

835. *A Physicochemical Investigation of the Methoxides of Lithium, Sodium, and Potassium.*

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The various solids that are formed when lithium, sodium, or potassium is dissolved in methanol have been characterized by chemical analysis, vapour-pressure measurements, and X-ray diffraction photographs. Lithium forms only LiOMe, the structure of which has been elucidated from powder photographs. Sodium forms NaOMe,2MeOH and NaOMe. Potassium forms KOMe,3MeOH, KOMe,MeOH, and KOMe.

INTEREST has recently been revived in the nature of metal alkoxides.¹ The less electro-positive metals tend to form polymeric, covalent alkoxides, but there is little information about the nature of the structure of the alkoxides of univalent metals.¹ It has been shown that thallium alkoxides tend to form tetramers, and a structure has been suggested for these molecules.² The evidence for the nature of the solids obtained when sodium is dissolved in methanol was for some time in doubt,³ but has apparently been settled in favour of NaOMe,2MeOH and NaOMe.⁴ No comparable information is available for the methoxides of lithium and potassium, except that unsolvated potassium methoxide can be obtained by heating a solution of potassium in methanol.^{3b} It is generally assumed that the alkali-metal alkoxides are ionic, but this assumption may be based on the fact that

¹ Bradley, *Nature*, 1958, **182**, 1211.

² Sidgwick and Sutton, *J.*, 1930, **1461**.

³ (a) Geuther and Scheitz, *Jenaische Zeitschr. für Medicin und Naturwiss.*, 1868, **4**, 16; (b) Wanklyn, *Annalen*, 1869, **150**, 200.

⁴ Geuther and Fröhlich, *Annalen*, 1880, **202**, 288.

these methoxides are normally used as synthetic agents in ionizing media. Indeed it has recently been suggested that lithium methoxide may be a giant polymer.⁵ In order to obtain more information about these systems, a physicochemical investigation has been undertaken of the solids formed when lithium, sodium, and potassium are dissolved in methanol. A preliminary report of the crystal structure of LiOMe has already appeared.⁶

EXPERIMENTAL

The metal was dissolved in an excess of pure, anhydrous methanol. After evolution of hydrogen had ceased, the flask was placed in a dry-box. When the moisture in the air of the dry-box had been removed (CaSO_4), the solution of the methoxide was filtered through glass wool on to a watch-glass inside a vacuum-desiccator, the desiccator sealed, and methanol pumped off until crystallization began. Some of the crystals were put into Lindemann glass tubes in order to record their powder photograph, some were placed in small sample bottles for transfer to the vapour-pressure apparatus, and some were abstracted for analysis. The remainder was left in the desiccator so that more methanol could be pumped off as desired. As additional phases were identified in the vapour-pressure apparatus, samples were taken for identification by means of X-rays and for chemical analysis. Water had to be rigorously excluded at all times, since all the solutions and solids are extremely hygroscopic.

The analyses were carried out by dissolving a known weight of solid in water and titrating the resulting solution against standard hydrochloric acid with Methyl Orange as indicator. The powder photographs were obtained in a 6-cm. diameter rotation camera with Cu-K_α radiation (λ 1.542 Å). Single crystals of two of the solvated methoxides were grown over a period of several months in capillaries, and the diffraction spectra of these crystals were recorded as Weissenberg and oscillation photographs.

RESULTS

It was observed qualitatively that the vigour of the reaction of the various solid phases with water increases with the atomic number of the alkali metal, and, for any given metal, increases with decreasing amounts of structural methanol.

Lithium.—The only detectable phase was LiOMe (Found: Li, 18.7, 18.2. Calc.: Li, 18.3%). The powder photographs could be indexed on a tetragonal cell with $a = 3.55_2$ and $c = 7.68_7$ Å. The systematic absence of the $hk0$ reflexions with $h + k$ odd corresponds to the space group $P4/nmm$ (No. 129). The density calculated on the assumption of two formula units in the cell is 1.300 g./c.c. The observed density, which could not be accurately determined by flotation, was between 1.2 and 1.5 g./c.c. A satisfactory interpretation of the diffracted intensities was obtained with a crystal structure similar to that of lithium hydroxide.⁷ The lithium ions lie at $\pm(1/4, 3/4, 0)$, the oxygen atoms at $\pm(1/4, 1/4, u_1)$, and the carbon atoms at $\pm(1/4, 1/4, u_2)$. The space group requires the methoxide ion to have four-fold symmetry so that the hydrogen atoms, which were ignored in this analysis, presumably adopt a statistical arrangement to conform to this symmetry. The two parameters u_1 and u_2 were determined by trial and error, and found to be 0.10₅ and 0.29, respectively. The observed and calculated results are shown in Table I. The scattering factors used were those of Berghuis *et al.*⁸ No temperature factor was found to be necessary. The agreement index, $R = \sum |I_{\text{obs.}} - I_{\text{calc.}}| / \sum I_{\text{obs.}}$, was 10%.

