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Relationship between Structure and Activity of Mixed Oxides as Oxidation Catalysts

I. Preparation and Solid State Reactions of Bi-molybdates*

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In order to study the catalytic properties of pure Bi-molybdate we have first examined the conditions which allow the preparation of pure Bi-molybdate by precipitation.

Low pH, low temperature and high concentration of molybdenum lead to the formation of $Bi_2(MoO_4)_3$. High temperature, high pH and high concentration of bismuth lead to the formation of $(BiO)_2MoO_4$. High temperature, high pH and low concentration of bismuth lead to the formation of $(BiO)_2Mo_2O_7$ (Erman phase).

We propose that the Erman phase and 2/3 Bi-molybdate are formed by precipitation of the bismuthyl salts of $Mo_2O_7^{2-}$ and $Mo_3O_{10}^{2-}$, respectively. By varying the precipitation conditions, these two anions are either present or absent.

In addition, we have found that $(BiO)_2Mo_2O_7$ exhibits an adsorption property toward Bi cations. $(BiO)_2MoO_4$ forms at high temperature in the reaction of $(BiO)_2Mo_2O_7$ with the Bi cations adsorbed.

We also report the solid state reactivity of the three Bi-molybdates towards the pure oxides Bi_2O_3 and MoO_3.

INTRODUCTION

Some discrepancies exist in the literature concerning the nature of Bi-molybdates prepared with ratios Bi/Mo = 1 and Bi/Mo = 2. The best known divergence concerns the presence or not of the so-called Erman phase in Bi-molybdates with a ratio Bi/Mo = 1. The presence of the Erman phase was always observed in Bi-molybdates prepared by precipitation. Erman *et al.* (*1*) found the so-called Erman phase in products obtained by precipitation from a solution of Bi^{III} with Mo^{VI} (ratio Bi/Mo = 1). Pasquon *et al.* (*2*) detected by X-rays the Erman phase in products obtained by coprecipitation of Bi^{III} and Mo^{VI} solutions (ratio Bi/Mo = 1) with SiO_2. However, ir analysis of this compound revealed the presence of bands characteristic of Bi-molybdate 2/3 (*3*). Béres *et al.* (*4*) observed the Erman phase also by coprecipitating Bi^{III} and Mo^{VI} from solution in the presence of H_3PO_4. According to Bleyenberg *et al.* (5), Rashkin *et al.* (*6*), Aykan (*7*), Batist *et al.* (*8*) and Kohlmuller *et al.* (*9*), Bi-molybdates with a ratio Bi/Mo = 1 obtained by solid state reaction may exclusively give mixtures of Bi/Mo 2/3 and Bi/Mo 2/1. Batist *et al.* (*8*) observed that the Erman phase can also be formed by solid state reaction between Bi/Mo 2/3 and Bi/Mo 2/1 at a temperature (600°C) higher than that of the normal activation of Bi-molybdates (500°C).

A lesser known divergence concerns the nature of Bi-molybdate with a ratio Bi/Mo = 2. This divergence was pointed out for the first time by Dewing (*10*), who re-

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ported that his ir spectrum of a Bi/Mo = 2/1 was quite different from that reported by Trifirò *et al.* (*11*). The same remark was also made by Schuit (*12*).

In order to clarify these discrepancies, we have tried to prepare pure Bi-molybdates with Bi/Mo ratios 2/3, 1/1, 2/1 by precipitation, avoiding solid state reaction. Care was taken to avoid coprecipitation of pure hydroxides and precipitation of bismuth salts of polymerized Mo ions with a very high Mo/Bi ratio. This was required owing to the fact that such salts, after activation at high temperature, can decompose to give one of the known Bi-molybdates plus MoO_3.

We have also investigated the solid state reactions of the single Bi-molybdates with Bi_2O_3 and MoO_3.

EXPERIMENTAL

Method of Preparation of Bi-molybdates

I. Coprecipitation. The choice of precipitation conditions was determined by the following criteria:

(1) no evaporation of the solution in order to avoid precipitation of pure hydroxides;
(2) precipitation pH must be kept low in order to avoid precipitation of $Bi(OH)_3$;
(3) control of the degree of polymerization of Mo anions, by adjustment of pH, temperature of precipitation, and concentration of molybdenum.

Several preparations of Bi-molybdates were obtained from a solution of Bi^{III} and Mo^{VI}, with different Bi/Mo ratios and by different procedures.

Nature of the Solutions

Solutions of Bi^{III} and of Mo^{VI} at different pH (1–2.2) and at different temperatures (0–80°C) were prepared by dissolving, respectively, $Bi(NO_3)_3 \cdot 5H_2O$ (Fluka) and H_2MoO_4 (B.D.H.) in distilled water (400–1500 ml) acidified with HNO_3.

Precipitation Procedure

Two methods of precipitation were used: the solution of Bi^{III} was added to Mo^{VI} solution or vice-versa. We shall call the first method A and the second B. After precipitation, solutions were immediately filtered and analysis of Bi^{III} and Mo^{VI} were carried out on the solution. Filtration was more difficult for precipitates obtained by method B than for those obtained by method A. In some cases the solutions of Bi^{III} and of Mo^{VI} were added very slowly.

Chemical Analysis

Bi^{III} in solution was analyzed as Bi_2O_3 by precipitation with $(NH_4)_2CO_3$ and calcination at 500°C. Mo^{VI} in solution was analyzed as $PbMoO_4$ by precipitation with $Pb(NO_3)_2$ at pH 3 in acetic acid.

