empty crucible. It shows that the sublimation of Bi_2O_3 or MoO_3, if it occurs at all, is within experimental error.

Differential thermal analysis (DTA). The differential thermal analysis of (i) Bi_2O_3, (ii) MoO_3, (iii) $(BiO)_2CO_3$, (iv) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, (v) a mixture of bismuth carbonate and ammonium molybdate in 7 : 3 molar ratio, (vi) 1 : 3 molar mixture of bismuth oxide and molybdenum trioxide, (vii) calcination products of 1 : 1, 1 : 2, 1 : 3, 2 : 1, and 3 : 1 molar mixtures of bismuth oxide and molybdenum trioxide, and (viii) products of 7 : 1, 7 : 2, 7 : 3, 14 : 1, and 21 : 1 molar mixtures of bismuth carbonate and ammonium molybdate was carried out using a manual differential thermal analyzer with a heating rate of 6°C min^{-1}. Results showed that calcination products of 1 : 2 and 1 : 3 molar mixtures of bismuth oxide and molybdenum trioxide melt below 900°C. Results are reported in Fig. 1 and Table I. Grzybowska *et al.* (*11*) have reported the decomposition of the 1 : 2 phase ($Bi_2Mo_2O_9$) below 550°C. Our results do not support this. DTA results of Batist *et al.* (*6*) for $Bi_2Mo_2O_9$ show two additional weak endotherms in addition to one strong endotherm at 690°C. Our results show only one endotherm at 680 ± 10°C. This discrepancy might be due to a difference in the heating rates in the two sets of experiments.

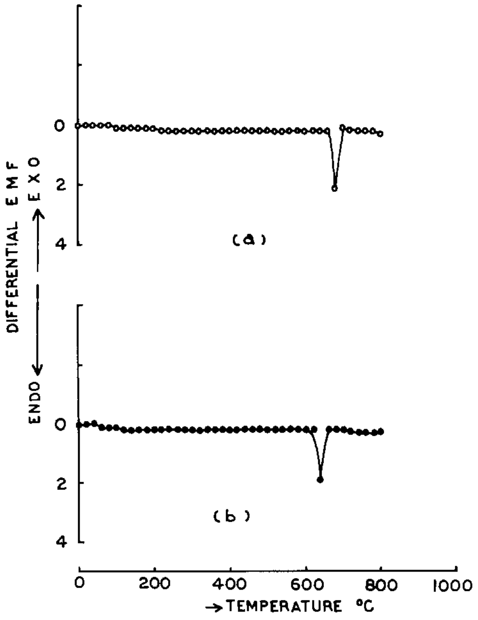

FIG. 1. DTA of reaction product of Bi_2O_3 and MoO_3 in the ratios (a) 1 : 2 and (b) 1 : 3.

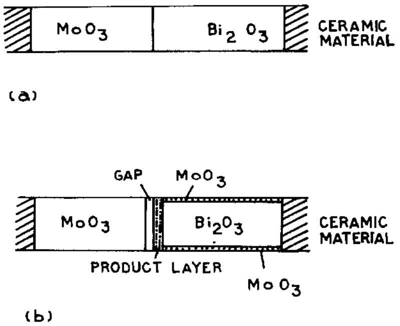

FIG. 2. Direction of diffusion of MoO_3 (a) before reaction and (b) after reaction.

Diffusion Study

(*i*) *Capillary Experiment*

In order to ascertain the direction of diffusion of reactant species, capillary experiments were performed. Corning glass capillaries of similar dimensions were filled with the two reactants Bi_2O_3 and MoO_3 as shown in Fig. 2a. These were tightly packed such that a clear boundary between the reactants was formed in the middle. The ends of the capillary were closed with a ceramic material. The capillaries were heated at 580 ± 10°C for different time intervals. After a while a gap was observed at the boundary and a shining layer of the product was formed on the side of Bi_2O_3, as shown in Fig. 2b. This experiment suggests that MoO_3 diffused toward Bi_2O_3.

