alcohols; most phenols; some ketones; simple carboxylic acids; most aromatic hydroxy acids; a few esters.

- (b) with decomposition: almost all unsaturated compounds; some aromatic hydrocarbons; most aliphatic hydroxy acids; most esters; sugars (brownish colours); some glycosides (red or other pronounced colours).
- (ii) Insoluble: saturated hydrocarbons; some aromatic hydrocarbons.
- B. Hot
 - (i) Gases evolved:
 - (a) with charring: aldehydes; ketones; acetals; carbohydrates; glycosides.
 - (b) without charring: simple alcohols of low mol. wt. (evolve gaseous unsaturated hydrocarbons); formic and oxalic acids and their derivatives (yield CO).
 - (ii) Pungent vapours evolved, without charring: simple phenols; certain simple carboxylic acids; many esters.
 - (iii) No gases evolved, with charring: most polyhydroxylic phenols; many aromatic hydroxy acids and certain of their derivatives.
 - (iv) Soluble unchanged: some carboxylic acids; some aromatic ketones of high mol. wt.
- V. Dissolve in water or alcohol and treat with one drop of FeCl₃ solution.
 - A. Reddish colouration or precipitate: almost all simple carboxylic acids.
 - B. Intense yellow colouration: aliphatic a-hydroxy acids.
 - C. Green, blue, or violet colourations: most phenols and phenolic compounds (some in alcoholic solution only); keto-enolic esters and similar compounds.

VI. Treat with a solution of $KMnO_4$ in dilute H_2SO_4 .

Decolourisation by:

- (a) almost all unsaturated compounds;
- (b) certain easily oxidisable substances such as formic acid and malonic acid and their esters; many aldehydes; simple quinones; some aliphatic hydroxy acids; many polyhydric alcohols and phenols; certain sugars.

VII. Treat with bromine water in the cold or warm.

A. Decolourisation without formation of much acid: almost all unsaturated compounds.

The acid formed should in every case be examined, after isolation by distillation with steam, filtration, or extraction with ether, according to the nature of the acid.

Phosphorus pentoxide reacts with amides, nitriles being produced on heating.

$$CH_{3}CONH_{2} \rightarrow CH_{3}CN + H_{2}O$$

These can best be isolated by distilling the nitrile from the resulting mixture, or failing this, by addition of cold water and extraction with ether.

Amides may be transformed into anilides by refluxing with aniline for 1-2 hr., ammonia being evolved

$$CH_{3}CONH_{2} + C_{6}H_{5}NH_{2} \rightarrow CH_{3}CONHC_{6}H_{5} + NH_{3}$$

Aromatic nitriles when treated with a warm alkaline solution of 20 volume hydrogen peroxide are converted into the corresponding amides

$$2C_{6}H_{5}CN + 2H_{2}O_{2} \rightarrow 2C_{6}H_{5}CONH_{2} + O_{2}$$

On reduction with tin and hydrochloric acid or by adding sodium to a boiling ethanolic solution of the substance, nitriles are converted into the related primary amines.

$$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$$

Imides of dicarboxylic acids present properties similar to those of simple amides, except that on treatment of a saturated methanolic solution with saturated methanolic potash a precipitate of the potassium derivative is formed.



On boiling with an alkaline solution of sodium hypobromite an amino acid is produced.



Closely related to the amides are *urea* and its *monosubstitution* products (pp. 71, 176, 181), which behave as amides derived from carbonic acid. On acid hydrolysis they yield carbon dioxide, an ammonium hydroxide to phenolphthalein. The addition of a few cm^3 of neutralised (phenolphthalein) formaldehyde causes the immediate disappearance of the pink colour, owing to the formation of a methylene derivative of an acidic nature. In a similar manner, acylating agents such as acetyl chloride, benzoyl chloride, *p*-toluenesulphonyl chloride yield derivatives which are strongly acidic.

Aromatic amino acids (pp. 73, 186) are more acidic than their aliphatic counterparts and cause a vigorous evolution of carbon dioxide from sodium bicarbonate. They usually give reddish colours with ferric chloride solutions. With nitrous acid (q.v.) they yield diazonium salts which couple normally with alkaline 2-naphthol solution to give azo dyes.

If the substance is hydrolysed by the action of alkaline reagents, yet yields no basic product, it may possibly be an ester of nitric acid or of nitrous acid.

