Molecular Weight Determination by Titration

WRAPPING IT UP

Flush all *filtrates* down the drain.

25.13 CARBOXYLIC ACIDS

Classification Test

One of the best qualitative tests for the carboxylic acid group is solubility in basic solutions. Carboxylic acids are soluble both in 1.5 *M* sodium hydroxide solution *and* in 0.6 *M* sodium bicarbonate solution, from which they are regenerated by acidification. Solubility properties are discussed in Section 25.3.

The acidity of carboxylic acids enables ready determination of the **equivalent mass** or **neutralization equivalent** of the acid by titration with standard base. The equivalent weight of an acid is that mass, in grams, of acid that reacts with one equivalent of base. As an example, suppose that 0.1000 g of an unknown acid requires 16.90 mL of 0.1000 *N* sodium hydroxide solution to be titrated to a phenolphthalein endpoint. This means that 0.1000 g of the acid corresponds to (16.90 mL)(0.1000 equivalent/1000 mL) or 0.0016901 equivalent of the acid, or that one equivalent of the acid weighs 0.1000/0.00169 or 59.201 g. Thus the following expression applies:

$$\text{Equivalent mass} \qquad \text{(Volume of base consumed in liters)(N)}$$

where *N* is the *normality* of the standard base.

Because each carboxylic acid function in a molecule is titrated with base, the equivalent mass corresponds to the molar mass of the acid divided by *n*, where *n* is the number of acid functions present in the molecule. For the example given, the molar mass is 59.2 for a single acid function, 118.4 for two, and 177.6 for three. If the molar mass of an unknown compound is known, then the number of acid groups in the molecule is calculated by dividing the molar mass by the equivalent mass. Hence, if the molar mass of the unknown compound is 118 and its equivalent mass is 59.2, the unknown must have *two* titratable acid functions.

EXPERIMENTAL PROCEDURE

Determination of Equivalent Mass of an Acid

Preparation Sign in at **www.cengage.com/login** to read the MSDSs for the chemicals used or produced in this procedure.

curately weigh about 0.2 g of the acid and dissolve it in 50–100 mL of water or % ethanol or a mixture of the two. It may be necessary to warm the mixture to solve the compound completely. Using phenolphthalein as the indicator, titrate the solution with a *standardized* sodium hydroxide solution having a concentration of about 0.1 *M* (Fig. From the data obtained, calculate equivalent

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Flush the *aqueous solution* down the drain.

Derivatives

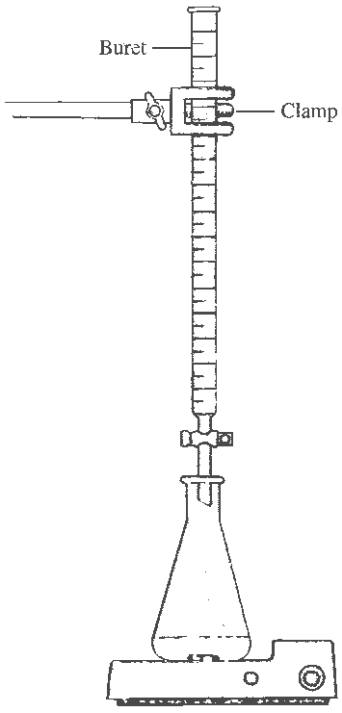


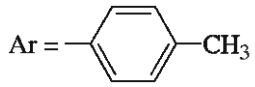
Figure 25.6
Apparatus for quantitative titration.

Three satisfactory solid derivatives of carboxylic acids are amides (Eq. 25.46), anilides (Eq. 25.47), and *p*-toluidides (Eq. 25.48). These derivatives are prepared by treating the corresponding acid chlorides with ammonia, aniline, or *p*-toluidine. The amides are generally less satisfactory derivatives than the other two because they tend to be more soluble in water and thus are harder to isolate. The acid chlorides are most conveniently prepared from the acid, or its salt, and thionyl chloride (Eq. 25.49).

$$\underset{\text{An acid chloride}}{RCOCl} + 2\,NH_3 \xrightarrow{\text{cold}} \underset{\text{An amide}}{RCONH_2} + NH_4Cl \qquad (25.46)$$

$$\underset{}{RCOCl} + 2\,\underset{\text{Aniline}}{H_2NC_6H_5} \longrightarrow \underset{\text{An anilide}}{RCONHC_6H_5} + C_6H_5NH_3^+\,Cl^- \qquad (25.47)$$

$$\underset{}{RCOCl} + 2\,\underset{p\text{-Toluidine}}{H_2NAr} \longrightarrow \underset{A\ p\text{-toluidide}}{RCONHAr} + ArNH_3\,Cl^- \qquad (25.48)$$



$$\underset{\text{A carboxylic acid}}{RCO_2H} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{An acid chloride}}{RCOCl} + \underset{\text{Sulfur dioxide}}{SO_2} + HCl \qquad (25.49)$$

14. SUPPLEMENTS (CONT.)