Calcination of Bi-molybdates

Calcinations were carried out at 120, 200, 300, 500°C for one hour.

II. Solid state reaction. Bi-molybdates were prepared by 1-hour reaction of $(BiO)_2Mo_2O_7$ with pure oxides at 500°C. Reactions between Bi_2O_3 and MoO_3 were also carried out for comparison.

III. Infrared analysis. Infrared spectra were recorded with the KBr technique by a grating infrared spectrometer (Perkin–Elmer model 457).

IV. X-Ray powder data. X-Ray diffraction patterns were recorded with a Geiger-counter Philips spectrogoniometer with Cu_α radiation.

V. Diffuse reflectance spectra. Diffuse reflectance spectra were recorded with a Cary 15 apparatus with a diffuse reflectance attachment.

RESULTS

Table 1 reports the precipitation conditions for 17 preparations.

The Bi/Mo ratio in the Bi-molybdates, calculated from the analysis of Bi^{III} and Mo^{VI} in the mother liquors, was generally different from the initial ratio in solutions. Ratios approached 1 except for Bi-molybdates prepared at the two extreme condi-

TABLE 1
Bismuth Molybdate Preparations

Preparation	Initial Bi/Mo ratio in solution	Concentration of		Concentration of		Mode of solution addition	Temp. (°C)	pH	Color of precipitate	Filtrate analysis	Ratio Bi/Mo in ppt. by analysis	Compounds revealed[a]
		Mo (mmoles)	H_2O ml	Bi (mmoles)	H_2O ml							
Bi-Mo-1	1	1.5	1500	1.5	1500	B	80	2.2	yellow	Mo No Bi	1.20	1/1 + 2/1
Bi-Mo-2	1	1.5	1500	1.5	1500	A	80	2.2	yellow	Mo No Bi	1.18	1/1 + 2/1
Bi-Mo-3	1	2.5	400	2.5	1500	A	80	2.2	pale yellow	Mo No Bi	1.15	1/1 + 2/1 traces
Bi-Mo-4	1	3.0	400	3.0	1500	A	80	2.2	pale yellow	Mo No Bi	1.10	1/1 + 2/1 traces
Bi-Mo-5	1	4.5	400	4.5	1700	A	80	2.2	pale yellow	trace Mo No Bi	1.0	1/1 + traces 2/1, 2/3
Bi-Mo-6	1	3.0	400	3.0	1500	B	80	2.2	pale yellow	trace Mo No Bi	1.0	1/1 + 2/1 traces
Bi-Mo-7	1	6.0	200	6.0	1500	A	20	1.5	white	No Mo Bi	0.75	2/3 + 1/1 traces

Bi-Mo-8	1	6.0	200	6.0	1500	A	20	1.0	no precipitate	—	—	
Bi-Mo-9	1	6.0	200	6.0	1500	A	0	1.5	no precipitate	—	—	
Bi-Mo-10	2/3	4.5	400	3.0	1500	A	80	2.2	pale yellow	trace Mo No Bi	0.85	1/1 + 2/3 traces +2/1 traces
Bi-Mo-11	2/3	4.5	400	3.0	1500	B	80	2.2	pale yellow	trace Mo No Bi	1.0	1/1 + 2/1 traces
Bi-Mo-12	2/3	9.0	200	6.0	1200	A	20	1.5	white	No Mo Bi	0.7	2/3
Bi-Mo-13	2/1	1.5	400	3.0	1500	B	80	2.2	yellow	No Mo Bi	1.5	2/1 + 1/1
Bi-Mo-14	2/1	1.5	400	3.0	1500	A	80	2.2	yellow	No Mo Bi	1.5	2/1 + 1/1
Bi-Mo-15	2/1	1.5	1500	3.0	1500	B	80	2.2	yellow	No Mo Bi	1.85	2/1 + 1/1 traces
Bi-Mo-16	2/1	1.5	400	3.0	1500	A very slow addition	80	2.2	yellow	No Mo Bi	1.3	1/1 + 2/1
Bi-Mo-17	1	3.0	400	3.0	1500	B	60	2.2	pale yellow	Mo No Bi	1.0	1/1 + traces 2/1, 2/3

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[a] Traces of Bi-molybdate 2/3 can be revealed by ir bands in 900–950 cm^{-1} range; traces of Bi-molybdate 2/1 can be revealed by ir band at 550 cm^{-1} and by high absorption at 450 mμ in diffuse reflectance spectra; traces of Bi-molybdate 1/1 can be revealed in Bi-molybdate 2/1 by ir band at 890 cm^{-1} and in Bi-molybdate 2/3 by higher intensity in X-ray spectra of the peak at d = 3.187.

tions, such as (a) high Mo^{VI} dilution, high T and high pH, where it approached 2, and (b) high Mo^{VI} concentration, low T and low pH, where it approached 2/3.

Analysis of X-ray Patterns

In Table 2 the bands of some Bi-molybdates activated at 500°C, are reported. The data were compared with those reported by Erman *et al.* (*1*), Aykan (*7*) and Batist *et al.* (*8*). Intensities of the single bands sometimes differ from those reported by the above authors.

Sample 1 showed the characteristic bands of the Erman phase (d = 3.187, 2.795, 2.699, 1.985, 1.681, 1.635) (*1, 8*). However the bands at d = 3.147, 2.742, 1.920 also revealed the presence of small amounts of Bi-molybdate 2/1 (*7, 8*).

Sample 4 showed only the characteristic bands of the Erman phase.

