MOLECULAR COMPOUNDS OF 1,4-DIOXANE

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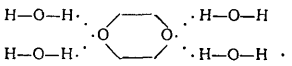
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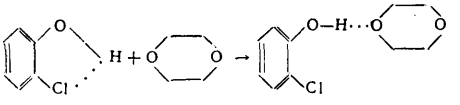
In contrast to its isomeric 1,3-dioxane, 1,4-dioxane is capable of forming molecular compounds (dioxanates) with many organic and inorganic compounds. The structure of dioxanates or other etherates has not yet been conclusively elucidated. It is considered that, depending on the properties of ether and ligand, the bond in these molecular compounds may be formed by: a) van der Waals forces; b) donor–acceptor interaction (resulting in compounds with an oxonium structure); c) hydrogen bonds with compounds containing active or mobile hydrogen atoms. Syrkin and Anisimov believe that the oxonium structure arises more frequently in dioxanates than in the molecular compounds of diethyl ether, for example[1].

1. MOLECULAR COMPOUNDS OF DIOXANE WITH COMPOUNDS CONTAINING ACTIVE OR MOBILE HYDROGEN ATOMS

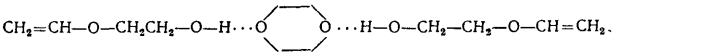
The ability of dioxane to dissolve, or mix with, compounds containing active or mobile hydrogen atoms is usually attributed to the formation of molecular compounds, involving the hydrogen bond. Physicochemical investigations of the water–dioxane system (vapour pressure, density, heat of mixing)[2-5] support this view. From their study of the heat of mixing of dioxane with water Fedos'eva *et al.*[4] inferred that dioxane forms with water a molecular compound of the type:



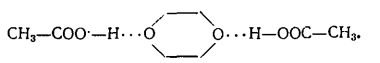
Freimann[5] and Gordy[6] measured the i.r. absorption spectra of dioxane and of ether solutions of alcohols and phenols and concluded that the OH groups of these hydroxylic compounds form hydrogen bonds with the oxygen atom in ethers. The reactivity of the OH group in *o*-chlorophenol, lowered by the *ortho*-effect, is increased[7] by the addition of 15% dioxane, which loosens the intramolecular hydrogen bond in *o*-chlorophenol and forms new hydrogen bonds between the phenolic OH group and the oxygen atoms in dioxane.



Measurements of the Raman spectra and the refractive index of the dioxane solution of ethylene glycol monovinyl ether[8] indicate unequivocally the presence of intermolecular hydrogen bonds:



The compounds of dioxane with organic acids are also formed primarily by hydrogen bonding. From their measurements of viscosity, density, surface tension, and refractive index in the dioxane–acetic acid system, the formation of the diacetate was inferred[9]:



The dioxanates of most strong acids are well-defined compounds with sharp melting points. They readily decompose in water, owing to the smaller proton affinity of dioxane compared with that of water[10]. Mezhennyi[11,12] found that at 20° dioxane dissolves, with heat evolution, up to 45 mole % of hydrogen chloride: the electrical conductivity of dioxane solutions of HCl is small (less than $10^{-7}\ \Omega^{-1}\ cm^{-1}$), and decreases with further dilution. This is in agreement with the earlier data by Meisenheimer[13], who found that the dissociation of HCl in dioxane is negligibly small.

Favorskii[14] was the first to show that a crystalline compound of composition $C_4H_8O_2.H_2SO_4$ (m.p. 101°) separates on mixing cold ether solutions of sulphuric acid with dioxane. A point corresponding to the dioxanate prepared by Favorskii has been identified[15] on the melting point diagram of the dioxane–sulphuric acid system. Syrkin and Anisimov[1] studied the polar properties of this dioxanate and found its dipole moment to be 4.63 D. The increase in the polarisation of the compound $D.H_2SO_4$† with dilution of the dioxane solution may, in the authors' opinion, be taken as evidence that both hydrogen bonds and oxonium structures are formed.

Pyrosulphuric acid forms dioxanate $D_2.H_2S_2O_7$, whose composition has been established by thermal analysis[16,17]. With 70% perchloric acid dioxane forms[18,19] in the cold a crystalline dioxanate hydrate, $D.HClO_4.H_2O$, m.p. 80°. Phosphoric acid dioxanate $D.2H_3PO_4$ (m.p. 87°) is recommended for use in reactions to be carried out in anhydrous media. The dioxanates $3D.4HNO_3$ and $2D.2HNO_3$ have also been described[21].

