CCLIII.—*The Influence of Structure on the Solubilities of Ethers. Part II. Some Cyclic Ethers.*

By George Macdonald Bennett and William George Philip.

A series of cyclic ethers has been examined with respect to the solubilities in water, the compounds (*a*) being isomeric, (*b*) differing from the series of open-chain ethers (preceding paper) only by two hydrogen atoms and the closure of the ring, and (*c*) having a cyclic structure with a 6-, 5-, 4-, or 3-membered ring. The substances chosen were pentamethylene oxide, α- and β-methyltetramethylene oxides, ββ'-*dimethyltrimethylene oxide*, αα'-*dimethyltrimethylene oxide*, and αα'-methylethylethylene oxide, all of the molecular formula $C_5H_{10}O$.

Preparation of Materials.—(i) Pentamethylene oxide was prepared as described by Clarke (J., 1912, **101**, 1788), and had b. p. 87°, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8814.

(ii) α-Methyltetramethylene oxide was obtained from the glycol resulting from the reduction of γ-acetylpropyl alcohol. The yields of the latter were consistently lower than those claimed by Possaner and von Ehrenthal (*Monatsh.*, 1903, **24**, 352): substitution of ethylene chlorobromide for ethylene dibromide caused no improvement, but the following method involving the use of ethylene chlorohydrin was much more satisfactory. To a solution of ethyl acetoacetate (65 g.) with sodium (12 g.) in ethyl alcohol (130 g.), ethylene chlorohydrin (45 g.) was added and the mixture boiled for 5 hours. The solution was filtered, evaporated, and the residue boiled for 5 hours with dilute hydrochloric acid (120 c.c.; 10%). The solution was made neutral and concentrated under reduced pressure until salt had separated copiously. An excess of acetone was then added, the solution filtered from salt, evaporated, and distilled under reduced pressure (yield, 40%). The ether had b. p. 80°, $d_{4^\circ}^{0^\circ}$ (vac.) 0·8732, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8540.

(iii) β-Methyltetramethylene oxide was prepared from ethyl methylsuccinate as described by Harries (*Annalen*, 1911, **383**, 170), and had b. p. 83°/738 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8850, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8642.

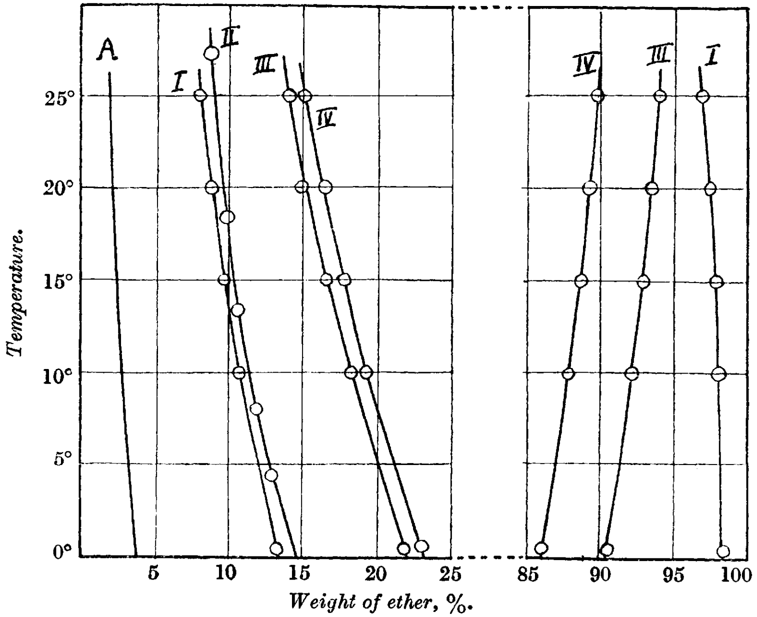
(iv) ββ′-*Dimethyltrimethylene oxide* was made from the corresponding glycol (Just, *Monatsh.*, 1896, **17**, 76) through its monobromohydrin (Franke, *ibid.*, 1913, **34**, 1898). An improved yield of the latter was furnished by heating the glycol (1 mol.) with the solution made by passing sulphur dioxide into bromine (100 g.) and ice (110 g.) until the colour is yellow. The mixture was heated on the steam-bath for 5 hours, at its boiling point for 1 hour, and then diluted. The product was extracted in ether, the extract washed with sodium carbonate solution, dried over sodium sulphate, and fractionated. The bromohydrin had b. p. 100°/25 mm. (yield, 41%). It was mixed with three times its weight of dry, powdered potassium hydroxide, and heated in an oil-bath at 130—180°. The ββ′-dimethyltrimethylene oxide, after drying and redistillation, was a mobile liquid of camphoraceous odour, b. p. 78°/742 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8550, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8348 (Found: C, 69·1; H, 11·5. $C_5H_{10}O$ requires C, 69·8; H, 11·6%).