(*ii*) *Study of Particle Size Distribution*

The procedure was similar to that described by Rastogi and co-workers (*15*) and others (*16*). A sedimentation column consisting of a long tube with a stopcock at the top and a ground glass joint at the bottom was used. The column was kept vertical. Sedimentation of the particles in the collecting tube was observed by a cathetometer, which could be read to ±0.002 cm. The experimental procedure follows.

The experiment was performed to ascertain the particle size distribution of MoO_3 before and after the reaction. A suspension of MoO_3 was prepared in water (~1.5 g/100 ml) and kept above the stopcock. The sedimentation column was filled beforehand with the suspension medium (water). The cathetometer was focused at the bottom of the collecting tube to record the height $h(0)$ of sedimented particles at zero time. The suspension in the upper chamber was stirred and the upper stopcock was opened and the particles were allowed to sediment. The height $h(t)$ of MoO_3 in the collecting tube was determined at different time intervals (~2 min). The sedimentation was allowed to proceed until all the material had settled in the tube. The height of the particles $h(\infty)$ was noted. The experiment was repeated with unreacted MoO_3 remaining after the reaction of a mixture of Bi_2O_3 and MoO_3 at 500 ± 10°C for 10 min. The reaction mixture was treated with concentrated HCl, which dissolves both bismuth molybdate and unreacted Bi_2O_3. The undissolved MoO_3 was filtered through a sintered glass crucible, washed with distilled water, and dried.

From the observed values of $h(0)$, $h(t)$, and $h(\infty)$ the ratio M_t/M_∞ was calculated by the relation

$$\frac{M_t}{M_\infty} = \frac{h(t) - h(0)}{h(\infty) - h(0)}, \qquad (1)$$

where M_t and M_∞ are the total mass sedimented at time t and infinity, respectively. Values of M_t/M_∞ were plotted against t and the slopes were obtained at different time intervals. From the values of slopes, the distribution function $f_w(r)$ was calculated by the relation

$$f_w(r) = \text{slope} \cdot 2t/r. \qquad (2)$$

The values of $r(t)$ (average radii of particles) were calculated with the help of the relation

$$r(t) = 9\eta L/(2(\rho P - \rho)gt), \qquad (3)$$

where η, L, ρP, ρ, and g are, respectively, viscosity of the suspension medium, length of the sedimentation column, density of the particles, density of the suspension medium, and acceleration due to gravity.

The particle size distribution curves were obtained by plotting $f_w(r)$ versus $r(t)$ as shown in Figs. 3a and b.

Kinetics of Reaction

Mixtures of Bi_2O_3 and MoO_3 in appropriate molar ratios were homogenized in an agate mortar using acetone, and subsequently were allowed to dry. The dried reaction mixture was heated at different temperatures in the range 400–650°C for different time intervals. The kinetics were studied by determining the fraction of MoO_3 unreacted gravimetrically. A small amount of reaction mixture was taken out at different intervals and weighed. Subsequently the reaction mixture was dissolved in concn. HCl (1 g/20 ml), filtered through a weighed sintered glass crucible, washed with dilute HCl and distilled water, and dried at 120°C. This was again weighed. Knowing the weight of unreacted MoO_3, the weight of reacted MoO_3 could be calculated at different temperatures and time intervals (Bi_2O_3 and bismuth molybdate formed were soluble in HCl). The fraction (α) of MoO_3 reacted at any time t was calculated by the expression

$$\alpha = \frac{\text{wt of } MoO_3 \text{ reacted at time } t}{\text{wt of } MoO_3 \text{ at time } t = 0}.$$

