XXI.—*On the Polyatomic Alcohols.*

A Discourse delivered before the Fellows of the Chemical Society of London.

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THE polyatomic alcohols are derived by replacing in n atoms of water n atoms of hydrogen, by an n -atomic basic radical, consisting either of $\frac{1}{2}$ carbon and hydrogen, or of carbon, hydrogen, and oxygen.* For glycol, which contains the diatomic radical C_2H_4 , we have $n = 2$.

And if we assume glycerine to contain the triatomic radical C_3H_5 , the formula for glycerine will be—

Compounds among the acids, the polybasic acids, which correspond to the polyatomic alcohols, have been known for several years. Mr. Graham's excellent researches on phosphoric acid and the phosphates led him to the conception of his theory of polybasic acids, which was afterwards adopted and further developed by Liebig. Our present mode of viewing these bodies, is chiefly founded on the investigations of Gerhardt and Williamson. The doctrine of polyatomic alcohols principally owes its development to the researches of Wurtz and Berthelot, undertaken within the last few years.

A. *Diatomic Alcohols.*

Glycol,† the first body of this class, was obtained three years ago by Wurtz, by placing iodide of ethylene‡ in contact with

* n is considered to represent a number greater than 1.

† Compt. rend. xliii, 199; Inst. 1856, 277; Ann. Ch. Pharm., c, 110.

‡ Faraday (1821), Ann. Phil. xviii, 118; Regnault, Ann. Chim. Phys. lix, 367.

acetate of silver; a lively reaction takes place, iodide of silver and acetate of glycol being produced:

The diatomic radical ethylene replaces the two atoms of silver in two atoms of acetate of silver, and thus unites the two molecules to form acetate of glycol. Iodide of ethylene stands to diacetate of glycol in the same relation as iodide of ethyle to acetic ether.*

If diacetate of glycol be distilled with hydrate of potash at 250° C., acetate of potash and glycol are obtained.

The best mode obtaining monacetate of glycol, is by Dr. Atkinson's process,† which consists in heating an alcoholic solution of one atom of bromide of ethylene with two atoms of acetate of potash, enclosed in a soda-water bottle, for two days at 100° C. The liquid is separated from the bromide of potassium, subjected to distillation, and those portions are collected as monacetate of glycol which come over at 182° C.

* $(\text{C}_2\text{H}_4)''\text{Cl}_2$ and $(\text{C}_2\text{H}_4)''\text{Br}_2$, contain in equal volumes of their vapours twice as much chlorine and bromine as $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{Br}$.

† Phil. Mag. Dec. 1858; Ann. Ch. Pharm. cix, 232.

By distilling monacetate of glycol with hydrate of potash, glycol can easily be prepared.* In a similar manner, the following glycols homologous to ethylo-glycol, have been obtained.

These bodies are syrupy liquids, volatile without decomposition, and soluble in water and ethylic alcohol. Ethylo-glycol boils at 197° C., propylo-glycol at 188° C., and amylo-glycol at 177° C.. The exceptional property of this class of homologous substances, to boil at a lower temperature, as they become richer in carbon and hydrogen, is very remarkable. Compounds of these glycols have been obtained by the action of the chlorides, bromides, or iodides of ethylene, propylene or amylene, on certain potash or silver salts; also by the action of acids on these glycols; and by decomposing potassium or sodium-glycol with iodides.

Chemical Properties of the Glycols.

1. With monatomic acids, they form two ethers by the successive replacement of two atoms of hydrogen by monatomic acid radicals.

* Ann. Ch. Pharm. cx, 317-8.

† Compt. rend. xlv, 306; Inst. 1857, 300; Ann. Ch. Pharm. cv, 202.

‡ Compt. rend. xlv, 244.

§ Ann. Ch. Pharm. cvi, 24.

a. Compound obtained by replacing in glycol *one* atom of hydrogen by a monatomic acid radical.*

Monacetate of glycol is formed, not only by the action of bromide of ethylene on acetate of potash, but also by heating equivalent quantities of glycol and anhydrous acetic acid at temperatures not exceeding 170° C.

b. Compounds obtained by replacing in glycols *two* atoms of hydrogen by two monatomic acid radicals, either of the same or of a different kind.†

These four compounds are formed by the action of the bromides of the radicals C_2H_4 , C_3H_6 , C_4H_8 , and C_5H_{10} , on acetate of silver.

Here also may be mentioned sulphocyanide of ethylene.‡

Brüning obtained, by the action of an alcoholic solution of potash on iodoform, a substance to which he attributes the formula

* Atkinson. Phil. Mag., Dec, 1858.

† Wurtz. Compt. rend. xlii, 244; xlv, 306; xliii, 199, Ann. Ch. Pharm. c, 112; cv, 203; cvi, 25.

‡ Buff. Ann. Ch. Pharm. xevi, 302; c, 229; Chem. Gaz. (1856), 416; Phil. Mag. [4] xiii, 374.