2. MOLECULAR COMPOUNDS WITH METAL HALIDES

A large number of dioxanates of metal halides are known. Salts of other anions do not normally react with dioxane. Dioxanates are prepared by allowing a mixture of dioxane and a metal halide to stand for several days, and subsequently evaporating the solution over sulphuric acid to incipient crystallisation. They are also prepared by mixing alcoholic solutions of metal halides with dioxane. They are crystalline compounds, coloured or colourless, readily soluble in alcohol, as a rule, and sometimes in acetone or ether. They are decomposed by water, and lose dioxane on being heated.

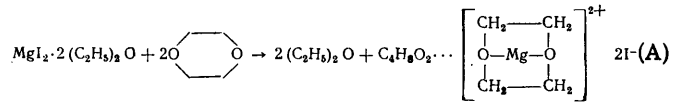
Lithium and caesium halides, from fluorides to iodides, are soluble in dioxane[22]. This property is particularly useful for separating lithium salts from the chlorides and bromides of other alkali metals[23]. Rheinboldt and his

† D stands for dioxane

coworkers[24-26] established that dioxane forms the following dioxanates with alkali halides: D.LiCl, D.LiBr, D_2.LiI, D_3.NaI, D.KI, as well as $D_2.NH_4I$. NaCl, KCl, NH_4Cl, NaBr, KBr, and NH_4Br do not form dioxanates.

A large group of dioxanates of bivalent metal halides has been described[25-33]: $D_2.MgCl_2$, $D_2.MgBr_2$, D_2MgI_2, $D.CaCl_2$, $D.CaBr_2$, $D.CaI_2$, $D.SrBr_2$, $D_2.SrI_2$, $D_2.BaI_2$, $D_2.ZnCl_2$, $D_2.ZnBr_2$, $D_2.ZnI_2$, $D.CdCl_2$, $D.2CdCl_2$, $D.CuCl_2$, $D.CuBr_2$, $D.HgCl_2$, $D_2.HgCl_2$, $D.HgBr_2$, $D_2.HgBr_2$, $D_2.HgI_2$, $D.HgI_2$, $D_2.CrBr_2$, $D_2.MnBr_2$, $D_2.MnI_2$, $D_2.FeCl_2$, $D_2.FeBr_2$, $D_2.FeI_2$, $D_2.CoCl_2$, $D_2.CoBr_2$, $D_3.CoI_2$, $D_4.CoI_2$, $D.NiCl_2$, $D.NiBr_2$, $D.NiI_2$, and of the mercuric salts of pseudo-halide groups[32], $D_2.Hg(CN)_2$ and $D_2.Hg(SCN)_2$. In addition to those enumerated, a large number of dioxanates of metal halide hydrates[34] are also known, *e.g.* $D.CuCl_2.H_2O$, $D_3.ZnCl_2.H_2O$, $D.CaCl_2.H_2O$, *etc.* $SrCl_2$, $BaCl_2$, and $BaBr_2$ do not form dioxanates[25].

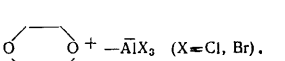
The tendency to form dioxanates, and the stability of the dioxanates, increase from chlorides to iodides in bivalent metal halides. Dioxanates are more stable than etherates. Esefov[33] showed that dioxane can displace diethyl ether from magnesium iodide etherate and form a stable dioxanate, whose structure he represented by the following formula (A):

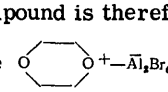


(A)

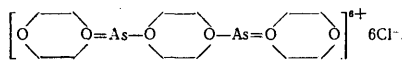
Dioxanate (A) does not decompose till 355°–365°.