Sample 7 revealed the bands at d = 3.187, 3.05, 2.779, characteristic of Bi-molybdates 2/3 (*7, 8*). The higher intensity of the band at d = 3.187 shows the presence of the Erman phase.

TABLE 2
X-RAY PATTERNS OF Bi-MOLYBDATES

Samples													
1		4		15		7		13		17		10	
d	o/o	d	o/o	d	o/o	d	o/o	d	o/o	d	o/o	d	o/o
6.55	1	6.55	2	8.4	4	6.2	1	8.04	3	8.04	2	6.82	1
												6.55	2
5.89	1	5.72	2	3.73	2	7.74	2	6.55	2	6.35	1	5.72	2
4.86	2	5.16	1	3.187	8	6.82	10	5.86	2	5.90	1	5.16	1
										5.72	2	4.861	2
4.74	1	4.861	3	3.15	100	6.227	3	5.21	2	5.16	1	4.815	3
3.767	1	4.746	2	2.179	2	5.32	2	4.87	3	4.861	3	4.746	2
3.187	100	3.767	2	2.740	33	4.815	22	4.74	2	4.146	2	3.767	2
3.147	15	3.187	100	2.683	9	4.552	8	3.73	2	3.767	2	3.580	3
2.795	28	3.147	4	4.595	2	3.739	2	3.187	100	3.187	100	3.248	2
												3.187	100
2.742	4	3.044	2	2.464	7	3.580	18	3.147	70	3.147	8	3.147	4
2.699	10	2.795	30	2.254	1	3.411	4	2.795	27	3.045	5	3.045	10
2.189	1	2.135	1	1.931	9	3.322	4	2.742	20			2.873	4
2.166	1	2.699	9	1.917	25	3.248	16	2.699	24	2.96	1	2.795	28
1.985	2	2.189	1	1.881	2	3.19	100	2.479	2	2.86	1	2.779	2
1.977	2	2.166	1	1.676	2	3.05	70	1.988	3	2.795	22	2.699	8
1.940	10	1.985	3	1.649	25	2.873	42	1.917	3	2.742	2	2.479	2
1.920	3	1.977	3	1.627	15	2.779	15	1.941	35	2.699	9	2.189	1
1.681	18	1.941	13	1.573	8	2.479	18	1.917	20	2.170	1	2.100	1
1.649	4	1.681	22			2.319	1	1.681	25	1.985	2	1.996	2
												1.985	3
1.635	8	1.635	9			2.269	1	1.632	25	1.977	2	1.977	3
1.627	2					2.		1.627	25				
1.595	5	1.595	6			2.240	4	1.393	10	1.941	21	1.941	12
						2.175	1	1.575	8	1.917	1	1.941	1
						2.119	1			1.881	1	1.871	1
						2.049	1			1.681	30	1.681	20
						1.996	13					1.635	9
						1.956	4					1.595	5
						1.910	10				2		
						1.871	13			1.64	2		
						1.842	4			1.637	10		
						1.800	4			1.595	8		

Sample 13 revealed both the bands of the Erman phase at d = 3.187, 2.795, 2.695 and those of Bi-molybdate 2/1 at d = 3.147, 2.742, 2.699, 1.917.

Sample 15 revealed the bands at d = 3.15, 2.740, 1.92 of Bi-molybdate 2/1. The presence of the band at 3.187 also revealed the presence of traces of the Erman phase.

Sample 17 revealed both the bands of the Erman phase at d = 3.187, 2.795, 2.699 and that at d = 3.05 of Bi-molybdate 2/3, which is present in low amount, and the bands at d = 3.15 (with a higher intensity than in the Erman phase), 2.740, 1.917 of Bi-molybdate 2/1 present in low amounts.

Sample 10 revealed the band of Erman phase and those at d = 3.05 typical of Bi-molybdate 2/3.

IR Spectra and Their Interpretation

Figures 1, 2 and 3 show the ir spectra of the Bi-molybdates activated at 500°C for 1 hour.