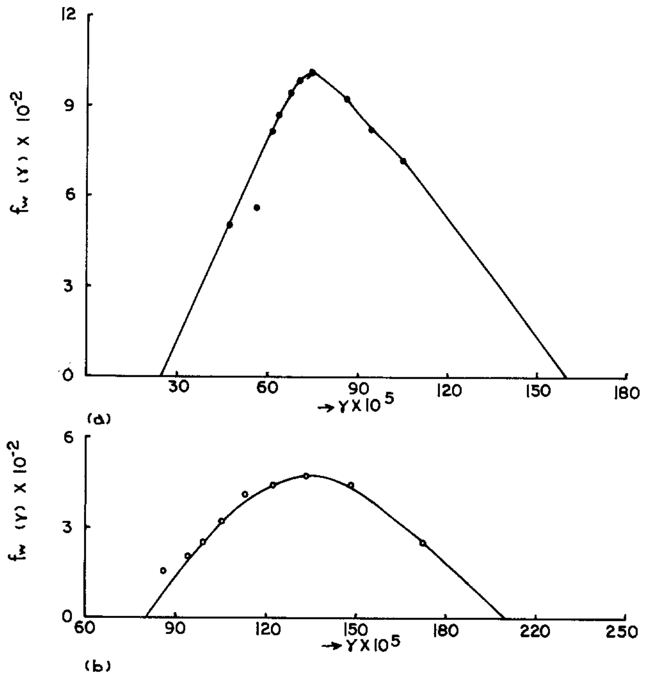

FIG. 3. Particle size distribution of MoO_3 (a) before reaction and (b) after reaction.

Discussion

The following solid-state reactions were studied by taking proportionate molar ratios of the reactants. The corresponding molybdates were isolated and characterized by chemical analysis, melting-point, and powder X-ray diffraction data.

$$(1)\ Bi_2O_3 + MoO_3 \xrightarrow[5\ \mathrm{hr}]{580^\circ\mathrm{C}} Bi_2MoO_6,$$

$$(2)\ Bi_2O_3 + 2MoO_3 \xrightarrow[5\ \mathrm{hr}]{580^\circ\mathrm{C}} Bi_2Mo_2O_9,$$

$$(3)\ Bi_2O_3 + 3MoO_3 \xrightarrow[5\ \mathrm{hr}]{580^\circ\mathrm{C}} Bi_2(MoO_4)_3,$$

$$(4)\ 2Bi_2O_3 + MoO_3 \xrightarrow[5\ \mathrm{hr}]{580^\circ\mathrm{C}} Bi_4MoO_9,$$

$$(5)\ 3Bi_2O_3 + MoO_3 \xrightarrow[5\ \mathrm{hr}]{580^\circ\mathrm{C}} Bi_6MoO_{12}.$$

These molybdates were also prepared by solid-state reaction between bismuth carbonate and ammonium molybdate in appropriate molar ratios. The latter reaction yielded products having finer particle size, which could be ascertained by visible microscopy. These compounds had earlier been prepared by coprecipitation from solution and subsequent calcination (*6*). However, preparation of catalysts by solid-state reactions is preferable on account of convenience and the possibility of obtaining a purer product having finer grains.

The X-ray diffraction patterns of the products of reactions (1) to (5) were obtained for characterization. The "*d*" values for our sample of Bi_2MoO_6 compare well with the values of the high-temperature form (750°C) prepared by the coprecipitation method (*6*). It should be noted that Janik (*17*) has reported that this form can also be prepared by solid-state reaction at about 600°C. The *d* values for $Bi_2Mo_2O_9$ are in agreement with the values reported by earlier workers (*6*) but the intensities do not match well. The X-ray diffraction pattern for $Bi_2(MoO_4)_3$ in the present case is also similar, but the earlier data include lines due to MoO_3 and Bi_2O_3 which are absent in the pattern for our samples. It appears that the 1 : 3 compound prepared by these workers had MoO_3 and Bi_2O_3 as impurity.

The X-ray diffraction patterns for Bi_4MoO_9 and Bi_6MoO_{12} are not easy to interpret. Many lines have similar *d* values which also occur in the patterns for the 1 : 1 and 1 : 2 compounds obtained in this investigation. However, the X-ray results in the present case do not entirely agree with those obtained by Batist and co-workers (*6*). In order to check the reproducibility of the X-ray patterns, the 3 : 1 compound was again prepared; its diffraction pattern was obtained and was found to be exactly the same. However, it is necessary to have phase diagram studies of the Bi_2O_3–MoO_3 system in order to understand the nature of the various molybdates.