Dioxanates formed by the halides of trivalent elements are also of interest. Boron trifluoride dioxanate, $D.BF_3.2H_2O$, is actually a salt-like compound with an ionic coordinate link[35]. With aluminium halides dioxane forms several compounds. Solutions of aluminium bromide in dioxane conduct electricity, and slowly deposit crystals of composition $D.AlBr_3$. Sheka and Karlysheva[37] prepared the dioxanates $D.AlCl_3$ and $D_2.AlCl_3$ and found their dipole elements (μ) to be 5.19 D and 5.21 D respectively. They also determined the dipole moment (μ = 5.23 D) of the dioxanate $D.AlBr_3$ obtained earlier[36]. The large dipole moments of these dioxanates are attributed to the considerable polarisation of the link between the oxygen atom in dioxane and the aluminium atom. The structure of these dioxanates can therefore be represented by the following general formula:



Characteristic in this respect[37] is the dioxanate $D.Al_2Br_6$, which is not dissociated in benzene solution. Its dipole moment is 4.62 D, and the compound is therefore assigned the unsymmetrical structure .

The dioxanate $D.SbF_3$ can be used[38] as a mild fluorinating agent. It reacts with $C_6H_5CCl_3$ forming a mixture of $C_6H_5CF_3$ and $C_6H_5CClF_2$. Arsenic trichloride froms two dioxanates, $D.AsCl_3$ (m.p. 68°) [39] and $D_3.AsCl_3$ (m.p. 62°) [40]. The latter is an ionic compound, whose complex cation contains arsenic, and whose outer sphere contains chloride ions. These can be precipitated from alcoholic solution with silver nitrate, although no such precipitation occurs with $AsCl_3$ itself. Accordingly the structure of arsenic trichloride dioxanate may be represented as follows:



The benzene solutions of the halides of tetravalent tin, titanium, and zirconium form the following crystalline dioxanates with dioxane: $D.SnCl_4$,[41,42] $D_2.SnCl_4$, $D.SnBr_4$,[41,43] $D_2.SnBr_4$,[40,43] $D.TiCl_4$,[44] $D_2.TiCl_4$,[44,45] $D_2.ZrCl_4$ and $D_2.ZrBr_4$.[45] Their composition was determined from analytical data and from cryoscopic molecular weight determinations. The stability of the dioxanates formed by the tetrachlorides of Group IV elements increases with the covalent radius of the metal atom[45].

Mixed alkyl and aryl magnesium halides also form crystalline dioxanates, as first observed by Schlenk and Schlenk[46]. They are prepared by precipitation with dioxane from ether solutions of Grignard reagents, the dialkyl- or diaryl-magnesium compounds remaining in solution. Wittig and his collaborators[47,48] described a large group of dioxanates of the phenyl derivatives of lithium, beryllium, magnesium, zinc, cadmium, and aluminium, for instance $D_2.[(C_6H_5)_3MgLi]$, $D_5.[(C_6H_5)_4AlLi]$, etc.

Metal halide dioxanates are used in organic synthesis. It has been reported[49] that the dioxanates of aluminium, zinc, tin, and iron halides can be used as catalysts in reactions between fumaric acid and butanol, triethyleneglycol, glycerol, etc. The stable crystalline lithium borohydride dioxanate, $D.LiBH_4$, obtained in 86% yield by mixing dioxane with a solution of $LiBH_4$ in tetrahydrofuran, can be used[50] to reduce esters. Unlike $LiBH_4$ itself, this material is stable and therefore convenient to handle.

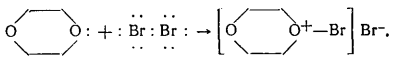
3. MOLECULAR COMPOUNDS WITH HALOGENS

There are no data in the literature regarding the reaction of dioxane with fluorine. With bromine, iodine, and interhalogen compounds dioxane forms crystalline molecular compounds. If bromine is added to dioxane in the cold, orange crystalline dioxane dibromine, $C_4H_8O_2.Br_2$, separates quantitatively[14,43,51]. Dioxane di-iodide $C_4H_8O_2.I_2$ is obtained[1,14,43,52] as dark crystals by mixing an ether solution of iodine with dioxane, and evaporating the solvent. The stability of halogen dioxanates (the strength of the oxygen–halogen bond) depends on the polarisation of the halogen molecule; the greater its polarisability, the stronger the molecular compound. Using the spectrophotometric method Lilich and Presnyakova[53] determined the stability constants (K_S) in 0.01 M carbon tetrachloride solutions of the dioxanates formed by halogens and interhalogen compounds (see Table). Their values for K_S