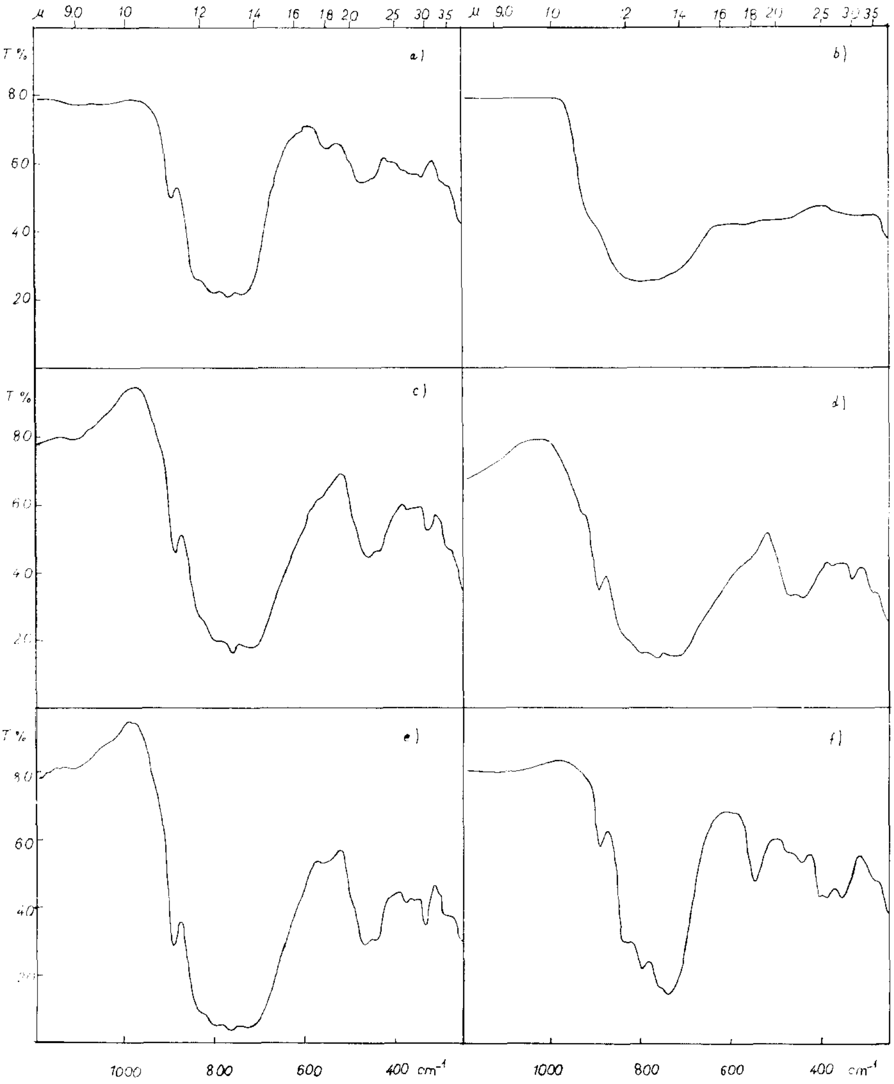

FIG. 1. Infrared spectra of Bi-molybdates: (a) Bi-Mo-1 calcined 1 hr 500°C; (b) Bi-Mo-4 calcined 1 hr 120°C; (c) Bi-Mo-4 calcined 1 hr 500°C; (d) Bi-Mo-5 calcined 1 hr 500°C; (e) Bi-Mo-11 calcined 1 hr 500°C; (f) Bi-Mo-6 calcined 1 hr 500°C.

Essentially three different types of spectra can be picked out in the three figures: (i) sample 4 (which by X-ray analysis was found to be the Erman phase) with a sharp band at 890 cm^{-1} and broad bands at about 800, 470, 440 and 350 cm^{-1}; (ii) sample 7 (which by X-ray analysis was found to be Bi-molybdate 2/3) with characteristic bands at 950, 935 and 900 cm^{-1}, and (iii) sample 15, (which by X-ray analysis was found to be Bi-molybdate 2/1) with bands at 840, 800, 730, 550, 360 cm^{-1}. All other spectra seem to be a combination of two or of all three of these.

In the spectra of sample 1 (Fig. 1*a*), sample 6 (Fig. 2*h*) and sample 11 (Fig. 1*e*), the characteristic bands of the Erman phase may be observed at 890, 470 and 440 cm^{-1}. However, the band at 550 cm^{-1} indicates the presence of Bi-molybdate 2/1.

The spectra of samples 2 and 3 are similar to that of sample 1 and are not reported.