A projection of the structure on the ab plane is shown in Fig. 1. The lithium atoms (small circles) lie in the plane of the paper, the large full circles denote oxygen atoms above the plane of the paper. Vertically above each of these oxygen atoms lies an attached methyl group. The large open circles represent oxygen atoms and their attached methyl

⁵ Bradley, *Nature*, 1959, **184**, 55.

⁶ Wheatley, *Nature*, 1960, **185**, 681.

⁷ Ernst, *Z. phys. Chem.*, 1933, **B**, **20**, 65; Dachs, *Z. Krist.*, 1959, **112**, 60.

⁸ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

groups lying below the plane of the paper. If the structure is viewed normal to the four-fold axis, it is seen to consist of layers ABCBAABCBA . . ., with A = Me, B = O, and C = Li. The oxygen atoms are bonded to a methyl group on one side and co-ordinated

TABLE 1. *Powder diffraction data for lithium methoxide.*

<i>hkl</i>	$\sin^2 \theta_{\text{obs.}}$	<i>d</i> (Å) *	$\sin^2 \theta_{\text{calc.}}$	<i>I</i> _{obs.} †	<i>I</i> _{calc.}	<i>hkl</i>	$\sin^2 \theta_{\text{obs.}}$	<i>d</i> (Å) *	$\sin^2 \theta_{\text{calc.}}$	<i>I</i> _{obs.} †	<i>I</i> _{calc.}
001	0.0100	7.710	0.0101	700	634	021	0.1977	1.734	0.1985	30	26
002	—	—	0.0402	Abs.	1	014	0.2078	1.692	0.2081	20	23
010	—	—	0.0471	Abs.	—	022	—	—	0.2286	Abs.	0
011	0.0572	3.223	0.0572	500	520	120	—	—	0.2355	Abs.	—
012	0.0869	2.616	0.0873	70	67	005	—	—	0.2414	Abs.	4
003	—	—	0.0905	Abs.	4	121	0.2451	1.557	0.2456	25	43
110	0.0938	2.517	0.0942	100	121	114	0.2552	1.526	0.2552	10	11
111	0.1040	2.391	0.1043	15	13	122	0.2746	1.471	0.2757	10	9
112 } 013 }	0.1358	2.092	0.1344 } 0.1376 }	40	40	023	—	—	0.2789	Abs.	0
004	—	—	0.1610	Abs.	1	015	—	—	0.2986	Abs.	0
113	—	—	0.1847	Abs.	3	123	0.3258	1.351	0.3260	5	3
020	0.1878	1.779	0.1884	50	58	115	0.3455	1.312	0.3457	10	5
						024	—	—	0.3493	Abs.	0

* *d*-spacings. † Abs., absent.

TABLE 2. *Interatomic distances (Å) and angles in lithium methoxide.*

O—Me	1.42	Me...Me	3.55, 4.09
Li...Li	2.51	LiOLi	80.3°
Li...O	1.95	LiOMe	114.5
O...O	2.99	OLiO	101.7, 131.1

to four lithium ions on the other to form square pyramids with oxygen atoms at the centres as shown in Fig. 2. The lithium ions are surrounded by a distorted tetrahedron of oxygen atoms, the tetrahedron being flattened in the *c* direction. The interatomic distances and angles are given in Table 2. These values are normal with the exception

FIG. 1. *Projection of the contents of the unit cell of lithium methoxide down [c]. Small circles denote lithium ions lying in the plane of the paper and large circles oxygen atoms lying in planes above and below that of the lithium ions.*