In order to understand the mechanism of reaction, it is necessary to ascertain which reactant species diffuses into which species. Therefore capillary experiments as described earlier were performed. The product layer was formed on Bi_2O_3, showing that MoO_3 diffuses into Bi_2O_3. Grain boundary diffusion followed by bulk diffusion is essentially involved in the process since, although it has been claimed from microgravimetric experiments that MoO_3 starts subliming at 500°C, giving gaseous MoO_3, the amount subliming is negligible as compared to the amount of MoO_3 interacting with the other reactant in the range 400–600°C. Particle size distribution of MoO_3 before and after the reaction was ascertained by sedimentation experiments. Results are shown in Figs. 3a and b. The area of the curves is proportional to the amounts of MoO_3. The original amount of MoO_3 was 0.3 g, while after the reaction it was 0.204 g. The maximum in curve 3a corresponds to radius $r \approx 74 \times 10^{-5}$ cm, while the maximum corresponding to curve 3b occurs when $r \approx 133 \times 10^{-5}$ cm. Since the particle size of MoO_3 cannot become larger, the only interpretation is that smaller particles are consumed in this reaction while bigger particles are left behind. This can certainly happen if MoO_3 diffuses into Bi_2O_3 grains. The smaller particles would be quickly used up in the process, affecting the particle size distribution and skewing it toward a larger particle size. The two types of experiments taken together show that MoO_3 diffuses into Bi_2O_3 grains. The kinetics of the following reactions were investigated.

$$\text{(i)}\quad Bi_2O_3 + MoO_3 \rightarrow Bi_2MoO_6,$$

$$\text{(ii)}^1\quad Bi_2O_3 + 2MoO_3 \rightarrow Bi_2Mo_2O_9,$$

$$\text{(iii)}\quad Bi_2O_3 + 3MoO_3 \rightarrow Bi_2(MoO_4)_3,$$

$$\text{(iv)}^2\quad Bi_2MoO_6 + MoO_3 \rightarrow Bi_2Mo_2O_9,$$

$$\text{(v)}\quad Bi_2Mo_2O_9 + MoO_3 \rightarrow Bi_2(MoO_4)_3.$$

An attempt was made to analyze the data with the help of Jander's equation

$$[1 - (1 - \alpha)^{1/3}]^2 = k_1 t, \qquad (4)$$

where α denotes the fraction of MoO_3 reacted at time *t*. The data do not satisfy Eq. (*4*). However, when log α was plotted against log *t*, straight lines were obtained in all cases, showing that the relation

$$\alpha^n = kt \qquad (5)$$

satisfied the data, where *n* and *k* are both constants. Typical results are plotted in Figs. 4 and 5. The values of *n* and *k* at different temperatures are recorded in Ta-

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[1] There is some controversy regarding reaction (ii) according to the studies reported by Janik (*17*) and Trifiro *et al.* (*12*). The reaction should be written as a consecutive reaction in the form

$$Bi_2O_3 + 2MoO_3 \rightarrow Bi_2Mo_2O_9 \rightarrow \tfrac{1}{2}Bi_2MoO_6 + \tfrac{1}{2}Bi_2(MoO_4)_3.$$

[2] In view of the remarks (*12, 17*) regarding reaction (ii), reaction (iv) should be written as

$$Bi_2MoO_6 + MoO_3 \rightarrow Bi_2Mo_2O_9 \rightarrow \tfrac{1}{2}Bi_2MoO_6 + \tfrac{1}{2}Bi_2(MoO_4)_3$$