The same body was prepared by Buttlerow from iodoform and ethylate of sodium, but he represents it as diiodide of methylene, CH_2I_2 . With acetate of silver, it furnished iodide of silver and a liquid which distilled at about 170°C ., and which Buttlerow considers to be diacetate of methylo-glycol. The latter, treated with baryta yielded, not methylo-glycol, but acetate and formiate of baryta. This subject requires further examination.*

2. If glycol and hydrochloric acid be heated together, water and chlorhydrine of glycol are formed.†

Chlorhydrine of glycol will probably yield, by renewed treatment with hydrochloric acid, under suitable conditions, dichloride of ethylene and water.

Propylo-glycol and hydrochloric acid form chlorhydrine of propylo-glycol and water.

Sulphuric acid, which is bibasic, and like glycol is derived from two atoms of water, yields similar derivatives.

* Ann. Ch. Pharm. cxi, 242. (August, 1859.)

† Compt. rend. xlviii, 101; Ann. Ch. Pharm. cx, 125.

‡ Williamson. Chem. Soc. Qu. J. vii, 180; Proc. R. S. vii, 11; Ann. Ch. Pharm. xcii, 242.

Hydriodic acid and glycol form, according to temperatures, either iodide of ethylene or iodhydrine of glycol, and water.

Chlorhydrine of glycol is rapidly decomposed by caustic potash, chloride of potassium, oxide of ethylene and water being produced.

Oxide of ethylene is isomeric with, and has the same vapour density as acetic aldehyde. Oxide of ethylene is decomposed with great violence by pentachloride of phosphorus, dichloride of ethylene and oxychloride of phosphorus being produced.

From oxide of ethylene, glycol compounds can be regenerated, which substances Wurtz could not obtain from aldehyde. Pentachloride of phosphorus and acetic aldehyde furnish a body which has the composition of dichloride of ethylene, but it is only isomeric, and not identical with Dutch liquid. Probably oxide of ethylene is the ether of glycol, for it stands to this alcohol as anhydrous sulphuric acid does to—

A substance, which would bear the same relation to glycol as common ether bears to ethylic alcohol, might be obtained by the action of dichloride of ethylene on—

The decomposition of chlorhydrine of propylo-glycol with caustic potash, yields oxide of propylene;

and no doubt similar derivatives will be formed from other glycols.*

3. If a mixture of hydrochloric and acetic acids be made to act on glycol, a body is produced which Simpson calls chloracetine of glycol.†

Chloracetine of glycol is a substance intermediate between Dutch liquid and diacetate of glycol. It is isomeric with chloracetine of ethylidine, which Simpson obtained by treating acetic aldehyde with chloride of acetylene.‡ It can be produced by passing a current of hydrochloric acid gas through monacetate of glycol at 100° C.

* Compt. rend. xlvii, 346; xlviii, 101; Ann. Ch. Pharm. cviii, 86, and cx, 126, 127; Chem. Gaz. vol. xvii, 155.

† Proc. R. S. ix, 726; x, 114.

‡ Compt. rend. Nov. 29, 1858.

Chloracetine of glycol and butyrate of silver, form butyroacetate of glycol.

If a stream of hydrochloric acid gas be passed through a mixture of equivalent quantities of butyric acid and glycol at 100°, chlorbutyrine of glycol is formed.

In a similar way chlorbenzoate of glycol,

has been produced.

Iodacetine of glycol is formed by passing a current of hydriodic acid gas, through a mixture of equivalent quantities of glacial acetic acid and glycol. This compound can also be prepared with great facility, by exposing monacetate of glycol to the action of hydriodic acid gas.

Chloracetine of glycol, chlorbutyrine of glycol, chlorbenzoate of glycol, iodhydrine of glycol, iodacetine of glycol as well as chlorhydrine of glycol are all decomposed by caustic potash, into oxide of ethylene, water and potash salts.

This process furnishes a convenient method of preparing oxide of ethylene, as the chloracetine can be obtained easily in large quantities. It is worthy of notice that in this reaction no glycol is reproduced; we also observe that bodies which yield oxide of ethylene in this manner with potash, are either glycol, in which one atom of hydrogen has been replaced by a monatomic acid radical, and the elements of peroxide of hydrogen by chlorine or iodine—or glycol in which only HO has been replaced by Cl or I.

On account of this decomposition with caustic potash, they might be regarded as compounds of oxide of ethylene with hydrochloric acid, chloride of acetylene, iodide of acetylene, &c.

4. Glycols produce with monatomic acids neutral compounds corresponding to the ethers of monatomic alcohols; with polyatomic acids, acid bodies analogous to sulphovinic acid. If from a polyatomic alcohol, one, two, or three atoms of peroxide of hydrogen be separated, the remaining part of the alcohol comports itself like a mono-, di-, or triatomic radical.

Under some conditions, glycol comports itself as if derived from one atom of water, and its composition may be represented by the formula

If it be mixed with sulphuric acid and heated to 150°C. , sulphoglycolic acid* is formed, which may be considered as sulphuric acid, wherein one atom of hydrogen is replaced by the atomic group $\text{C}_2\text{H}_5\text{O}$.

Sulphoglycolic acid appears to be monatomic.