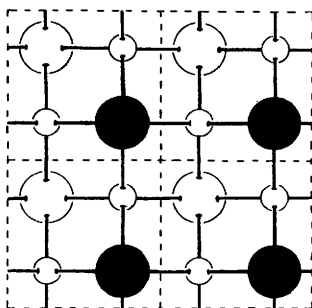
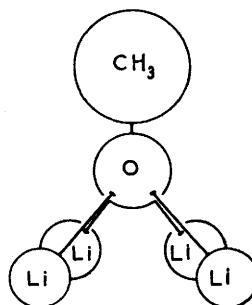


FIG. 2. *The co-ordination of the oxygen atoms in lithium methoxide.*



of the methyl-methyl contacts. In the *c* direction the methyl-methyl contact has the expected value of about 4 Å. In the *a* and *b* directions, however, the methyl groups are very closely packed. It seems reasonable to associate this short contact of 3.55 Å with an enhanced interaction between the lithium ions and the oxygen atoms of the methoxide ions.

The structure has features which can be associated with an approach towards covalency. Apart from the short methyl-methyl contacts, there is a pronounced layer effect which

suggests that, in solvents that are not too polar, sheets of atoms ABCBA, protected by the close-packed methyl groups, might be formed.

Sodium.—Two phases were detected, NaOMe,2MeOH and NaOMe, in agreement with the findings of Geuther and Fröhlich⁴ (Found in NaOMe,2MeOH: Na, 19.6, 19.9, 18.7, 18.6. Calc.: Na, 19.5%. Found in NaOMe: Na, 42.0. Calc.: Na, 42.6%). No evidence for the intermediate NaOMe,MeOH, was found.⁹ The vapour pressure of the equilibrium $\text{NaOMe,2MeOH} \rightleftharpoons \text{NaOMe} + 2\text{MeOH}$ is 20 mm. at 20°. All the methanol can be removed from this dimethanolate by pumping at room temperature for several hours. The methanol is removed almost instantaneously at 190°.

The powder photographs of the dimethanolate could not be satisfactorily indexed. The observed lines are given in Table 3. The photographs of unsolvated sodium methoxide

TABLE 3. Powder diffraction data for sodium methoxide dimethanolate.

Line	Strength *	$\sin^2 \theta_{\text{obs.}}$	d (Å)	Line	Strength *	$\sin^2 \theta_{\text{obs.}}$	d (Å)
1	vs	0.0062	9.792	9	s	0.0904	2.564
2	m	0.0095	7.910	10	w	0.0985	2.457
3	m	0.0244	4.936	11	vw	0.1050	2.379
4	mw	0.0363	4.047	12	Broad	—	—
5	vs	0.0474	3.541	13	ms	0.1609	1.922
6	m	0.0545	3.303	14	m	0.1824	1.805
7	m	0.0746	2.823	15	Broad	—	—
8	mw	0.0816	2.699				

* vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak.

could be interpreted in terms of an orthorhombic cell with $a = 4.32$, $b = 7.42$, $c = 8.73$ Å, although this solution cannot be considered unique. If this cell is correct and if it contains four formula units, the calculated density is 1.282 g./c.c. The density could not be determined directly by flotation. The observed powder lines of sodium methoxide are given in Table 4.

TABLE 4. Powder diffraction data for sodium methoxide.

Line	Strength *	$\sin^2 \theta_{\text{obs.}}$	d (Å)	Line	Strength *	$\sin^2 \theta_{\text{obs.}}$	d (Å)
1	s	0.0078	8.730	15	m	0.2512	1.538
2	vs	0.0108	7.419	16	m	0.2621	1.506
3	vs	0.0427	3.731	17	m	0.2958	1.418
4	s	0.0742	2.830	18	m	0.3305	1.341
5	vw	0.0827	2.681	19	m	0.3583	1.288
6	w	0.1020	2.414	20	m	0.4158	1.196
7	s	0.1061	2.367	21	w	0.4563	1.142
8	s	0.1268	2.165	22	w	0.4904	1.101
9	s	0.1379	2.076	23	m	0.1554	1.074
10	w	0.1638	1.905	24	w	0.5520	1.038
11	ms	0.1698	1.871	25	w	0.5834	1.009
12	m	0.2037	1.708	26	m	0.6394	0.964
13	w	0.2291	1.611	27	w	0.6773	0.937
14	m	0.2355	1.589				

* See footnote to Table 3.