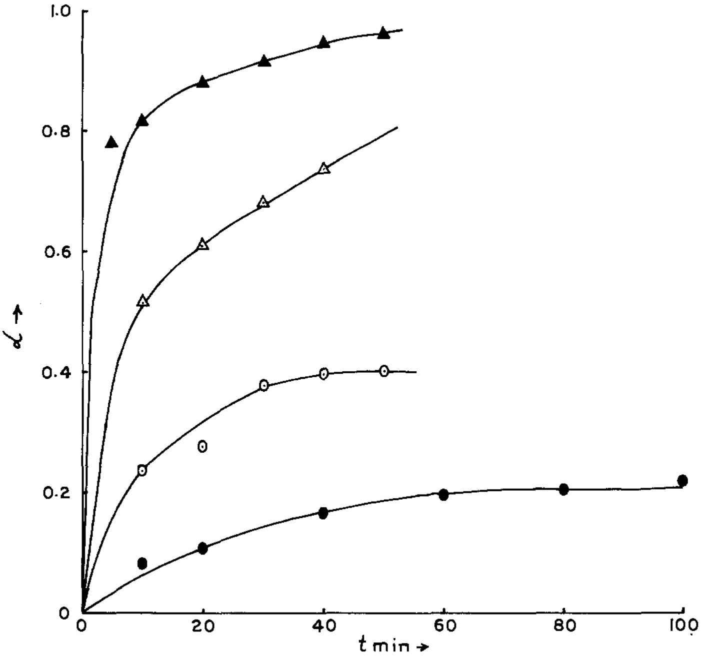

FIG. 4. Typical kinetic data for the reaction between Bi_2O_3 and MoO_3 (molar ratio 1 : 3): ▲, 620°C; △ 580°C; ⊙, 540°C; ●, 500°C.

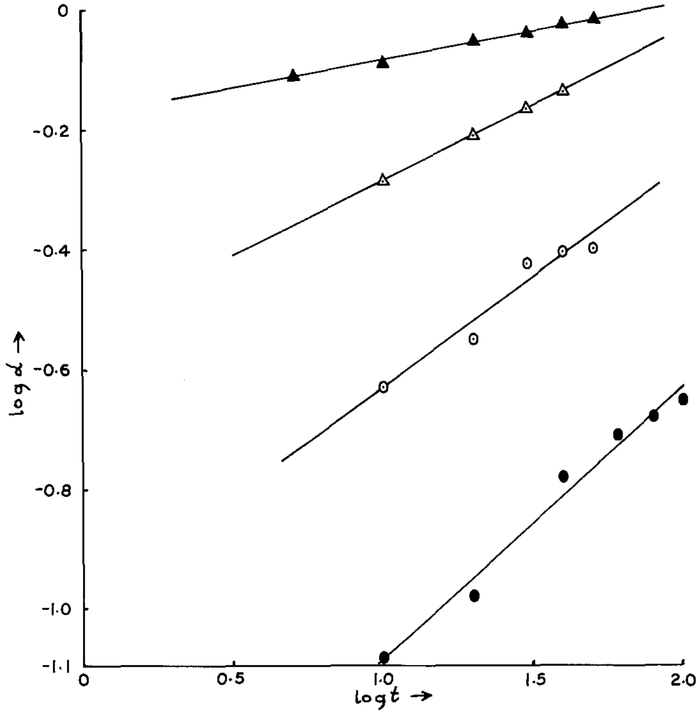

FIG. 5. Test of Eq. (5): ▲, 620°C; △, 580°C; ⊙, 540°C; ●, 500°C.

TABLE III

KINETIC DATA FOR THE REACTIONS

Solid-state reaction		420°C	460°C	500°C	540°C	580°C	620°C
(i)	n	2.6	2.6	2.6	11.5	—	—
	$k \times 10^4$	1.50	4.80	46.0	10.2		
(ii)	n	—	2.3	2.7	4.0	4.0	—
	$k \times 10^4$	—	9.70	40.0	58.0	174	—
(iii)	n	—	—	2.2	2.8	4.0	10.5
	$k \times 10^4$	—	—	3.90	15.8	69.0	129
(iv)	n	—	—	2	1.7	3.0	7.8
	$k \times 10^4$	—	—	10.6	123	282	329
(v)	n	—	—	—	2.1	2.9	4.6
	$k \times 10^4$	—	—	—	10.9	93	199

Note. k is expressed as min^{-1}.

ble III. These were obtained by the method of least squares. Both n and k were found to depend on temperature. Similar behavior has been observed for the heterogeneous reaction between NO_2 and *ortho*-toluidine nitrate (*18*). The plot of $\log k$ versus $1/T$ is linear (Fig. 6).