The reactions of glycol with hydrogen and diatomic acids, may be conveniently expressed by adopting for glycol, the formula

the diatomic radical C_2H_4 , is here represented as combined with peroxide of hydrogen, which is monatomic. The formulæ of several compounds noticed, are accordingly ;

$(\text{C}_2\text{H}_4)''(\text{HO})$	Cl	Chlorhydride of glycol.
$(\text{C}_2\text{H}_4)''\text{Cl}$	Cl	Dichloride of ethylene.
$(\text{C}_2\text{H}_4)''(\text{HO})$	I	Iodhydride of glycol.
$(\text{C}_2\text{H}_4)''\text{I}$	I	Diiodide of ethylene.
$(\text{C}_2\text{H}_4)''(\text{C}_2\text{H}_3\text{O}_2)$	Cl	Chloracetine of glycol.
$(\text{C}_2\text{H}_4)''(\text{C}_2\text{H}_3\text{O}_2)$	I	Iodacetine of glycol.
$(\text{C}_2\text{H}_4)''(\text{C}_4\text{H}_7\text{O}_2)$	Cl	Chlorbutyrine of glycol.
$(\text{C}_2\text{H}_4)''(\text{C}_7\text{H}_5\text{O}_2)$	Cl	Chlorbenzoate of glycol.

The radicals $\text{C}_2\text{H}_3\text{O}_2$, $\text{C}_4\text{H}_7\text{O}_2$ and $\text{C}_7\text{H}_5\text{O}_2$, have the composition of the peroxides of the acid radicals of Mr. Brodie, and these peroxides would be the radicals of the monatomic oxygen-acids, if such acids be regarded as hydrogen-acids constructed on the type HCl . The above formulæ of glycol and several of its derivatives, are only meant to express the composition of these bodies in a more simple manner with regard to certain changes.

5. In contact with potassium or sodium, ethyl-glycol loses one

* Proc. R. S. ix, 725.

or two atoms of hydrogen, which are replaced by metal. The following two compounds have been prepared.

Propylo-, butylo-, and amylo-glycol comport themselves with potassium or sodium very probably in a similar manner.

each other, and produce iodide of sodium and bodies which may be respectively considered as glycol, wherein one or both atoms of hydrogen are replaced by ethyl.

Monethylate of glycol, $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ (\text{C}_2\text{H}_4)'' \\ \text{H} \end{array} \right\} \text{O}_2$, in contact with potassium,

loses hydrogen, and a compound is produced which may be considered as glycol, wherein one atom of hydrogen has been replaced by ethyl, the other by potassium.

Iodide of ethyl acts on $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ (\text{C}_2\text{H}_4)'' \\ \text{K} \end{array} \right\} \text{O}_2$ and produces iodide of potassium and diethyl-glycol.

The latter is isomeric with acetal.*

* Wurtz. Compt. rend. xlvii, 346; Ann. Ch. Pharm. cviii, 84.

6. Pentachloride of phosphorus and ethylo-glycol form hydrochloric acid, oxychloride of phosphorus and dichloride of ethylene.*

7. Chloride of zinc abstracts water from ethylo- and propylo-glycol, and converts the one into acetic-, the other into propylic aldehyde.

8. In contact with air or oxygen, and platinum-black, the glycols oxidize with great rapidity. Nitric acid converts ethylo-glycol into glycolic, glyoxylic and oxalic acids. From propylo- and amylo-glycol, lactic and butylo-lactic acids have been obtained.†

The acids contain two atoms of hydrogen less, and one atom of oxygen more, than their corresponding glycols. The same relation exists between the fatty acids and their alcohols. If in glycolic acid two atoms of hydrogen be replaced by one atom of oxygen, oxalic acid is formed. From lactic, and butylo-lactic acids, compounds homologous to oxalic acid will probably be obtained.

* Comp. rend. xlv, 228; Ann. Ch. Pharm. civ, 174.

† Compt. rend. xlv, 306; xlv. 1306; xlv. 1232; Ann. Ch. Pharm. ciii, 366; ex, 316; cvii, 197; cv, 205; Chem. Gaz. xvii, 8; xvi, 441; xv, 341.

The composition of these acids and their corresponding glycols may also be expressed by the following formulæ.

According to the formulæ 2, 5 and 8, glycolic-, lactic-, and butylo-lactic acids ought to be bibasic. Our present experience is very deficient on this point, and further experiments are required for its elucidation.

If glycol be oxidized by nitric acid, glyoxylic acid* is formed, together with glycolic and oxalic acids. Glyoxylic acid is an intermediate compound between glycolic and oxalic acids, just as oil of bitter almonds is intermediate between benzylic alcohol and benzoic acid.

And as oil of bitter almonds and solution of potash decompose each other and produce benzylic alcohol and benzoate of potash, so the same alkali with glyoxylic acid forms glycolate and oxalate

* "On the action of nitric acid on alcohol." Phil. Mag., Nov., 1856.

of potash ; and as oil of bitter almonds oxidizes with great ease and yields benzoic acid, so glyoxylic acid takes up oxygen readily, and becomes converted into oxalic acid.

These acids combine with the potash present.

