2. *The Effect of Solvents on the Molecular Complexities of Tantalum* n-*Alkoxides.*

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The molecular weights of tantalum alkoxides Ta(OR)_5, where R = Me, Et, Pr^n, or Bu^n, have been determined ebullioscopically in toluene, acetonitrile, pyridine, and di*iso*propyl ether. These results are discussed in comparison with the values previously found in benzene and in the parent alcohols and it is suggested that the donor power of the solvent has the major influence in determining the molecular complexity of the alkoxide.

EARLIER work (*J.*, 1955, 726) on the normal alkoxides of tantalum, Ta(OR)_5 where R = Me, Et, Pr^n, or Bu^n, showed these compounds were practically dimeric in boiling benzene whilst in the boiling parent alcohols the order of molecular complexities was : ethoxide > propoxide > butoxide > methoxide. It was suggested that the main factors likely to cause the peculiar order of complexities in the parent alcohols were (i) boiling point, (ii) dielectric constant, and (iii) " donor power " of the alcohol. In an attempt to assess the different contributions made by these factors we have determined the molecular weights of these alkoxides ebullioscopically in various solvents. Although it was not possible to choose suitable solvents in which the effects of these factors could be completely isolated from each other the results, which are presented in Table 1, show some significant features.

TABLE 1.

	Molecular complexity in :					
R in Ta(OR)_5	C_6H_6 (b. p. 80°, *D* 2·28)	PhMe (b. p. 110°, *D* 2·38)	MeCN (b. p. 82°, *D* 38·8)	Pyridine (b. p. 114°, *D* 12·5)	Pr^i_2O (b. p. 68°, *D* ~3)	ROH
Me	1·98	1·83	1·50	1·01	1·75	1·20
Et	1·98	1·83	1·50	0·99	1·84	1·78
Pr^n	1·95	1·83	1·50	0·99	1·84	1·70
Bu^n	2·02	1·83	1·48	0·99	1·84	1·40

The values for the boiling point and the dielectric constant (at 20°) are recorded in parentheses for each solvent.

The general picture is that for benzene, toluene, acetonitrile, or pyridine there is no appreciable variation of molecular complexity from one alkoxide of tantalum to another, although the complexities are clearly dependent on the nature of the solvent. The pentamethoxide appears anomalous in di*iso*propyl ether in which the other alkoxides all have the same complexity. We suggest that the difference in the complexities found in benzene and toluene is caused by the effect of temperature alone because these solvents are very similar in dielectric constant and " donor power." Moreover, the decrease in complexity with increase in boiling point is in accord with the prediction that increase in temperature should promote the dissociation of the dimeric alkoxides.

The results in Table 1 suggest a value of ~40 kcal./mole as a rough estimate of the energy of dimerisation. This gives the energy of each intermolecular Ta–O bond as ~20 kcal. in the dimer. Next we consider the effect of dielectric constant bearing in mind that solvents of high dielectric constant usually have marked donor properties. However the data for acetonitrile and pyridine lead us to the opinion that dielectric constant cannot be of major importance. Thus, when allowance is made for the effect of temperature, the complexity in acetonitrile (*D* 38·8) should be 1·35 to be comparable with the value 1·00 in boiling pyridine (*D* 12·5) and, the influence of donor power being ignored, it appears that increase in dielectric constant causes an increase in complexity. However, if the intermolecular bonding were electrostatic, *i.e.* $\overset{\delta+}{\text{Ta}}\cdots\overset{\delta-}{\text{O}}$, we should expect an increase in dielectric constant to decrease the molecular complexity by lowering the energy of dissociation. If the intermolecular bonding is essentially covalent, *i.e.*, $\overset{-}{\text{Ta}}\text{–}\overset{+}{\text{O}}$, then the formal charge separation in the covalency may neutralise the dipole $\overset{\delta+}{\text{Ta}}\text{–}\overset{\delta-}{\text{OR}}$ originally present in the monomer and thus cause a net reduction of charge separation in the dimer. In this case the effect of dielectric constant would be similar to that in the system involving electrostatic bonding. Only in a system where the formal charge separation due to covalency gave rise to a higher charge separation (of opposite sign) in the dimer would the increase in dielectric constant cause an increase in molecular complexity, *viz.*:


Monomer Dimer

where $\delta_2+ > \delta_1+$, and $\delta_2- > \delta_1-$

This last possibility seems extremely unlikely and we conclude that in this comparison of pyridine with acetonitrile the effect of dielectric constant is overshadowed by differences in donor power. By donor power we mean the tendency of the solvent molecule to co-ordinate with the tantalum alkoxide by donating a lone pair of electrons to the electrophilic tantalum atom as shown in the equation:

$$[\text{Ta(OR)}_5]_2 + 2\text{S:} \rightleftharpoons 2\text{S:Ta(OR)}_5$$

According to this equation we should expect a solvent with a high donor power to promote dissociation of the dimeric tantalum alkoxide. Both acetonitrile and pyridine could be donors by virtue of their nitrogen, but the much higher basicity of the pyridine suggests that it has the higher donor power. Therefore, although pyridine has a much lower dielectric constant than acetonitrile its greater donor power is seen to be more effective in dissociating the dimeric tantalum alkoxide. The importance of donor power is confirmed by the fact that the complexity falls from benzene (*D* 2·28) to di*iso*propyl ether (*D* ~3) in spite of the opposing effect due to the lowering in boiling point. Nevertheless, the effect of the ether on the complexity is not very marked but this may well be due to stereochemical factors. Thus the donor tendency of the ether molecule may be opposed by the steric hindrance to co-ordination caused by repulsion between the alkoxide groups in the tantalum compound and the branched alkyl groups of the ether. Moreover this would explain the anomalous behaviour of tantalum methoxide in this solvent because steric hindrance should be smallest for this alkoxide.

