Assay of Phthalic Anhydride and Some Related Compounds by Volumetric Methods

P.K. DUBEY*, S.M. GHOUSE MOHIUDDIN and D. RAMESH

Chemistry Department
J.N.T. University, Kukatpally, Hyderabad-500 872, India

Three simple methods are described for the assay of phthalic anhydride. The first method involves titration of a methanolic solution of phthalic anhydride with standardised methanolic alkali. In the second method, phthalic anhydride is hydrolysed with boiling water, subsequently titrated with standardised aq. alkali. In the third method, phthalic anhydride is treated with a large excess of aq. alkali and the unconsumed alkali is titrated against standardised aq. acid (back-titration method). All the three methods are comparable and give good results.

INTRODUCTION

Phthalic anhydride is a petrochemical intermediate which finds use extensively as raw-material in the manufacture of several commercial products[1, 2]. Phthalic anhydride has three major uses which account for 95% of its total production. Thus, it is used in the manufacture of dialkyl phthalates which find application as plasticisers for polymers like polyvinyl chloride (PVC), polyvinyl acetate (PVA) *etc.* The second important use of phthalic anhydride is in the production of unsaturated polyesters which when properly cross-linked are used for making glass-fibre-reinforced plastics. The third major application of phthalic anhydride is in alkyd resins made by its polymerisation with glycerol, vegetable oils and/or fatty acids. The alkyd resins, sometimes referred to as glyptolic resins, are used in surface coatings, *e.g.*, in oil-based paints.

It is obvious from the above data that phthalic anhydride is a valuable industrial raw-material and its accurate assay is very important. The standard method as given by ISI[3] for the assay of phthalic anhydride involves hydrolysis with excess aq. alkali followed by titration of unreacted alkali with a standard acid.

RESULTS AND DISCUSSION

In the present investigation, for the assay of phthalic anhydride, three simple methods are described. The first method involves titration of a methanolic solution of phthalic anhydride with standardised methanolic alkali. In the second method, phthalic anhydride is hydrolysed with boiling water and subsequently titrated with standardised aq. alkali. In the third method, phthalic anhydride is treated with a large excess of aq. alkali and the unconsumed alkali is titrated against standardised aq. acid (back-titration method). All the three methods are comparable and give good results. The methods are fairly general and can be applied to other compounds like acetic anhydride, succinic anhydride, phthalic acid and tere-phthalic acid.

1. Method-I (Methanolic medium)
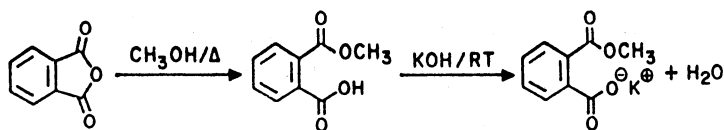
Procedure: Methanol was titrated (by adding a few drops) with standardised KOH solution in the presence of phenolphthalein indicator till the appearance of light pink colour took place. This methanol was called as neutral methanol.

Accurately weighed anhydride was taken in a conical flask. Natural methanol was added and heated for about 5 min. The solution was cooled to room temperature and titrated against standardised methanolic KOH till light pink end point was obtained. The readings were noted. Methanolic KOH was standardised by titration against primary standard potassium hydrogen phthalate using phenolphthalein as indicator.

Calculations:

Wt. of the sample of anhydride taken $= W_1$ gms.

Normality of the methanolic KOH solution $= N_1$ gm-equiv./litre

Vol. of standard KOH solution consumed $= V_1$ mL

From the above reaction (eq. 1), it is evident that gram-equivalents of KOH is equal to gram-equivalents of monoestermonoacid which in turn is equal to gram-equivalents of the anhydride.

That a monoestermonocarboxylic acid, *i.e.*, monomethylphthalate, is formed in the reaction of methanol with phthalic anhydride is demonstrated by the following experiment: A mixture of phthalic anhydride (1.48 gms, 10 mmoles) and methanol (15 mL) is heated on a steam-bath for 5–10 min. and evaporated to dryness. The residue was triturated with n-hexane at room temperature and filtered to obtain an insoluble solid, yield = 1.656 gms. (92% molar), m.p. 82–84°C.[4] Its IR (KBr) showed absorptions at ($\bar{v}$) around 2800 cm^{-1} (very broad, strong, —OH), 1730 cm^{-1} (very strong, ester carbonyl), 1690 cm^{-1} (very strong, acid carbonyl), 1600 cm^{-1} (C=C) etc. Its ^{1}H NMR in DMSO-d^6/TMS showed signals at δ 3.95 (s, 3H, —CH$_3$), δ 7.6–8.0 (complex multiplet, ABCD, 4H, aryl protons), δ 13.35 (broad s, 1H, —COOH). Proton-noise decoupled ^{13}C NMR spectrum of the compound recorded in DMSO-d^6 using TMS as lock signal showed peaks at δ 52.394 (—CH$_3$), 129.213, 129.935, 131.029, 131.324, 132.100, 132.499 (six aryl carbons), 189.183, 189.193 (two aryl carbons). The mass spectrum of the compound showed peaks at m/z 180 (3.1%, C$_9$H$_8$O$_4$, M$^+$), 163 (2.3%, M—OH), 149 (100%, M —OCH$_3$), 136 (35.2%, M—CO$_2$), 135 (22.5%, 163—CC), 121 (24.1%, 149—CO), 105 (53.5%, 121—O), 104 (15.2%, 105—H), 93 (40.6%, 121—CO), 92 (48.8%, 136—CO$_2$), 91 (23.4%, 92—H), 77 (34.5%, C$_6$H$_5^+$), 76 (37.3%, C$_6$H$_4^+$), 51 (23.1%, 77—C$_2$H$_2$), 50 (47.9%, 76—C$_2$H$_2$).