(v) αα′-*Dimethyltrimethylene oxide* was prepared in a similar manner (yield, 43%) from the chlorohydrin, b. p. 72°/13 mm., obtained by the action of magnesium methyl iodide on ethyl β-chloropropionate (yield, 53%) as described by Henry (*Compt. rend.*, 1906, **142**, 133). The *oxide* had b. p. 71°/750 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8490, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8279. It is a liquid of pleasant odour, and dissolves with evolution of heat in water, becoming hydrated to the corresponding glycol. Great difficulty was experienced in analysing this and the foregoing substance: apart from their volatility, the *gem*-dimethyl group may have caused low values. This substance was also hygroscopic. The specimens were always redistilled immediately before use, but no direct evidence of their freedom from impurity is available.

(vi) αα′-Methylethylethylene oxide was prepared as described by Tiffeneau (*Compt. rend.*, 1902, **134**, 775; 1907, **145**, 437). It had b. p. 80·5°/755 mm., $d_{4^\circ}^{0^\circ}$ (vac.) 0·8425, $d_{4^\circ}^{20^\circ}$ (vac.) 0·8220 (Found: C, 70·2; H, 11·4. Calc.: C, 69·8; H, 11·6%).

Methods of Measurement.—The experimental method was as described in the preceding paper. The solubilities of β-methyltetramethylene oxide were determined by the synthetic method. With this, and with one or two other substances, a difficulty was sometimes met with in using the volumetric method described. A trace of a solid was produced in the tubes which made the separation of the phases and the reading of the meniscus difficult. The effect was slight and in some cases entirely absent. It was found by repeated experiment to be unconnected with any possible impurity in the mercury, and was finally recognised as due to the oxidation of the metal to an oxide by a trace of ether peroxide (compare Richardson, J., 1891, **59**, 51). The moist ether is thus a catalyst which causes reaction between mercury and oxygen. If this explanation had been realised originally, the whole phenomenon could doubtless have been suppressed by avoiding the presence of oxygen. The measurements here recorded are free from errors due to this difficulty, but the alternative method of measurement was adopted for the one ether.

FIG. 1.



Mutual solubilities of isomeric cyclic ethers and water.

I. *Pentamethylene oxide.* III. *a-Methyltetramethylene oxide.*
II. *β-Methyltetramethylene oxide.* IV. *ββ'-Dimethyltrimethylene oxide.*
(A, *Ethyl* n-*propyl ether.*)

As a check on the behaviour of these substances in the pure state, the solubilities of naphthalene in them and in three open-chain ethers at several temperatures were determined, following the method of Ward (*J. Physical Chem.*,. 1926, **30**, 1316). The naphthalene was carefully purified and melted completely between 80·05° and 80·07°.

Results.—The mutual solubilities of four cyclic ethers and water are shown by the curves in Fig. 1, a curve for ethyl *n*-propyl ether being included for comparison. The data in Table I are smoothed values for these substances. The remaining two ethers, αα′-dimethyltrimethylene oxide and αα′-methylethylethylene oxide, dissolve completely in water with considerable evolution of heat. The resulting solutions were found to contain only the corresponding glycols, and these two ethers could not be recovered.

TABLE I.

Mutual solubilities of cyclic ethers and water.

A = weight % of ether in aqueous phase. B = weight % of water in ether phase.

Oxide.		25°.	20°.	15°.	10°.	0°.
Pentamethylene	A	8·02	8·76	9·64	10·70	13·40
$Q + 3300$ cals.	B	3·14	2·70	2·27	2·08	1·63
α-Methyltetramethylene......	A	13·87	15·05	16·52	18·20	22·10
$Q + 3150$ cals.	B	6·08	6·65	7·05	7·72	9·54
β-Methyltetramethylene......	A	8·8	9·5	10·2	11·25	14·6
$Q + 2800$ cals.						
ββ′-Dimethyltrimethylene ...	A	15·04	16·26	17·71	19·31	23·28
$Q + 2800$ cals.	B	10·20	10·67	11·32	12·15	13·96

TABLE II.

Solubilities of naphthalene in open-chain and in cyclic ethers.

(*t* = temperature; *N* = molar fraction of naphthalene.)

Di-*n*-butyl ether	*t*	42·6°	45·7°	52·9°
	N	0·3773	0·4153	0·5078
Ethyl *n*-propyl ether	*t*	29·9°	39·7°	42·3°
	N	0·2708	0·3650	0·3936
Ethyl *iso*propyl ether	*t*		43·9°	52·3°
	N		0·4026	0·5136
Pentamethylene oxide	*t*	26·4°	30·1°	40·2°
	N	0·3421	0·3705	0·4608
ββ′-Dimethyltrimethylene oxide	*t*	29·2°	38·9°	
	N	0·3460	0·4173	
αα′-Dimethyltrimethylene oxide	*t*	33·8°	39·9°	44·7°
	N	0·3010	0·4087	0·4557
αα′-Methylethylethylene oxide ...	*t*	27·4°	38·2°	46·6°
	N	0·3256	0·4223	0·5052

Discussion of Results.