A substance between glycol and glycolic acid, or glycol and oxalic acid, has not yet been obtained from glycol. But from ethylic alcohol, by oxidizing it with nitric acid, a body of the composition $\text{C}_2\text{H}_2\text{O}_2$ has been obtained. This body combines with bisulphite of ammonia and soda; acts on ammonia like oil of bitter almonds; yields, like acetic aldehyde, sulphur-compounds with sulphuretted hydrogen; and is easily oxidized by nitric acid into glyoxylic and oxalic acids, two substances which are also produced by the oxidation of glycol; $\text{C}_2\text{H}_2\text{O}_2$ seems to be a true aldehyde to glycol and oxalic acid.

B. Compounds of the aldehydes $\text{C}_n\text{H}_{2n}\text{O}$ and $\text{C}_n\text{H}_{2n-2}\text{O}$.

a. *Acetic aldehyde.*

Acetic aldehyde is, as has already been stated, isomeric with oxide of ethylene. From aldehyde a series of bodies can be prepared isomeric with several glycol-compounds, and their composition is, as if they were derived from a diatomic alcohol of the formula,

With regard to these compounds, aldehyde may be represented as the oxide of the diatomic radical C_2H_4 , *ethylidine*, isomeric, but not identical, with ethylene.

1. Acetic aldehyde and pentabromide of phosphorus form bromide of ethylidine and oxybromide of phosphorus.*

Pentachloride of phosphorus and aldehyde decompose each other in a similar manner.

Chloride of ethylidine,† which is isomeric only with chloride of

* Wurtz & Frapollin. Compt. rend. xlvii, 418; Ann. Ch. Pharm. cviii, 225.

† Ann. Ch. Pharm. cv, 323.

ethylene, is decomposed by caustic potash into chloride of vinyl and hydrochloric acid, the same products of decomposition which are obtained under similar conditions from chloride of ethylene.

2. Hydrochloric acid and aldehyde form water and oxychloride of ethylidene.*

Oxychloride of ethylidene is decomposed by water into aldehyde and hydrochloric acid: it is isomeric with chlorethral.

3. Chloride of acetylene and aldehyde combine and form

This body is also produced by the action of chlorine on aldehyde. With solution of potash it forms aldehyde, chloride of potassium, and acetate of potash.

4. If acetic aldehyde and anhydrous acetic acid be heated in a sealed tube to 180°C. both unite and form

which boils at 168°C. and is isomeric with diacetate of glycol. Hydrate of potash decomposes this compound, acetate of potash and aldehyde being produced.

5. Bromide of ethylidene and $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{Na} \end{array} \left\{ \begin{array}{c} \text{O} \\ \text{O} \end{array} \right\}$ form bromide of sodium and acetal.

* Compt. rend. xlv, 662; Ann. Ch. Pharm. cvi, 336.

† Compt. rend. xlvii, 874; Ann. Ch. Pharm. cix, 156.

‡ Geuther. Ann. Ch. Pharm. cvi, 249.

Ethylic alcohol, acetic aldehyde, and hydrochloric acid produce a liquid which boils at 95°C. and has the formula

This compound is decomposed by ethylate of sodium acetal and chloride of sodium being formed.

Acetal, which is isomeric with diethyl-glycol, is also formed by the oxidation of ethylic alcohol. If hydrochloric acid acts on acetal, chloride of ethyl occurs amongst the products of decomposition.

When chlorine acts on ethylic alcohol, the following substances are obtained.

Chloral stands to trichlorinated acetal as aldehyde does to acetal.

6. If a mixture of sulphuric acid, water, peroxide of manganese, and ethylic and methylic alcohols be distilled, the following two compounds are obtained.

Acetal wherein one or both atoms of ethyl have been replaced by methyl.

The following is a list of those compounds, derived from glycol and acetic aldehyde, which are isomeric.

Aldehyde	C_2H_4O	Oxide of ethylene	C_2H_4O
Chloride of ethylidene	$(C_2H_4)''Cl_2$	Chloride of ethylene	$(C_2H_4)''Cl_2$
Chloracetine of ethylidene	$\left. \begin{matrix} C_2H_3O \\ (C_2H_4)'' \end{matrix} \right\} O, Cl$	Chloracetine of glycol	$\left. \begin{matrix} C_2H_3O \\ (C_2H_4)'' \end{matrix} \right\} O, Cl$
Acetate of aldehyde	$\left. \begin{matrix} C_2H_3O \\ (C_2H_4)'' \\ C_2H_3O \end{matrix} \right\} O_2$	Diacetate of glycol	$\left. \begin{matrix} C_2H_3O \\ (C_2H_4)'' \\ C_2H_3O \end{matrix} \right\} O_2$
Acetal	$\left. \begin{matrix} C_2H_5 \\ (C_2H_4)'' \\ C_2H_5 \end{matrix} \right\} O_2$	Diethylo-glycol	$\left. \begin{matrix} C_2H_5 \\ (C_2H_4)'' \\ C_2H_5 \end{matrix} \right\} O_2$

b. *Valerianic aldehyde.*

The aldehyde of valerianic acid has also been combined with acetic and benzoic acids.

Acetic acid compound	$\left. \begin{matrix} C_2H_3O \\ C_2H_3O \\ (C_5H_{10})'' \end{matrix} \right\} O_2$	Benzoic acid compound	$\left. \begin{matrix} C_7H_5O \\ C_7H_5O \\ (C_5H_{10})'' \end{matrix} \right\} O_2$
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These compounds are respectively decomposed by caustic potash into valerianic aldehyde, and acetate and benzoate of potash.* Acetate of valerianic aldehyde is isomeric with diacetate of amylo-glycol.

c. *Benzoic aldehyde.*

Pentachloride of phosphorus and oil of bitter almonds form oxychloride of phosphorus and chlorobenzole.