So, the gram-equivalents of consumed standard methanolic KOH solution

$$= \frac{N_1 \times V_1}{1000}$$

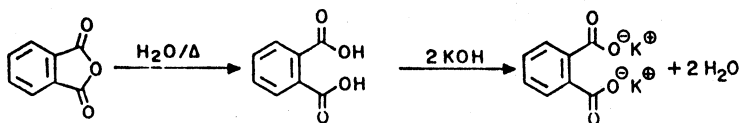$\therefore$ The gram. equivalents of anhydride $= \dfrac{N_1 \times V_1}{1000}$

$\therefore$ Weight of anhydride present in the smaple (U_1)

= (gram equivalents of anhydride) × (molecular wt. of anhydride)

$$U_1 = \frac{N_1 \times V_1}{1000} \times M_1$$

% Purity of the sample $= \dfrac{U_1}{W_1} \times 100$

The above method has been used for the assay of (i) phthalic anhydride, (ii) acetic anhydride and (iii) succinic anhydride.

2. Method-II (Aqueous medium)

Procedure: Accurately weighed anhydride was taken in a conical flask. To this was added distilled water and the mixture was heated to 100°C on a steam-bath for 5 min. After this, the solution was cooled to room temperature, a few drops of phenolphthalein indicator were added and the solution titrated against standardised aq. KOH from the burette until a light pink end point resulted. Aq. KOH solution was itself standardised by titration against primary standard potassium hydrogenphthalate solution using phenolphthalein as indicator. The readings were noted.

Calculations:

Weight of the sample of anhydride taken $= W_2$ gms.

Normality of aq. KOH solution used $= N_2$ gm-equiv. litre^{-1}

Volume of standard KOH solution consumed $= V_2$ mL

From the above reaction, it is evident that one gm.-equiv. of anhydride requires two gm-equiv. of aq. KOH solution.

So, the gram-equivalents of consumed standard aq. KOH solution

$$= \frac{N_2 \times V_2}{1000}$$

$\therefore$ The gram. equivalents of anhydride $= \dfrac{N_2 \times V_2}{2 \times 1000}$

$\therefore$ Weight of anhydride present in the smaple (U_2)

= (gram-equivalents of anhydride) × (molecular wt. of anhydride)

$$U_2 = \frac{N_2 \times V_2}{2 \times 1000} \times M_1$$

% Purity of sample $= \dfrac{U_2}{W_2} \times 100$

The above method has been used for the assay of (i) phthalic anhydride, (ii) acetic anhydride, (iii) succinic anhydride, (iv) phthalic acid and (v) terephthalic acid.

3. Method-III (Back-titration)
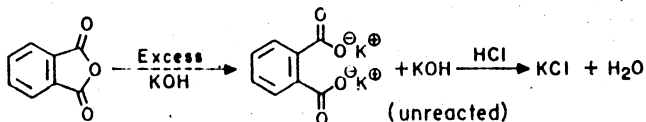
Back-titration means the anhydride is dissolved in excess of standardised aq. KOH solution. The unreacted aq. KOH solution is estimated by titration against standardised aq. hydrochloric acid.

Procedure: Measured quantity of aq. KOH solution was pipetted out into a conical flask and titrated against standardised aq. hydrochloric acid solution using phenolphthalein as indicator to colourless end point. The reading is noted. This reading is called blank reading.

In another conical flask, accurately weighed anhydride (or acid) was taken and measured quantity of aq. KOH solution was pipetted in. The contents are slightly warmed when a clear solution resulted. Few drops of phenolphthalein indicator were added and the solution titrated against aq. standardised hydrochloric acid till colourless end point was obtained. This reading was called sample reading.

The aq. hydrochloric acid solution itself was standardised by titration against primary standard sodium carbonate solution using methyl orange as an indicator.

Calculations: Normality of standardised aq. HCl solution $= N_3$ gm-equiv. litre^{-1}

Weight of the sample of anhydride taken $= W_3$ gms.

Blank reading $= B$ mL

Sample reading $= S$ mL

Volume of alkali consumed for the anhydride $= V_3$ mL $= (B - S)$ mL.