TABLE. Halogen dioxanates

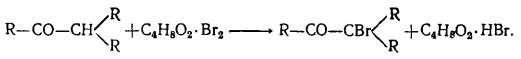
$D.X_2$	M.p. °C	K_S	μ, D
$D.Br_2$	66	3.75	1.3
$D.I_2$	85	10.5	0.95
D.BrI	58	163	—
D.ClI	65	632	—

accord well with the polarisability of the halogens. Compared with the constants for bromine and iodine dioxanates, K_S values for the dioxanates of interhalogen compounds are considerably higher, which is in full agreement with the high polarisability of ClI and BrI. Syrkin and Anisimov[1] compared the electron polarisation and dipole moments of $D.Br_2$ and $D.I_2$ at infinite dilution and found that dioxane dibromide is strongly ionised

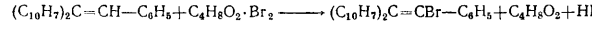


This is further confirmed by the distance between bromine atoms, 2.31 Å, in crystalline dioxane dibromide[54] as compared with 2.28 A in the bromine molecule.

Dioxane dibromide has recently been recognised as a specific brominating agent[55]. Equimolar amounts of dioxane dibromide and a carbonyl compound react in ether solution or in the absence of solvent to give good yields of α-bromo-derivatives of aldehydes and ketones[55-63]:



R may be a hydrogen atom, alkyl, or a heterocyclic radical. The bromination of spiran compounds has been reported[64]. Dioxane dibromide is a mild reagent for brominating the carbon–carbon multiple bond in unsaturated compounds[65-67]. In the reaction with triarylethylenes dioxane dibromide replaces the single hydrogen atom by bromine[68,69]:



Benzene does not undergo bromination even on heating, while toluene, heated only to 40° forms quantitatively *p*-bromotoluene[55,62]. Depending on the relative amount of the reagent, phenol and its ethers yield mono- or di-substituted products[55,64,70,71]. Aromatic amines, (aniline, toluidines), their *N*-substituted derivatives[62,72], and *N*-arylamides of sulphonic acids[73] react similarly. Acid-labile compounds such as furan, thiophen, pyrrole derivatives, indole, and 2-methylindole, whose bromination by usual reagents is complicated by side-reactions, react with dioxane dibromide to give quantitative yields of substituted derivatives with one bromine atom in the heterocyclic nucleus[55,62].

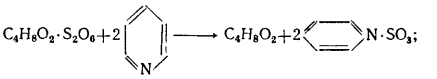
Dioxane di-iodide does not appear to have iodinating capacity[74]. For substitution iodination Terent'ev *et al.*[62] used the molecular compound formed by dioxane and iodine monochloride, $C_4H_8O_2.ClI$. With this reagent they carried out the iodination of phenol, salicylic acid, β-naphthol, resorcinol, and 2-methylindole, and obtained the corresponding mono-iodo derivatives in satisfactory yields.

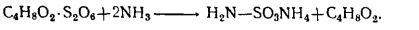
4. MOLECULAR COMPOUNDS WITH VARIOUS OXIDES

With nitrogen dioxide, dioxane forms a crystalline dioxanate, $D.N_2O_4$, which has been used for nitrosating unsaturated compounds[75]. With sulphur dioxide it forms the dioxanates $D.SO_2$ and $D.2SO_2$,[76,77] which have been recommended for use as pesticides[78]. A dioxanate formed by rhenium oxide, $Re_2O_7.3C_4H_8O_2$ has also been described[79].

The dioxanate formed by sulphur trioxide is the most interesting. It was first obtained by Suter and his collaborators[80], who used it for sulphonating organic compounds. The direct action of sulphur trioxide upon dioxane produces decomposition and resinification. However, on mixing a sulphur trioxide solution (*e.g.* in dichloroethane) with dioxane in the cold a crystalline dioxanate of composition $D.S_2O_9$ is formed[81].