* Guthrie and Kolbe. Ann. Ch. Pharm. cix, 298.

If chlorobenzole be placed in contact with $\left. \begin{smallmatrix} \text{CH}_3 \\ \text{Na} \end{smallmatrix} \right\} \text{O}$, chloride of sodium and $\left. \begin{smallmatrix} (\text{C}_7\text{H}_6)'' \\ \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_3 \end{smallmatrix} \right\} \text{O}_2$ are produced.

In a similar manner we obtain

Acetate, benzoate, and chloride of benzole can be decomposed with caustic potash, acetate and benzoate of potash and chloride of potassium, together with oil of bitter almonds, being respectively formed; a corresponding alcohol of the formula $\left. \begin{smallmatrix} \text{C}_7\text{H}_6 \\ \text{H}_2 \end{smallmatrix} \right\} \text{O}_2$ could not be obtained.*

With regard to these compounds, oil of bitter almonds may be regarded as the oxide of the diatomic radical $(\text{C}_7\text{H}_6)''$.

d. *Cuminic Aldehyde.*

Chlorocumole and benzoate of silver yield chloride of silver and benzoate of cumole.†

* Ann. Ch. Pharm. cii, 356, 373.

† Ann. Ch. Pharm., cvi, 253; cix, 367. Petersb. Acad. Bull. xvii, 125.

Acetate of cumole has also been prepared from acetate of silver and chloride of cumole.

Caustic potash decomposes these bodies in a manner analogous to that in which it decomposes the benzole compounds.

Meconine and saligenine may perhaps be added to the diatomic alcohols. Berthelot obtained

Saligenine appears to be the alcohol of salicylous and salicylic acids. Salicylous acid is produced from saligenine by oxidation with chromic acid, as aldehyde and acetic acid are from ethylic alcohol. Benzole-alcohol, $\left\{ \begin{array}{c} (\text{C}_7\text{H}_6)'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$, derived from chlorobenzole, $(\text{C}_7\text{H}_6)''\text{Cl}_2$, will be, if it at all exist, isomeric with saligenine.

Saliretine, formed by the action of sulphuric acid on saligenine, is perhaps the ether of saligenine.

Salicine may be represented as saligenine wherein one atom of hydrogen has been replaced by $\text{C}_6\text{H}_{11}\text{O}_5$

and populine as saligenine wherein one atom of hydrogen has been replaced by benzoyl, $\text{C}_7\text{H}_5\text{O}$ and another by $\text{C}_6\text{H}_{11}\text{O}_5$.

Very little is known of the alcohol of anisic acid, $\text{C}_8\text{H}_{10}\text{O}_2$.*

C. Triatomic Alcohols.

GLYCERINE

represents three atoms of water, wherein three atoms of hydrogen have been replaced by the triatomic radical $(\text{C}_3\text{H}_5)'''$.

1. This substance combines with monatomic acids with elimination of water, and produces neutral compounds which, by respective treatment with caustic potash or soda, hydrochloric and acetic acids and water, are decomposed into glycerine and acid. As one, two or three atoms of hydrogen can be replaced in glycerine, three compounds may be formed from glycerine and the same acid.

These bodies are obtained by heating mixtures of glycerine and

* Cannizaro and Bertagnini, *Cimento* i, 99; *Ann. Ch. Pharm.* xviii, 188.
Liebig and Kopp's *Jahresbericht*, (1855) 623.

acid in sealed tubes at temperatures varying from 100° to 300° C. for several hours. According to temperature, pressure, and the relative quantity of materials employed, one, two, or three atoms of hydrogen are replaced in glycerine by acid radicals. The product is treated with slaked lime or carbonate of soda, in order to remove the uncombined acid, and digested with ether. The compound is left as a residue when the ethereal solution is evaporated. The glycerides, as these compounds may be called, of the volatile fatty acids are oily liquids; stearine and palmitine are solids; only few are volatile without decomposition.

The following is a list of those compounds which contain a monatomic acid or basic radical that have already been prepared.*

MONOGLYCERIDES.

DIGLYCERIDES.

* Compt. rend. xxxvii, 398; xxxviii, 668; Ann. Ch. Pharm. lxxxviii, 304; xcii, 301, 305; Chem. Soc. Qu. J. vi, 280; vii, 222. Chem. Gaz. (1853) 421; (1854) 340. Jahresbericht, (1853) 451; (1854) 448; Ann. Ch. Phys. [3] xli, 216; Proc. R. S. vii, 130.

Berthelot considers divalérine, dipalmitine, distearine, and dioleinc to contain one atom of water more than represented by the above formulæ.

TRIGLYCERIDES.

Some of these compounds, as monostearine, diethyline, distearine, tribenzoycine, &c., crystallize. Chevreul, Pelouze and Gélis, Duffy, Heintz, and especially Berthelot, have furnished important researches on the glycerides. According to the method which the latter chemist employed, it seems that some of the compounds obtained by him were not quite pure, and the analy-

tical results bear out this supposition. But considering the general chemical comportment of glycerine, the formulæ given in the above list are most probably a correct representation of the composition of these compounds.