The above set of reactions is unusual in the sense that n can depend on temperature. It appears that this feature is probably related to the nature of the product layer, and the diffusion coefficient of the reactant species through the product layer progressively decreases as the thickness of the product layer increases. One may imagine that initially a porous layer is formed which becomes incoherent in the course of time.

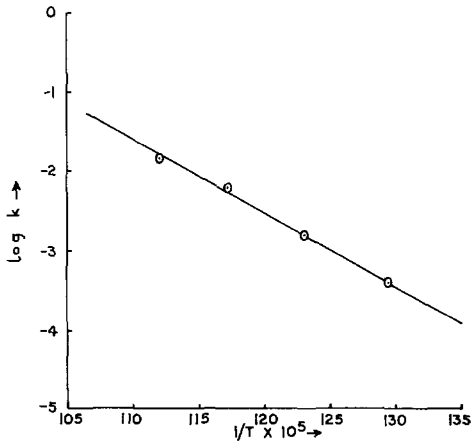

FIG. 6. Temperature dependence of k.

The kinetic data were analyzed with the help of the equation

$$\alpha = k_2 t^{1/2} - k_3 t, \qquad (6)$$

which also satisfied the data, where k_2 and k_3 are constants. The fit of the data was better in the case of Eq. (6) as compared to Eq. (5). Typical plots demonstrating the applicability of Eq. (6) are given in Figs. 7 and 8. Equation (6) is easier to interpret physically. We can rewrite Eq. (6) as

$$\alpha = t^{1/2}[k_2 - k_3 t^{1/2}]. \qquad (7)$$

The quantity within brackets would be proportional to the square root of the diffusion coefficient. Although it is difficult to derive Eq. (7) theoretically, intuitively it appears that two types of diffusion are involved in the above set of reactions. These are (a) grain boundary diffusion and (b) bulk diffusion. The diffusion coefficient depends on the number of grain boundary contact points, which decrease as the reaction progresses or as the temperature increases. In this picture, the constant k_2 would be asso-

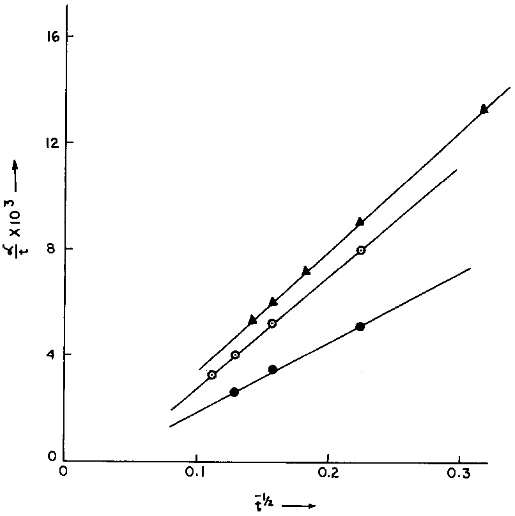

FIG. 7. Test of Eq. (6): ●, 420°C (1 : 1); ⊙, 460°C (1 : 1); ▲, 460°C (1 : 2).

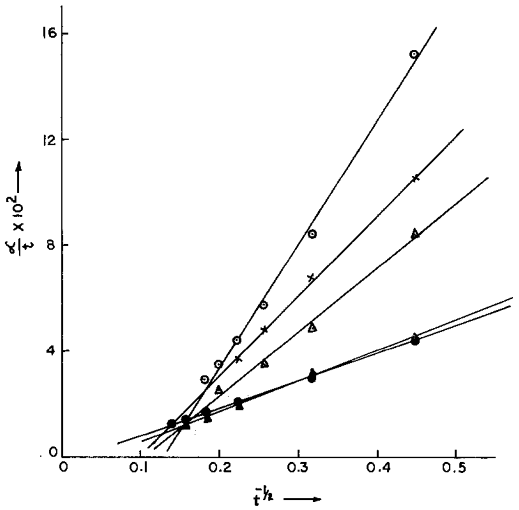

FIG. 8. Test of Eq. (6): ●, 500°C (1 : 1); ⊙, 540°C (1 : 1); ▲, 500°C (1 : 2); △, 540°C (1 : 2); ×, 580°C (1 : 2).