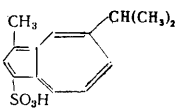
Mezhennyi and Kovganich[82] recently proposed a method for the preparation of sulphur trioxide dioxanate by direct reaction of dioxane vapours with gaseous sulphur trioxide. In the absence of moisture this compound is stable for several weeks. It is stable up to 80°, but above this temperature it decomposes violently with evolution of sulphur trioxide. It is practically insoluble in dichloroethane, benzene, and ligroin, but is readily soluble in dioxane, where it is present as $D.S_2O_6$. Mezhennyi and Martynenko[83] confirmed cryoscopically that in very dilute dioxane solutions sulphur trioxide is dimeric and that such solutions are completely non-conducting. Water instantly decomposes this dioxanate into sulphuric acid and dioxane. The dioxanate reacts violently and with the evolution of heat with pyridine[84] and ammonia[85], forming the adduct and ammonium sulphamate, respectively:



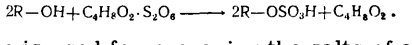


Sulphur trioxide dioxanate has the remarkable property of sulphonating many acid-labile organic compounds which are resinified or polymerised by the usual sulphonating agents[86]. Sulphonation with sulphur trioxide dioxanate is carried out under mild conditions, usually at 0–20°, in an indifferent solvent (dichloroethane, methylene dichloride, ether). The resulting dioxanates of sulphonic acids can easily be decomposed into sulphonic acids and dioxane, and with alkalis and carbonates they form the salts of sulphonic acids, which are easily isolated.

Sulphonations of alkenes[80,87-89], alkynes[81], and cyclic alkenes[90-92] by sulphur trioxide dioxanate have been reported. In unsaturated aliphatic–aromatic compounds (*e.g.* styrene and its derivatives) the sulphonate group assumes a position in the side-chain, not in the aromatic nucleus[93-100]. At 20° benzene and *m*-xylene[80] form quantitatively the respective monosulphonic acids. Sulphonation of naphthalene[80], tetralin[101], anthracene, and guaiazulene[102] has also been described. The last compound gives a sulphonic acid of the following structure, in 53% yield:



Alcohols and phenols form rapidly and quantitatively acid sulphate esters[103-104]



This reaction is used for preparing the salts of acid sulphonic esters derived from higher alcohols, which are surface-active[105]. It has also been used as the basis of a method for the quantitative determination of mono- and poly-hydric alcohols[104,106]. Similarly primary aromatic

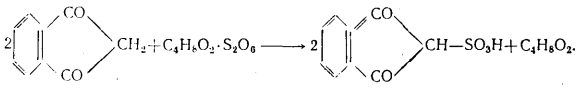
amines are transformed quantitatively into sulphamic acids [104,107] by sulphur trioxide dioxanate:

$$2Ar-NH_2+C_4H_8O_2\cdot S_2O_6 \longrightarrow 2Ar-NH-SO_3H+C_4H_8O_2.$$

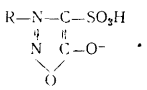
Sulphur trioxide dioxanate is an effective and specific sulphonating agent for aliphatic aldehydes [55,108], ketones [55,60,108-111], including cyclic ketones [55,108], and carboxylic acids and their derivatives [112,113]. The α-hydrogen atoms in these compounds undergo substitution by the sulphonate group, forming the corresponding sulphonic acids:

$$2R-CH_2-C(=O)-X+C_4H_8O_2\cdot S_2O_6 \longrightarrow R-CH(SO_3H)-C(=O)-X+C_4H_8O_2,$$

where X = H, Alk, OH, OAlk. Depending on the relative amount of reagents, α-mono- or α,α'-disulphonic acids may be obtained. Sulphonation of acetonitrile and isovaleronitrile proceeds likewise [112]. One H atom in the methylene group of the following 1:3 diketones is substituted by the sulphonate group (70–80% yields): 2-phenyl-1,3-indandione, dimedone, 5-phenyl-1,3-cyclohexadione, peri--1,3-naphthindandione, and dibenzoylmethane [114,115]. For example, the reaction with 1,3-indandione proceeds as follows:



The majority of heterocyclic compounds seem to be typical acid-labile substances. Terent'ev and Yanovskaya [116,117] showed however, that pyrrole and thiophen, as well as their alkyl derivatives, undergo sulphonation by sulphur trioxide dioxanate, forming good yields of mono-C-sulphonic acids. In sydnones [118] the single hydrogen atom in the heterocyclic ring undergoes substitution resulting in a sulphonic acid of the general formula:



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ANODIC SUBSTITUTION REACTIONS

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