Alkyl nitrates (p. 211), on hydrolysis with aqueous potash under reflux, yield potassium nitrate and the corresponding alcohol.

$$\rm C_2H_5ONO_2 + \rm KOH \rightarrow \rm C_2H_5OH + \rm KNO_3$$

This normal hydrolysis is nevertheless always accompanied to a greater or less degree by an abnormal reaction, whereby the alkyl group is partially oxidised at the expense of the nitrate, potassium nitrite being produced. Alkyl nitrates are reduced on treatment with tin and hydrochloric acid, with formation of hydroxylamine.

$$C_2H_5ONO_2 + 6[H] \rightarrow C_2H_5OH + NH_2OH + H_2O$$

Care must be exercised when purifying by distillation or determining the boiling point of an alkyl nitrate, as these esters are liable to undergo explosive decomposition on rapid heating, this property being forcibly exemplified in the case of nitroglycerol (glyceryl trinitrate) and nitrocellulose.

Alkyl nitrites (p. 211), on hydrolysis with alkaline reagents, yield the corresponding alcohols and a metallic nitrite.

 $C_5H_{11}ONO + KOH \rightarrow C_5H_{11}OH + KNO_2$

They are readily reduced, even by hydrogen sulphide, yielding the corresponding alcohol and ammonia,

$$C_{5}H_{11}ONO + 3H_{2}S \rightarrow C_{5}H_{11}OH + NH_{3} + H_{2}O + 3S$$

the same effect being also produced by more powerful reducing agents. On treatment of one molecular proportion of aniline dissolved in absolute alcohol in the presence of one-and-one-quarter molecular proportions of sulphuric acid with a slight excess of an alkyl nitrite, diazobenzene hydroxide is produced.

$$C_6H_5NH_2 + C_5H_{11}ONO \rightarrow C_6H_5N_2OH + C_5H_{11}OH$$

basic than the hydroxides of the alkali metals; the free bases cannot for this reason be prepared by the action of caustic soda upon solutions of their salts. The process commonly employed for this purpose involves the action of silver oxide upon a solution of sulphonium halide.

$$2(CH_3)_3^{+}SOH^- + Ag_2O + H_2O \rightarrow 2(CH_3)_3^{+}SOH^- + 2AgI$$

Sulphonium salts in acetone solution dissolve mercuric iodide with formation of addition compounds, which crystallise out on evaporation of the solvent.

If the substance is practically neutral to litmus, it may be a sulphone, a sulphoxide, a sulphide or a disulphide, or a mercaptan. Due allowance must be made for the possible presence of carboxyl groups, and the fact is to be borne in mind that the presence in the molecule of a sulphone grouping considerably augments the acidic character of phenolic hydroxyl groups.

Sulphones (p. 218) exhibit no specific reactions, being extremely stable. They are unattacked by the action of the most powerful acids, alkalis, or oxidising or reducing agents. Aromatic sulphones may thus be boiled with fuming nitric acid with no further effect than nitration, while the simpler aliphatic members of this class are unaffected even by this violent treatment. They are, however, broken up into sulphinates and hydrocarbons on treatment with sodium in boiling toluene.

$$2C_6H_5SO_2C_6H_5 + 2Na \rightarrow 2C_6H_5SOONa + C_6H_5C_6H_5$$

The simpler sulphones may be distilled unchanged under atmospheric pressure; some disulphones such as sulphonal, on the other hand, break down on strongly heating, yielding carboxylic acids, mercaptans, sulphur dioxide, and other products.

Sulphones may be detected by the fusion test described under sulphonic acids; sulphur dioxide is evolved upon acidification of the cold melt.

Sulphoxides (p. 218) may exhibit faintly basic properties. Many give Smiles' test (*cf.* aromatic sulphinic acids),* and are far less stable than the sulphones. They may be oxidised by nitric acid, or better, by adding finely powdered potassium permanganate to a solution in glacial acetic acid, with formation of sulphones, and may be reduced to the corresponding sulphides by boiling with tin or zinc in hydrochloric acid.

Sulphides and mercaptans (thiols) are generally liquids with unpleasant odours. Upon fusion with potassium hydroxide and treatment with

^{*} It is to be observed that aromatic sulphoxides which contain hydroxyl and similar groups dissolve in concentrated sulphuric acid with a more or less pronounced blue colour.