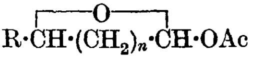
The deviation of the solubilities of naphthalene in the ethers from the ideal value may be shown by the slope of the curve relating log N to $1/T$ (Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1416; 1923, **45**, 633). The mean values of $\Delta \log N/\Delta(1/T)$ derived from the data in Table II are: Dibutyl ether 1245, ethyl *n*-propyl ether 1190, ethyl *iso*propyl ether 1200, pentamethylene oxide 920, ββ′-dimethyltrimethylene oxide 980, αα′-dimethyltrimethylene oxide 1120, αα′-methylethylethylene oxide 985. The ideal value may be taken to be 970, and the value recorded by Mortimer for ethyl ether is 1180. The figures show that these liquids are normal and differ very little in internal pressure from naphthalene, the cyclic oxides having a slightly higher internal pressure than the others. The figures for the last two ethers in the above list are possibly subject to error owing to the hygroscopic nature of the substances. The observed points for the cyclic ethers are close to the ideal curve, and the internal pressures may be taken to be approximately equal to that of naphthalene (1·00 on Mortimer's scale). This slightly greater internal pressure is also apparent from a consideration of the following boiling points: *n*-Hexane 69°, *cyclo*hexane 81°, ethyl *n*-propyl ether 64°, methyl *n*-butyl ether 70°, pentamethylene oxide 87°.

The solubilities of the cyclic ethers in water increase with falling temperature, but their relative order is independent of this change. The solubilities are in the order: Ethyl *n*-propyl ether (2·74), pentamethylene oxide (10·70), β-methyltetramethylene oxide (11·25), α-methyltetramethylene oxide (18·20), ββ′-dimethyltrimethylene oxide (19·31), the figures in brackets being the solubilities at 10·0°.

The difference between the solubilities of α- and β-methyltetramethylene oxides once more illustrates the effect of substituting a secondary for a primary radical attached to the oxygen atom, as discussed in Part I of this investigation. The extreme development of chemical reactivity due to a tertiary radical is seen in αα′-dimethyltrimethylene oxide and αα′-methylethylethylene oxide by the immediate rupture of the ring on solution in water.

The most striking feature of the results is the large increase of solubility caused by the closure of the ring, and this is also true of the solubilities of water in the ethers, the values of which are considerable.

The work of Menschutkin (J., 1906, **89**, 1532) and of Petrenko-Kritschenko (*Annalen*, 1905, **341**, 165) proved that the reactivity of an alcohol or a ketone is increased when its open chain is closed into a ring. If the open-chain substance be regarded as behaving normally, ring closure evidently confers an enhanced reactivity. This effect, which is of the nature of a negative steric hindrance, may be termed "steric activation." Menschutkin realised that this phenomenon should also arise in the closing of a heterocyclic ring, and cited as an illustration the greater velocity of alkylation of piperidine than of *n*-amylamine. The much greater strength of piperidine as a base in comparison with diethylamine and dipropylamine may also be ascribed to steric activation. The measurements recorded in this paper are evidence of a similar effect with oxygen as the hetero-atom. To show that the solubility developed by closure of the ring is a property of the oxygen atom in particular, the solubilities of *n*-hexane and *cyclo*hexane in water were examined. Direct experiment showed that water dissolves less than 0·005% of either at 17°.

The increase of solubility due to the closure of the ring is also larger the smaller the ring, in accordance with expectation. Considering only the ethers with unsubstituted methylene groups attached to the oxygen atom, the figures to be compared are 10·70, 11·25, and 19·31% for 6-, 5-, and 4-membered rings, respectively. The fact that the difference between the first two is small is perhaps due to the strainless configuration in the 6-membered ring, which will consequently have a similar angle to that of its 5-membered isomeride. The observation of Bergmann and Kann (*Annalen*, 1924, **438**, 278), that acetoxypolymethylene oxides of the type  $R{\cdot}\overset{\lceil\quad O\quad\rceil}{CH{\cdot}(CH_2)_n{\cdot}CH}{\cdot}OAc$ are polymerised to a greater extent the smaller the value of *n*, is evidence of a similar increase of chemical reactivity in the oxygen atom with diminishing size of the ring.

It may also be pointed out that the large majority of stable oxonium compounds arise from the chemical reactivity of an oxygen atom which is a member of a ring. This can hardly be accidental, but must be a consequence of the steric activation of such atoms.

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