2. The compounds, produced by the action of sulphuric, tartaric, and phosphoric acids on glycerine, possess an acid character; combine with bases; decompose very easily into glycerine and acid by treatment with water; and may be compared to sulphovinic acid. If the latter be considered as sulphuric acid wherein one atom of hydrogen has been replaced by ethyl, then the corresponding compound of glycerine may be represented as sulphuric acid wherein one atom of hydrogen has been replaced by the monatomic radical $C_3H_7O_2$, derived from glycerine. The same remark applies equally to tartro- and phospho-glyceric acids.

Sulphoglyceric acid* is formed by mixing one part of glycerine with two parts of sulphuric acid.

Sulphoglyceric acid is monobasic; the following salts are known:—

Tartroglyceric acid is formed by heating equivalent quantities of glycerine and tartaric acid to $150^\circ C$.

* Pelouze. (1836.) Ann. Ch. Phys. lxiii, 21; Ann. Ch. Pharm. Liebig & Wöhler, xix, 211.

It appears that only the lime-salt of this acid is known.

Phosphoglyceric acid* is formed by mixing glycerine with solid phosphoric acid

A compound of this acid is supposed to exist in the yolk of eggs and in the brain; it is dibasic, and has furnished the following salts:—

Sebacine, being a derivative from glycerine and a bibasic acid, has to be mentioned.

Sebacine is neutral, and is decomposed by oxide of lead into glycerine, and a lead-salt of sebacic acid.

* Compt. rend. xxi, 718; Goble. J. Pharm. [3] ix, 161; xi, 409; xii, 5.

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Chlorhydrine boils at 227° C., dichlorhydrine at 178° C., and epichlorhydrine at about 120° C. Chlorhydrine and dichlorhydrine regenerate glycerine by treatment with oxide of lead or potash.

4. On heating glycerine saturated with hydriodic acid, to 100° C. for forty hours, iodhydrine is generated.*

Iodhydrine is not volatile without decomposition; when treated with potash, it yields iodide of potassium, a substance resembling glycerine and a body, $\text{C}_6\text{H}_{10}\text{O}_3$, which is probably the ether of glycerine.

5. The chlorides of phosphorus and glycerine produce the same substances which are obtained by acting with hydrochloric acid on glycerine; monochlorhydrine, dichlorhydrine, and epichlorhydrine, as well as small quantities of trichlorhydrine and epidichlorhydrine are formed. The last two substances are formed abundantly by the action of PCl_5 on dichlorhydrine.†

* Compt. rend. xxxix, 748; Ann. Ch. Phys. (3) xliii, 279; Ann. Ch. Pharm. xcii, 311; Jahresbericht von Liebig & Kopp, (1854), 453.

† Ann. Ch. Phys. (3), lii, 433; Jahresbericht von Liebig, (1857), 477.

Trichlorhydrine boils at about 155° C., and epidichlorhydrine at about 120° C.; both, if heated to 100° C. with moist oxide of silver, regenerate glycerine.

6. The derivatives from glycerine and the bromides of phosphorus are very numerous; monobromhydrine, dibromhydrine, tribromhydrine, epibromhydrine, hemibromhydrine, acroleine, and two compounds $C_{18}H_{27}BrO_7$ and $C_6H_9Br_2P$, have been obtained in a tolerably pure state.* Glycerine and terbromide of phosphorus act upon each other as follows:—

The distillation of dibromhydrine with pentabromide of phosphorus yields tribromhydrine and a compound, $C_3H_7Br_3O$.

Epibromhydrine is obtained in large quantities by the action of liquid bromide of phosphorus on glycerine.

Along with monobromhydrine, dibromhydrine, and epibromhydrine, Berthelot and Luca obtained three substances, the formulæ of which, according to these chemists, are $C_6H_9BrO_2$, $C_6H_9Br_2P$, and $C_{18}H_{27}BrO_7$.

* Ann. Ch. Phys. (3) xlviii, 304; Ann. Ch. Pharm. ci, 68; Jahresbericht. von Liebig & Kopp, (1856), 599.

The two formulæ $C_6H_9BrO_2$ and $C_{18}H_{27}BrO_7$ seem to be not well established, and the substances which they represent require further investigation. $C_6H_9Br_2P$ will be considered with the nitrogen derivatives of glycerine.

The formation of acroleine, by the action of PBr_3 on glycerine, is easily understood.

The water which separates from the glycerine unites perhaps with the phosphorous acid, produced at the same time.

Monobromhydride, dibromhydride, epibromhydride and hemibromhydride, by treatment with potash, and tribromhydride and $C_3H_7Br_3O$, by treatment with moist oxide of silver, regenerate glycerine. Dibromhydride is the chief product obtained by the action of PBr_3 on glycerine. Epibromhydride boils at $138^\circ C.$; dibromhydride at $219^\circ C.$; hemibromhydride below $200^\circ C.$; tribromhydride at about $180^\circ C.$; and monobromhydride in vacuo at about $180^\circ C.$ These five substances are neutral liquids. Tribromhydride $(C_3H_5)'''Br_3$, brominated bromide of propylene $(C_3H_5Br)''Br_2$, and terbromide of allyle, obtained by the action of bromine on iodide of allyle, are isomeric, but not identical; only the first and last are able to furnish glycerine.