The behaviour of the tantalum alkoxides in their parent alcohols remains to be discussed. We are inclined to the view that the fall in complexity from ethoxide to propoxide to butoxide is mainly due to the steady rise in boiling point of the solvent. The anomalous behaviour of tantalum methoxide in methyl alcohol is probably the result of several factors but the main cause is presumably that methyl alcohol has a higher donor power than the other alcohols.

It is of interest that the behaviour of thallous methoxide in boiling methyl alcohol also appears anomalous. Thus it was shown by Sidgwick and Sutton (*J.*, 1930, 1461) that in freezing benzene both thallous methoxide and ethoxide were tetrameric. However, whilst the ethoxide was also tetrameric in boiling ethyl alcohol the methoxide was monomeric in boiling methyl alcohol.

EXPERIMENTAL

The tantalum alkoxides were prepared and purified by the methods previously described (*loc. cit.*).

Purification of Solvents.—Toluene (" AnalaR ") was refluxed over sodium for several hours and then distilled. Pyridine (" AnalaR ") was dried azeotropically with benzene and then fractionally distilled. Acetonitrile was purified by extraction with saturated aqueous potassium carbonate, dried by storage over repeated batches of fresh phosphoric oxide, and finally distilled. Di*iso*propyl ether was treated with ferrous sulphate solution to remove peroxides, then dried ($CaCl_2$ under nitrogen) in a dark bottle, sodium was added, and the ether fractionally distilled.

Ebullioscopy.—The construction and operation of the ebulliometer have been described (*J.*, 1955, 3977). To improve the precision of the molecular-weight determinations to *ca.* ±0·5% several " runs " were made on freshly distilled samples. In addition, a new technique of " internal calibration " was employed. Several additions of alkoxide were made to the boiling solvent and the elevations of boiling point recorded. Then several additions of a pure inert organic solute (fluorene) were made. The graph of ΔT *versus* m then took the form of two intersecting straight lines from whose slopes, and together with the molecular weight of fluorene, the apparent molecular weight of the alkoxide was calculated. In this method the result is independent of the ebullioscopic constant for the solvent or the weight of solvent. Azobenzene was also tried in place of fluorene in the " internal calibration " but was sometimes unsatisfactory owing to interaction with the tantalum alkoxide, presumably by co-ordination through nitrogen. Thus the addition of azobenzene to a benzene solution of the methoxide gave a non-linear ΔT–m, consistent with interaction of azobenzene with the methoxide (where m is the amount of solute added). However, in boiling methyl alcohol there appeared to be no interaction because two straight lines were obtained from which the correct molecular weight of the methoxide was deduced. Clearly, the donor tendency of the azobenzene was swamped by the overwhelming excess of methyl alcohol which is a donor solvent. Similar behaviour was found when azobenzene was used as an internal calibrating agent for tantalum ethoxide. Before acetonitrile, pyridine, or di*iso*propyl ether was used as solvent their effect on the tantalum alkoxides was investigated. In all cases the pure alkoxide was recovered unchanged after removal of solvent. When ethyl methyl ketone was tried with either the methoxide or the ethoxide the remaining tantalum compound had a low tantalum content. Thus it appears that a Meerwein–Ponndorf reduction occurs with partial conversion of the original tantalum alkoxide into the *sec.*-butoxide. This reaction precluded the use of ethyl methyl ketone or other ketones as ebulliometric solvents. Typical results are presented in Table 2.

TABLE 2.

				M	
Alkoxide	Range of m (g.)	Toluene (g.)	$\Delta T/m$	Found	Calc.
$Ta(OMe)_5$	0·024—0·227	15·19	202 *	614	336
$Ta(OEt)_5$	0·048—0·215	17·18	148	741	406
$Ta(OPr^n)_5$	0·076—0·272	15·96	130	903	476
$Ta(OBu^n)_5$	0·053—0·268	15·99	114	1033	546
		MeCN (g.)			
$Ta(OMe)_5$	0·024—0·349	14·71	0·146°	502	336
$Ta(OEt)_5$	0·092—0·549	16·23	0·108	612	406
$Ta(OPr^n)_5$	0·110—0·389	14·29	0·106	712	476
$Ta(OBu^n)_5$	0·063—0·341	14·96	0·089	810	546
		Pyridine (g.)			
$Ta(OMe)_5$	0·040—0·243	17·08	256 *	338	336
$Ta(OEt)_5$	0·052—0·336	17·05	216	401	406
$Ta(OPr^n)_5$	0·094—0·276	19·76	158	473	476
$Ta(OBu^n)_5$	0·069—0·233	18·43	147	545	546
		Pr^i_2O (g.)			
$Ta(OMe)_5$	0·042—0·435	12·84	0·514°	588	336
$Ta(OEt)_5$	0·070—0·524	12·27	0·424	747	406
$Ta(OPr^n)_5$	0·074—0·437	12·34	0·363	867	476
$Ta(OBu^n)_5$	0·067—0·629	13·92	0·279	1000	546

* ΔT = Elevation of b. p. in terms of mm. of water pressure difference in the water thermometer.

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