ciated with the bulk diffusion coefficient. Incidentally, the plot of log k_2 against $1/T$ yields a straight line and the overall energy of activation comes out to be 20–40 kcal/mole (Table IV), which is very close to the value expected for bulk diffusion.

The values of k_2 and k_3 are recorded in Table IV. Whereas the values of k_2 and k_3 are of the same order for 1 : 1 and 1 : 2 compounds, the corresponding value for 1 : 3 compounds is considerably lower. This is probably due to the difficulty in getting a suitable orientation for solid grains of Bi_2O_3 and MoO_3 to produce the 1 : 3 compound. For such a case, grain boundary geometry favorable for the reaction would also be

TABLE IV

VALUES OF k_2 AND k_3 FOR VARIOUS REACTIONS AT DIFFERENT TEMPERATURES AND ENERGY OF ACTIVATION

Solid-state reaction		420°C	460°C	500°C	540°C	580°C	620°C	E
(i)	$k_2 \times 10^2$	2.66	4.21	10.4	46.6	—	—	26
	$-k_3 \times 10^4$	7.81	14.2	23.7	595	—	—	
(ii)	$k_2 \times 10^2$	—	4.57	11.4	24.3	30.5	—	20
	$-k_3 \times 10^4$	—	11.5	54.2	259	307	—	
(iii)	$k_2 \times 10^2$	—	—	2.65	8.58	21.2	44.0	32
	$-k_3 \times 10^4$	—	—	3.08	39.6	159	477	
(iv)	$k_2 \times 10^2$	—	—	3.61	7.61	27.1	48.5	31
	$-k_3 \times 10^4$	—	—	4.10	−53.9	189	618	
(v)	$k_2 \times 10^2$	—	—	—	3.66	16.9	34.7	40
	$-k_3 \times 10^4$	—	—	—	−0.02	89.4	375	

Note: k_2 is expressed as $\min^{-1/2}$, and $-k_3$, as $\min^{-1}$; E is given as kcal/mole.