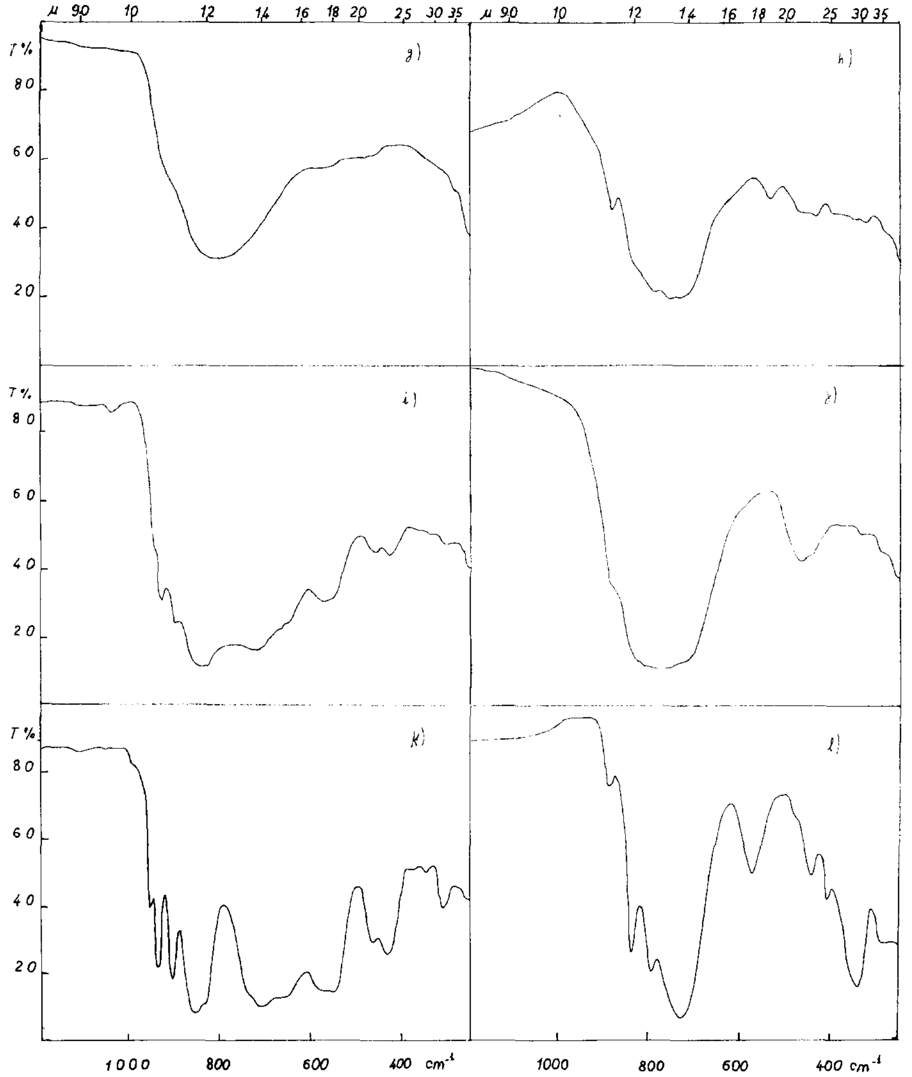

FIG. 2. Infrared spectra of Bi-molybdates: (g) Bi-Mo-7 calcined 1 hr 120°C: (h) Bi-Mo-6 calcined 1 hr 500°C; (i) Bi-Mo-7 calcined 1 hr 200°C; (j) Bi-Mo-15 calcined 1 hr 300°C; (k) Bi-Mo-7 calcined 1 hr 300°C; (l) Bi-Mo-15 calcined 1 hr 500°C.

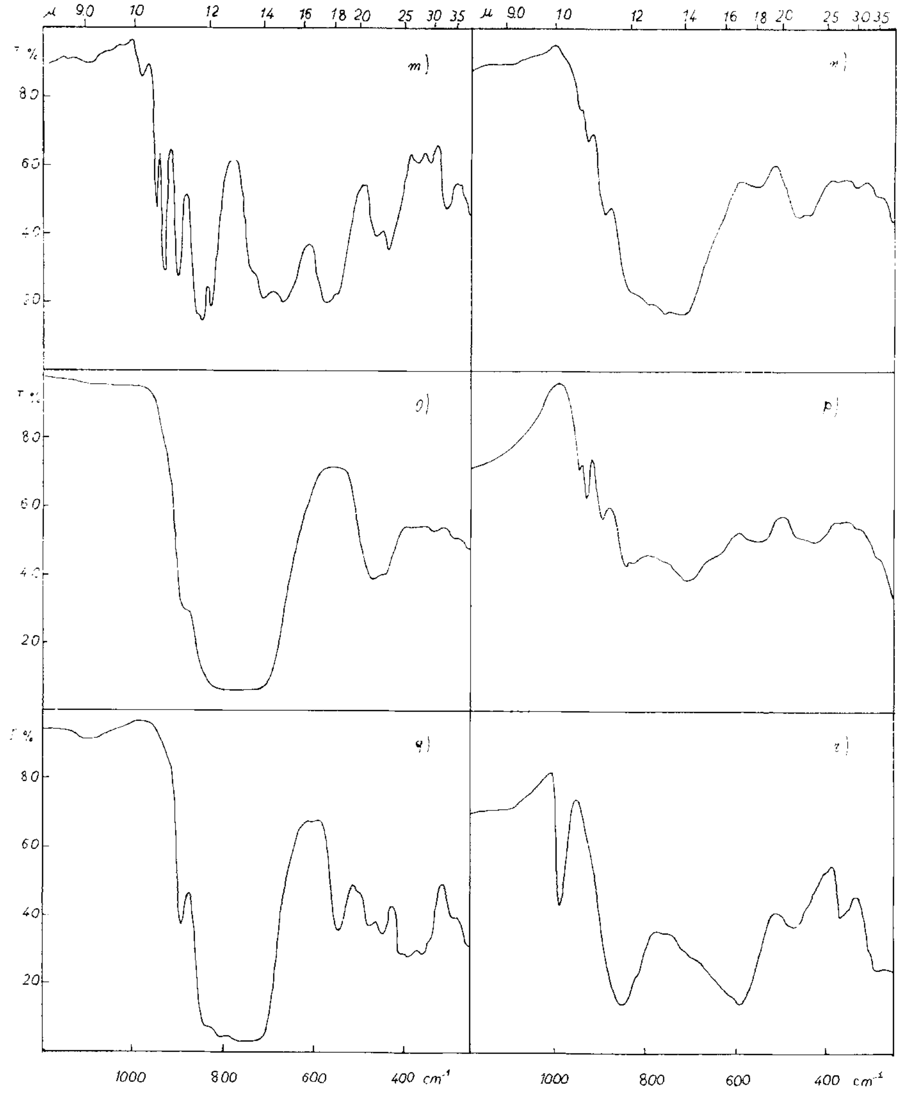

FIG. 3. Infrared spectra of Bi-molybdates: (m) Bi-Mo-12 calcined 1 hr 500°C; (n) Bi-Mo-17 calcined 1 hr 500°C; (o) Bi-Mo-4 calcined 1 hr 300°C; (p) Bi-Mo-10 calcined 1 hr 500°C; (q) prepared by adding Bi-Mo-4 freshly prepared in a solution of Bi^{3+} and calcined 1 hr at 500°C; (r) $Bi_2Mo_2O_7 + MoO_3$—reaction temp. 300°C.

The spectra of sample 10 (Fig. 3*p*) show the presence of bands at 960, 935, 900 cm^{-1} of Bi-molybdates 2/3.

The spectra of sample 3 (Fig. 1*d*) show mainly the bands of the Erman phase. However, the shoulder at about 935 cm^{-1} reveals the presence of traces of Bi-molybdates 2/3.

The spectra of samples 7 (Fig. 2*i*) and 12 (Fig. 3*m*) show the presence of the bands of the 2/3 compound at 950, 935 and 900 cm^{-1}. The band at 980 cm^{-1} in the spectrum of sample 12 is characteristic of MoO_3.