7. The action of iodide of phosphorus on glycerine is represented by the following equation.*

The teratomic radical glycyle, $(C_3H_5)'''$, changes in this reaction and becomes converted into the monatomic radical, allyle. Besides iodide of allyle some propylene, C_3H_6 , is formed, in consequence of a secondary reaction.

* Ann. Ch. Phys. (3) xliii, 257; Ann. Ch. Pharm. xcii, 306; Jahresbericht (1854), 451.

8. Compounds derived from glycerine with more than one acid, chloride or bromide, have next to be considered.* Dibromhydride and pentachloride of phosphorus produce hydrochloric acid, oxychloride of phosphorus and chlorhydrodibromhydride.

From dichlorhydride and pentabromide of phosphorus, bromhydrodichlorhydride is obtained.

Chlorhydrodibromhydride and bromhydrodichlorhydride are neutral liquids, which regenerate glycerine by treatment with moist oxide of silver.

Instead of chlorine or bromine, the atomic group $(\text{C}_2\text{H}_3\text{O})'\text{O}$, derived from acetic acid, may be introduced into these substances.

Chloride of acetylene and glycerine form acetochlorhydride, acetodichlorhydride and water.

Acetochlorhydride and acetodichlorhydride are neutral liquids, volatile without decomposition.

The action of chloride of acetylene on a mixture of glycerine and acetic acid, produces diacetochlorhydride.

* Ann. Ch. Phys. (3), lii, 432; Liebig's Jahresbericht (1857), 476.

If a mixture of equivalent quantities of chloride and bromide of acetylene be allowed to act on glycerine, aceto-chlorhydrine is formed.

Glycerine, in contact with hydrochloric acid and benzoic acid, produces benzochlorhydrine.

Diaceto-chlorhydrine and aceto-chlorhydrine are neutral liquids, volatile without decomposition.

The majority of the compounds, enumerated under 3, 5, 6, and 8, may be considered to be formed according to the subjoined equation,

where n is equal to 1, 2, or 3, A stands for one atom of monatomic acid, and B denotes the compound formed.

The formation of trichlorhydrine may be taken as an example.

Nevertheless there are some compounds which are not formed in accordance with this equation, as exemplified in epidichlorhydrine.

Epidichlorhydrine is able, nevertheless, if treated with moist oxide of silver, to regenerate glycerine.

In most cases, if hydrochloric acid or the chlorides or bromides of phosphorus act on glycerine, the elements of peroxide of hydrogen separate from the latter, and for HO, one atom of chlorine or bromine enters the compound; but if oxygen acids, such as acetic acid, act on glycerine, the latter exchanges HO for the peroxides of the acid radicals, discovered by Mr. Brodie.

The formula of glycerine may therefore be written

and expressions for its derivatives obtained by substituting for HO, either bromine, chlorine, or one of the peroxides of the acid radicals. This mode of representation has been adopted in the following list, which contains the compounds mentioned under 3, 5, 6, and 8. But I wish it to be understood that I do not mean to say that peroxide of hydrogen preexists in glycerine, but merely that in certain reactions the elements HO are exchanged for chlorine, bromine, or compound bodies.

$(C_3H_5)'''(HO)$	(HO)	(HO)	Glycerine.
$(C_3H_5)'''(HO)$	(HO)	Cl	Monochlorhydrine.
$(C_3H_5)'''(HO)$	(HO)	Br	Monobromhydrine.
$(C_3H_5)'''(HO)$	Cl	Cl	Dichlorhydrine.
$(C_3H_5)'''(HO)$	Br	Br	Dibromhydrine.
$(C_3H_5)''' Cl$	Cl	Cl	Trichlorhydrine.
$(C_3H_5)''' Br$	Br	Br	Tribromhydrine.
$(C_3H_5)''' Br$	Cl	Cl	Bromhydrodichlorhydrine.
$(C_3H_5)''' Cl$	Br	Br	Chlorhydrodibromhydrine.
$(C_3H_5)'''(HO)$	$(C_2H_3O_2)$	Cl	Acetochlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	$(C_2H_3O_2)$	Cl	Diacetochlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	Cl	Cl	Acetodichlorhydrine.
$(C_3H_5)'''(C_2H_3O_2)$	Br	Cl	Acetochlorhydrobromhydrine.
$(C_3H_5)'''(C_7H_5O_2)$	(HO)	Cl	Benzochlorhydrine.

The following compounds cannot be derived in this manner from glycerine, because their formation does not take place according to the equation mentioned on page 252.

9. Glycerine and hydrate of potash form, with evolution of hydrogen, formiate and acetate of potash.*

* Dumas and Stass. Ann. Ch. Phys. lxxiii, 148; Ann. Ch. Pharm. xxxiv, 129.