Potassium.—Three phases were detected, KOMe,3MeOH, KOMe,MeOH, and KOMe (Found in KOMe,3MeOH: K, 22.7, 23.0, 22.4. Calc.: K, 23.5%. Found in KOMe,MeOH: K, 38.5, 37.6. Calc.: K, 38.3%. Found in KOMe: K, 55.4. Calc.: K, 55.7%). The vapour pressure of the equilibrium $\text{KOMe,3MeOH} \rightleftharpoons \text{KOMe,MeOH} + 2\text{MeOH}$ is 15 mm. at 19°. The trimethanolate can be converted into the monosolvate by pumping off methanol during several hours at room temperature. The monomethanolate appears to be thermally stable at room temperature, although the remaining methanol can readily be removed by heating to 190°.

⁹ de Forcrand, *Ann. Chim. Phys.*, 1887, **11**, 456.

Powder photographs of KOMe can be indexed on a primitive cubic cell with $a = 8.77 \text{ \AA}$. If there are eight formula units in the cell, the calculated density is 1.382 g./c.c., which appears to be the most likely value. If there are six or twelve formula units, the calculated density is 1.036 and 2.072 g./c.c., respectively. The density could not be observed directly because of the immense affinity of the powder for water. It has not proved possible to obtain a structure for these crystals. The powder diffraction data are given in Table 5.

A solitary single crystal was obtained of what was probably KOMe, MeOH. The unit cell is monoclinic with $a = 14.75 \text{ \AA}$, $b^* = 0.0665 \text{ \AA}^{-1}$, and $c^* = 0.1071 \text{ \AA}^{-1}$. There are

TABLE 5. *Powder diffraction data for potassium methoxide.*

$(h^2 + k^2 + l^2)$	Strength *	$\sin^2 \theta_{\text{obs.}}$	$d \text{ (\AA)}$	$\sin^2 \theta_{\text{calc.}}$	$(h^2 + k^2 + l^2)$	Strength *	$\sin^2 \theta_{\text{obs.}}$	$d \text{ (\AA)}$	$\sin^2 \theta_{\text{calc.}}$		
1	vs	0.0077	8.786	0.0077	40	}	m	0.3122	1.380	{	0.3092
2	w	0.0149	6.317	0.0154	41						0.3169
4	w	0.0308	4.393	0.0309	45	}	vw	0.3519	1.300	{	0.3479
9	s	0.0696	2.923	0.0696	46						0.3556
10	s	0.0773	2.773	0.0773	50		m	0.3856	1.242	{	0.3865
11	m	0.0849	2.646	0.0850	54		vw	0.4168	1.194	{	0.4174
14	m	0.1083	2.343	0.1082	57		vw	0.4409	1.161	{	0.4406
16	m	0.1245	2.185	0.1237	61		vw	0.4695	1.125	{	0.4715
19	m	0.1474	2.008	0.1469	66		vw	0.5109	1.079	{	0.5102
20	m	0.1548	1.960	0.1546	70		vw	0.5407	1.048	{	0.5411
21	mw	0.1627	1.912	0.1623	81	}	vw	0.6289	0.972	{	0.6261
26	m	0.2020	1.716	0.2010	82						0.6339
29	ms	0.2242	1.628	0.2242	89	}	vw	0.6920	0.927	{	0.6880
34	w	0.2621	1.506	0.2628	90						0.6957
36	}	w	0.2822	1.451	{	0.2783	99	0.7681	0.857	{	0.7653
37				0.2860	100	0.7730					

* See footnote to Table 3.

probably sixteen formula units in this cell, giving a calculated density of 1.312 g./c.c. There was no means of checking the constitution of this crystal which was grown in a sealed capillary. If the above interpretation of these single photographs is not correct, at least one other potassium methoxide methanolate must be capable of existence, though no evidence was found for this existence from the vapour-pressure measurements, the analyses, or powder photographs. Powder photographs of the monomethanolate were very diffuse, and showed only three measurable lines. The positions of these lines were consistent with the above cell, but can hardly be considered as confirming it.

Single crystals of the trimethanolate could be grown relatively readily, but always with the unique b axis parallel to the axis of the capillary. The crystals are monoclinic, space group $P2_1/n$ (No. 14), with $a = 14.96$, $b = 7.68$, $c = 13.24 \text{ \AA}$, $\beta = 93.8^\circ$. There are eight formula units in the cell, and the calculated density is 1.455 g./c.c.

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