In the spectra of samples 13, 14, 15 (Fig. 2*l*) the bands of the 2/1 compound are mainly present. The weak band detected at 890 cm^{-1} also shows the presence of 1/1 compound. The spectrum of Bi-molybdate Bi–Mo-16 (Fig. 1*f*) shows the presence both of the bands at 890 and 470 cm^{-1}, typical of 1/1, and of the bands at 840 and at 550 cm^{-1} typical of 2/1.

The spectrum of sample 17 (Fig. 3*n*) is very similar to that of the Erman phase, but weak bands at 935 and 950 cm^{-1} belonging to the 2/3 are present. Figure 1*b* and Fig. 3*o* show the spectra of sample 4 after activation at 120 and 300°C, respectively. These two spectra are very similar to that of the sample subjected to activation at 500°C.

We also ran the spectrum of sample 15 after activation at 300°C (Fig. 2*j*). It differs from that of the sample activated at 500°C, but is similar to that of the typical 1/1 sample. This means that the Bi-molybdate 2/1 structure occurs at a high temperature.

The spectra of sample 7 after activation at 120, 200 and 300°C are reported in Fig. 2. The spectra of the samples activated at 500°C and 300°C are similar. Bands in the range between 900 and 950 cm^{-1}, typical of Bi-molybdate 2/3, are still present after activation at 200°C.

Diffuse Reflectance Spectra and their Interpretation

From the diffuse reflectance spectra of bismuth molybdate, the absorption function $(A/R)^{1.383}$ (where R = percentage reflectance; $A = 100\text{-}R$) was calculated at 450 mμ according to the method employed by Doyle and Forbes (*13*). The results are reported in Table 3.

Very low values of $(A/R)^{1.383} = 0.01$ indicate the presence of Bi-molybdate 2/3 (samples 7 and 12), and values near 0.1 indicate the presence of Erman phase (samples 4 and 5).

TABLE 3
DIFFUSE REFLECTANCE. VALUES OF ABSORPTION FUNCTION $(A/R)^{1.383}$ AT 450 mμ

Samples	$(A/R)^{1.383}$
Bi-Mo-15	0.25
Bi-Mo-1, 2, 13, 14	0.15–0.22
Bi-Mo-3, 4, 5, 6, 10, 11	0.11–0.13
Bi-Mo-7, 12	0.01

Values of $(A/R)^{1.383} > 0.1$ suggest the presence of Bi-molybdate 2/1 (see the high value found for sample 15, which from X-ray analysis was found to consist mainly of Bi-molybdate 2/1).

Products of Solid State Reaction

Table 4 shows the results of 1-hr reactions carried out at 300°C and 500°C of $(BiO)_2Mo_2O_7$, $(BiO)_2MoO_4$ and $Bi_2(MoO_4)_3$, respectively, with Bi_2O_3 and MoO_3. $(BiO)_2MoO_4$ and $Bi_2(MoO_4)_3$ were prepared at 500°C by solid state reaction between $(BiO)_2Mo_2O_7$ and Bi_2O_3 or MoO_3, respectively.

The reaction extent was followed by ir analysis: ir spectra showed the disappearance of the band at 980 cm^{-1} characteristic of M=O in MoO_3; the decrease or appearance of the bands at 935, 950 cm^{-1} characteristic of $Bi_2(MoO_4)_3$ (*7*); the decrease or disappearance of the band at 890 cm^{-1} characteristic of $(BiO)_2Mo_2O_7$ (*7*). Only in the case of the reaction between $Bi_2(MoO_4)_3 + Bi_2O_3$ did we also use X-ray spectroscopy in order to detect the possible presence of $(BiO)_2MoO_4$.

DISCUSSION

Table 5 summarizes the results obtained. We can deduce from it that in order to obtain a particular bismuth molybdate, with higher or lower degree of purity, very specific precipitation conditions must be adopted.

The type of product formed at the first stage may be determined by what is known in the field of the chemistry of Bi and Mo solution. Bismuth can give salts of the following two cations, Bi^{3+} and $(BiO)^+$. Bismuthyl compounds generally are very slightly soluble: therefore, in our opinion, bismuth precipitates as bismuthyl salts. The chemical behavior of Mo^{VI} in solution is determined by the degree of polymerization of MO^{VI} anions from $(MoO_4)^{2-}$ to $(Mo_2O_7)^{2-}$, (Mo_3O_{10}) (*10*) and to highly polymerized species.

At high molybdenum concentration, at low pH and low temperature, the precipitate predominantly consists of compound 2/3, which forms from some trimolybdate