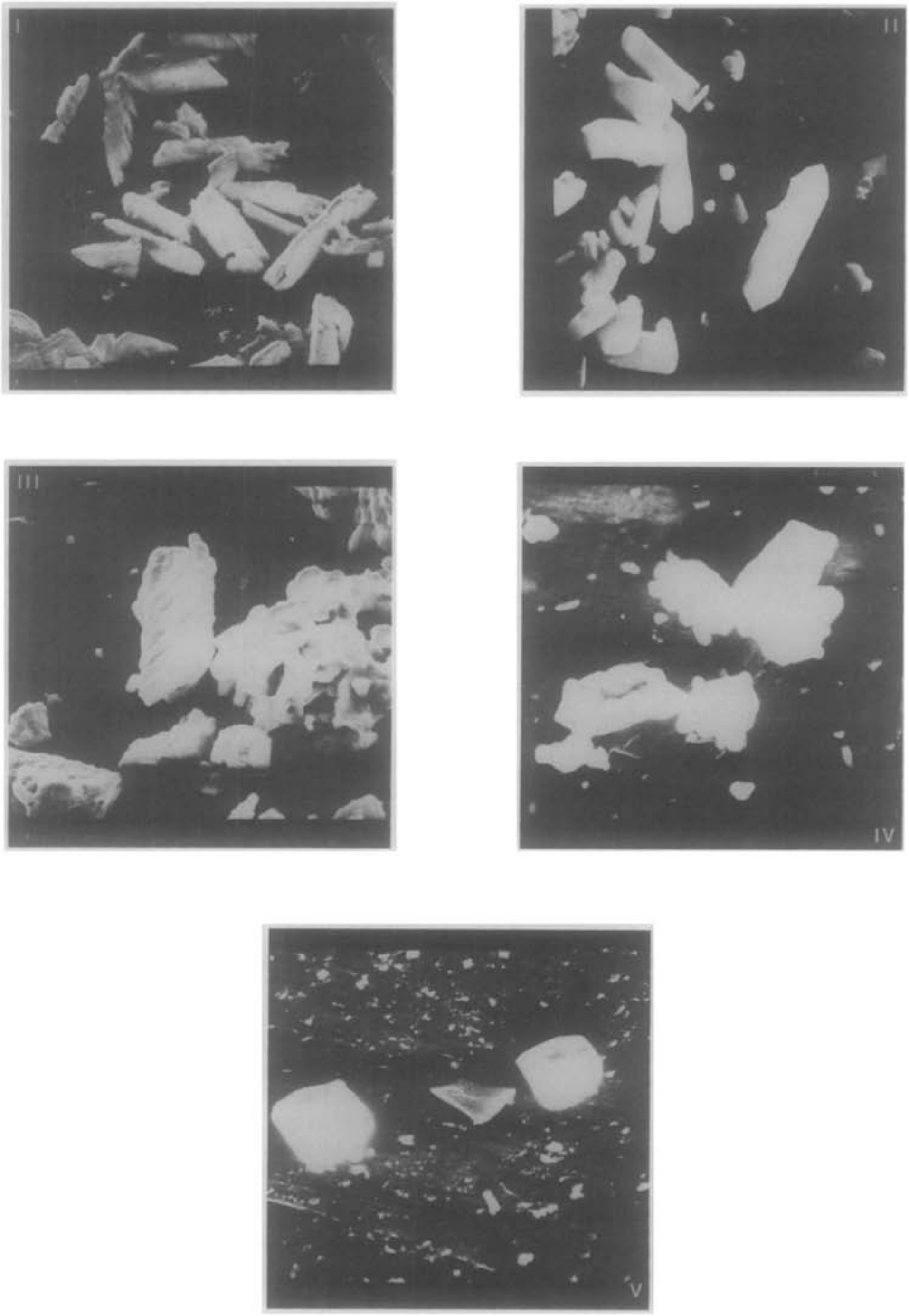

FIG. 9. SEM photographs of (I) Bi$_2$O$_3$, ×1560; (II) MoO$_3$, ×1560; (III) Bi$_2$O$_3$ · MoO$_3$, ×1680; (IV) Bi$_2$O$_3$ · 2MoO$_3$, ×1650; (V) Bi$_2$O$_3$ · 3MoO$_3$, ×840.

more difficult to achieve, since the grains of reactants have plate habit. The scanning electron micrographs of Bi_2O_3, MoO_3, and aged samples of $Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot 2MoO_3$, and $Bi_2O_3 \cdot 3MoO_3$ are shown in Fig. 9 (plates I to V).

It should be noted that only a plausible mechanism can be inferred from formal kinetics and one cannot furnish an irrefutable proof of mechanism. One cannot prove a mechanism; one can only falsify it. So long as it is not falsified, it will hold the field. Nevertheless, one can collect useful information about the mechanism from kinetic studies.

We will now comment on the mechanism of the solid-state reaction for the formation of the 1 : 3 compound. Since 1 : 3 compound can be prepared by solid-state reaction between 1 : 2 compound and MoO_3, it may be that when 1 mole of Bi_2O_3 and 1 mole of MoO_3 are mixed, 1 : 1 compound would be the first to be produced and then 1 : 2 and finally 1:3 compound. This is not supported by experimental evidence. Results show that MoO_3 is consumed in the reaction and stoichiometric calculations further show that neither 1 : 1 nor 1 : 2 compounds nor solid–solid solutions can be formed since some residue of MoO_3 would always be left. The X-ray studies do not give evidence of unreacted MoO_3 in the diffraction pattern of the 1 : 3 compound. This is further supported by the fact that the melting point of the compound is found to be sharp and is in agreement with previous data.

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