10. A mixture of anhydrous phosphoric acid and glycerine, on being subjected to distillation, yields acroleine.

11. Monochlorhydrine acts on ammonia* and forms the hydrochlorate of a base which Berthelot calls glyceramine.

According to Berthelot, if a stream of ammonia gas be passed through a solution of dibromhydrine in anhydrous alcohol, bromide of glyceramine is formed. The production of the latter from ammonia and dibromhydrine is intelligible only when we assume that one atom of water takes part in the reaction.

Tribromide of allyle† acts easily on ammonia, and forms a base called dibromallylamine.‡

and—

In this instance two atoms of the monobrominated radical allyle replace two atoms of hydrogen in ammonia and form the base in question. The presence of another atom of hydrogen in

* Ann. Ch. Pharm. ci, 76.

† Ann. Ch. Pharm. civ, 247.

‡ Phil. Mag. [4], xvi, 257; Ann. Ch. Pharm. cix, 362.

the latter, replaceable by other radicals, was proved by treating dibromallylamine with iodide of ethyl; ethyldibromallylamine was thus obtained.

By treating glycerine with liquid bromide of phosphorus, Berthelot obtained a substance* of the composition $\text{C}_6\text{H}_9\text{Br}_2\text{P}$. If in this formula the phosphorus be replaced by nitrogen, we have the formula of dibromallylamine. It is probable that these two substances have a similar constitution, and are related to each other as triethylamine is to triethylphosphine.

12. Nitric acid oxidizes glycerine with great ease, the result of the reaction being an acid called glyceric acid.†

Glyceric acid is formed from glycerine, in a manner analogous to that of acetic acid from alcohol, or glycolic acid from glycol; two atoms of the hydrogen of the alcohol being replaced by one of oxygen. The acid, which stands to glyceric acid in the same relation as oxalic does to glycolic acid, or malonic‡ to lactic acid, appears to be the tartronic acid of Dessaignes.§

Although the formation of tartronic acid from glyceric acid has not yet been experimentally established, other properties point out the existence of an intimate connexion between these two substances.

The oxidation of propylo-glycol yields, according to the conditions of the experiment, lactic or glycolic acid.||

* Ann. Ch. Pharm. ci, 73.

† Phil. Mag., March, 1858; Ann. Ch. Pharm. cvi, 81.

‡ Ann. Ch. Pharm. cvii, 251.

§ Compt. rend. xxxiv, 731; Ann. Ch. Pharm. lxxxii, 362; lxxxix, 339; Jahresbericht (1852), 475.

|| Ann. Ch. Pharm. cv, 204-5.

Glyceric acid may be converted into lactic acid,* and tartronic into glycolic acid. The transformations of glyceric and tartronic acids, and their composition, support the view, therefore, that they are connected in the same manner as oxalic and glycolic acids.

According to our knowledge of several salts of glyceric acid, this substance appears to be monatomic. But if we consider its derivation from glycerine, the view of M. Wurtz,† who considers glyceric acid to be triatomic, is very probably correct.

This point, however, requires further investigation.

Thus by a variety of reactions, we recognize glycerine to be derived from three atoms of water, and to contain three atoms of hydrogen, replaceable by other radicals and the triatomic radical (C_3H_5) . Accordingly we obtain from glycerine and a monatomic acid, at least three compounds, corresponding to the ethers of common alcohol, and with hydrochloric acid at least three chlorides, the formation of which takes place in a manner analogous to that of chloride of ethyl from $\left\{ \begin{array}{c} C_2H_5 \\ H \end{array} \right\} O$, or of chloride of potassium from $\left\{ \begin{array}{c} K \\ H \end{array} \right\} O$. The same reaction, which occurs *once* in these two instances, repeats itself in the case of glycerine *three* successive times. The great number of compounds, which can be prepared in this way by changing the acids, may be considerably augmented by employing two or three different acids at the same time, as illustrated by the following examples.

* Ann. Pharm. cix, 227; Phil. Mag., December, 1858.

† Société Chimique de Paris (13 Mai, 1859), 38.

$$\begin{array}{l} (\text{C}_3\text{H}_5), \text{monatomic in } . \quad . \quad . \quad . \quad \frac{\left(\text{C}_3\text{H}_5' \right)'}{\text{H}} \Bigg\} \text{O} \\ \hspace{60em} \text{Allylic alcohol.} \\ (\text{C}_3\text{H}_5)'', \text{triatomic in } . \quad . \quad . \quad . \quad \frac{\left(\text{C}_3\text{H}_5'' \right)'}{\text{H}_3} \Bigg\} \text{O}_3 \\ \hspace{60em} \text{Glycerine.} \\ (\text{C}_3\text{H}_5)'', \text{H} . = (\text{C}_3\text{H}_6)', \text{diatomic in } . \quad \frac{\left(\text{C}_3\text{H}_6' \right)'}{\text{H}_2} \Bigg\} \text{O}_2 \\ \hspace{60em} \text{Propylo-glycol.} \\ (\text{C}_3\text{H}_5)'', \text{HH} . = (\text{C}_3\text{H}_7)', \text{monatomic in } . \quad \frac{\left(\text{C}_3\text{H}_7' \right)'}{\text{H}} \Bigg\} \text{O} \\ \hspace{60em} \text{Propylic alcohol.} \end{array}$$