TABLE 4
RESULTS OF PREPARATION BY SOLID STATE REACTION

Reaction	T (°C) of reaction	Products
$Bi_2O_3 + MoO_3$ (Bi/Mo = 1)	300	Formation of $Bi_2(MoO_4)_3$ presence of free MoO_3
$Bi_2O_3 + MoO_3$ (Bi/Mo = 1)	500	Formation of $Bi_2(MoO_4)_3$ disappearance of free MoO_3
$Bi_2O_3 + MoO_3$ (Bi/Mo = 2)	500	Formation of $(BiO)_2MoO_4$
$(BiO_2)Mo_2O_7 + MoO_3$ (Bi/Mo = 2/3)	300	no reaction observed (Fig. 3*r*)
$(BiO)_2Mo_2O_7 + MoO_3$ (Bi/Mo = 2/3)	500	Formation of $Bi_2(MoO_4)_3$ disappearance of free MoO_3 (Fig. 4*w*)
$(BiO)_2(MoO_4) + MoO_3$ (Bi/Mo = 1)	300	no reaction (Fig. 4*v*)
$(BiO)_2(MoO_4) + MoO_3$ (Bi/Mo = 1)	500	Formation of $Bi_2(MoO_4)_3$ disappearance of free MoO_3 (Fig. 4*u*)
$Bi_2(MoO_4)_3 + Bi_2O_3$ (Bi/Mo = 1)	300	no reaction
[a]$Bi_2(MoO_4)_3 + Bi_2O_3$ (Bi/Mo = 1)	500	Partial reaction (Fig. 4*x*)
$(BiO)_2Mo_2O_7 + Bi_2O_3$ (Bi/Mo = 2)	300	Partial reaction (Fig. 4*t*)
$(BiO)_2Mo_2O_7 + Bi_2O_3$ (Bi/Mo = 2)	500	Complete reaction to $(BiO)_2MoO_4$ (Fig. 4s)

[a] The reaction extent was detected by the increase in intensity of the IR band at 700 cm^{-1} (see Fig. 4) and by the presence in the X-ray pattern of the characteristic peaks of Bi-Mo 2/1.

species $(Mo_3O_{10})^{2-}$ precipitated during addition of the bismuth solution (sample 7) (Fig. 2*k*). It is also possible that tetra- or higher molybdates are precipitated, since during calcination, elimination of MoO_3 takes place with formation of the 2/3 compound (Fig. 3*m*) (sample 12). The presence of traces of Bi-molybdate 2/3 may also be observed in preparations at high T and high pH by the method of type A, where the molybdenum concentration at the initial stage of precipitation is very high (sample 10, Fig. 3*p*, sample 5 (Fig. 1*d*)).

The decrease of the precipitation temperature below 80°C leads to the formation of Bi–Mo 2/3, even when operating at high pH and relatively low concentrations of Mo (sample 17, Fig. 3*n*). At higher temperature, higher pH and lower molybdenum concentration Bi-molybdate 1/1 2/1 are found (samples 1, 2, 3). These two Bi compounds could precipitate from molybdenum anions, assumed to be $Mo_2O_7^{2-}$ and MoO_4^{2-}, respectively. The existence of these two anions was hypothesized (*14*) at $pH > 4$ for $Mo_2O_7^{2-}$ and $pH \simeq 6$ for MoO_4^{2-}; however, at high temperature and

TABLE 5
RANGE OF CONDITIONS UNDER WHICH Bi-MOLYBDATES FORM

⟶ increasing Mo concentration

2/1 + 1/1	2/1 + 1/1 + 2/3	2/3 + 1/1	2/3 + MoO_3	No precipitate
pH 2.2 80°C				0°C pH = 1.0

⟵ increasing temperature
⟵ increasing pH

low concentration of Mo^{VI} anion, a depolymerization may take place. Therefore, it is reasonable to postulate their existence also at the lower pH adopted in this work. Temperature, concentration and pH may be so adjusted until the precipitate virtually consists of the 1/1 compound with only traces of the 2/1 compound. A higher dilution of the molybdenum solution favors the formation of the 2/1 compound (Table 1), which might be attributed to the presence of higher amounts of MoO_4^{2-} in solution (*15*).

However, unlike the formation of 1/1 and 2/3, formation of 2/1 depends considerably on the Bi/Mo ratio in solution and on the activation temperature. In fact, as may be seen from the ir spectra (Fig. 2*j*–2*l*) the characteristic bands of 2/1 (840, 550 cm^{-1}) appear only after activation at 500°C. At 300°C the spectrum is similar to that of the 1/1 (Erman phase, Fig. 3*o*).

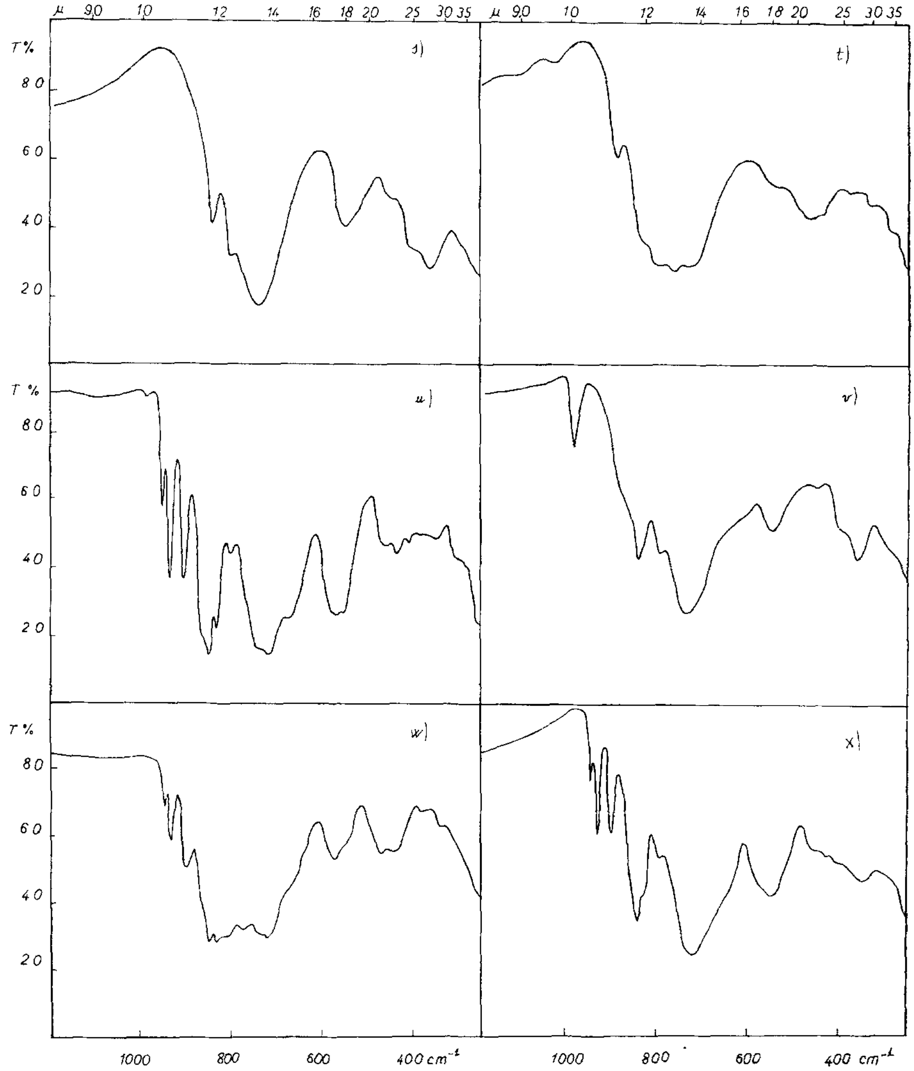

FIG. 4. Infrared spectra of Bi-molybdates prepared by solid state reaction: (s) $(BiO)_2Mo_2O_7 + Bi_2O_3$—reaction temp. 500°C; (t) $(BiO)_2Mo_2O_7 + Bi_2O_3$—reaction temp. 300°C; (u) $(BiO)_2MoO_4 + MoO_3$—reaction temp. 500°C; (v) $(BiO)_2MoO_4 + MoO_3$—reaction temp. 300°C; (w) $(BiO)_2Mo_2O_7 + MoO_3$—reaction temp. 500°C; (x) $Bi_2(MoO_4)_3 + Bi_2O_3$—reaction temp. 500°C.

Therefore, under the conditions adopted in this work, the 2/1 compound is not formed by precipitation but by solid state reaction between the Erman phase and some Bi compound.

Since preparations were carried out at a pH low enough to avoid precipitation of $Bi(OH)_3$, we put forward the hypothesis that the Erman phase has some adsorption properties for the Bi cations. In fact, by introducing freshly prepared Bi–molybdate 1/1 (Bi_2-Mo-4, Erman phase) in a solution of bismuth at 80°C and at pH 2.2, some Bi-molybdate 2/1 (Fig. 3*q*) forms (band at 550 cm^{-1}). It is known that $(TiO)_2Mo_2O_7$ (*16*) shows cationic exchange properties for Bi^{3+}. The structure of this compound cannot be much different from that of $(BiO)_2Mo_2O_7$. In our opinion, the impossibility of precipitating large amounts of $(BiO)_2MoO_4$ is due to the low pH adopted in order to avoid precipitation of $Bi(OH)_3$, which, under the precipitation conditions adopted, determines that the least polymerized Mo anion is essentially $Mo_2O_7^{2-}$.

To confirm that this formation of Bi-molybdate 2/1 occurs by reaction at high temperature between Erman phase and Bi^{3+}, we carried out solid state reactions between the Erman phase and Bi_2O_3. From the results obtained we may see that no practically reaction occurs at 300°C (Fig. 4*t*), after 1 hr, whereas at 500°C, conversion to Bi-Mo 2/1 takes place after 1-hr (Fig. 4*s*).

The adsorption property of Bi-molybdate 1/1 towards Bi cations is higher if the Erman phase precipitates in a solution with excess of Bi rather than if we contact Bi solutions with a precipitated $(BiO)_2Mo_2O_7$ sample. In fact the precipitation by method B leads to higher amounts of Bi-molybdate 2/1 than precipitation by method A (Table 1).

The formation of Bi-molybdate 2/3 seems to occur at low temperature. At 200°C it is already partially formed; in fact, the characteristic bands of 2/3 are present; at 300°C it is completely formed. This does not seem to occur by a solid state reaction, since $(BiO)_2Mo_2O_7$ and $(BiO)_2MoO_4$ practically do not react at 300°C, with MoO_3 (see Table 4). However, the bands of Bi-molybdate 2/3 appear during activation between 120–200°C; this may possibly be explained by assuming that there is $(BiO)_2Mo_3O_{10}$ in the compound that precipitates, and that in activation at $T > 120°C$ it is transformed into $Bi_2(MoO_4)_3$.

Reactivity of Bi-molybdates

$(BiO)_2Mo_2O_7$ shows high reactivity at 500°C both toward Bi_2O_3, with formation of $(BiO)_2MoO_4$ (Fig. 4*s*), and toward MoO_3, with formation of $Bi_2(MoO_4)_3$ (Fig. 4*w*). Table 4 shows some data of the reactivity of $(BiO)_2Mo_2O_7$ towards the pure oxides, compared with that of $Bi_2(MoO_4)_3$ and $(BiO)_2MoO_4$. As a measure of reactivity, we assumed the occurrence or not of reaction at 300°C in the solid state reaction with pure oxides. The following scale of reactivity may be deduced from Table 4: in reactivity towards Bi_2O_3, $MoO_3 >$ Erman phase $= (BiO)_2MoO_4$; in reactivity towards MoO_3, $Bi_2O_3 >$ Erman phase $> Bi_2(MoO_4)_3$.

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