From the above reaction it is evident that the gram-equivalents of KOH solution consumed for the anhydride was equal to gram-equivalents of hydrochloric acid. Hence, gram-equivalents of hydrochloric acid consumed was equal to gram-equivalents of anhydride. But, each anhydride molecule has two acid groups. So, half gram-equivalent of anhydride will require one gram-equivalent of hydrochloric acid solution.

So, gram-equivalents of standard hydrochloric acid solution consumed

$$= \frac{N_3 \times V_3}{1000}$$

Gram-equivalents of anhydride $= \dfrac{N_3 \times V_3}{2 \times 1000}$

Weight of anhydride present in the sample (U_3)

$= $ (gram-equivalents of anhydride) $\times$ (molecular wt. of anhydride)

$$= \frac{N_3 \times V_3}{2 \times 1000} \times M_1$$

$$\% \text{ Purity of sample} = \frac{U_3}{W_3} \times 100$$

The above method has been used for the assay of (i) phthalic anhydride, (ii) acetic anhydride, (iii) succinic anhydride, (iv) phthalic acid and (v) terephthalic acid.

Results obtained from the above study using the three methods of assay for the five compounds are summarised in Table-1.

TABLE-1
ASSAY OF PHTHALIC ANHYDRIDE AND RELATED COMPOUNDS

S.No.	Compund Name	Mol. Wt.	Titration Procedure	Assay obtained
1.	Phthalic anhydride	148	Method-I	99.87%
2.	Phthalic anhydride	148	Method-II	100.40%
3.	Phthalic anhydride	148	Method-III	101.10%
4.	Acetic anhydride	102.1	Method-I	97.55%
5.	Acetic anhydride	102.1	Method-II	98.34%
6.	Acetic anhydride	102.1	Method-III	98.26%
7.	Succinic anhydride	100.07	Method-I	101.34%
8.	Succinic anhydride	100.07	Method-II	100.10%
9.	Succinic anhydride	100.07	Method-III	101.10%
10.	Phthalic acid	166	Method-II	100.70%
11.	Phthalic acid	166	Method-III	99.10%
12.	Terephthalic acid	166	Method-II	92.70 %
13.	Terephthalic acid	166	Method-III	92.63 %

EXPERIMENTAL

Assay of phthalic anhydride (Method-I)

Chemicals required: (a) Standard methanolic KOH, (b) Phenolphthalein indicator, (c) Methanol, (d) Potassium hydrogenphthalate.

Procedure: 0.397 gm. of phthalic anhydride was taken in a 150 mL conical flask. 25 mL of neutral methanol was added to it and heated for 5 min. on a steam-bath. After obtaining clear solution, it was titrated with standard methanolic KOH from the burette in the presence of phenolphthalein indicator till light pink end point was obtained (26.8 mL). 20 mL of 0.08747 N primary standard aq. potassium hydrogenphthalate required 17.5 mL methanolic KOH solution.

Calculations:

Weight of the sample taken $(W_1) = 0.397$ gm.

$$\text{Normality of methanolic KOH solution } (N_1) = \frac{20 \times 0.08747}{17.5} \text{ N}$$

$$= 0.09997 \text{ N}$$

Volume of standard KOH solution consumed (V_1) = 26.8 mL

Molecular weight of phthalic anhydride = 148

$$\text{Purity of sample} = \frac{0.09997 \times 26.8 \times 148 \times 100}{1000 \times 0.397} = 99.87\%$$

The titrations with acetic anhydride and succinic anhydride were done exactly as above except that molecular weight of acetic anhydride and succinic anhydride were taken as 102.1 and 100.07 respectively.

Assay of phthalic anhydride (Method-II)

Chemicals required: (a) Standard aq. KOH, (b) Phenolphthalein indicator (c) Potassium hydrogenphthalate (primary standard).

Procedure: 0.2626 gm. of phthalic anhydride was taken in a 150 mL conical flask. To this flask, 40 mL of distilled water was added and the mixture heated on a steam-bath for 5 min. The clear aq. solution was titrated against aq. KOH from the burette using phenolphthalein indicator till light pink end point resulted (22.4 mL). 20 mL of 0.08747 N primary standard aq. potassium hydrogen-phthalate required 11.0 mL of aq. KOH solution.

Calculations:

Weight of the sample of anhydride taken (W_2) = 0.2626 gm.

$$\text{Normality of aq. KOH solution } (N_2) = \frac{20 \times 0.08747}{11.0} = 0.1591 \text{ N}$$

Volume of standard KOH solution consumed = V_2 = 22.4 mL

Molecular weight of phthalic anhydride = 148

$$\text{Purity of the sample} = \frac{0.1591 \times 22.4 \times 148 \times 100}{2 \times 1000 \times 0.2626} = 100.4\%$$

The titrations with acetic anhydride, succinic anhydride, phthalic acid and terephthalic acid were done exactly as above except that their molecular weights (for calculation purposes) were taken as shown in Table-1.

Assay of phthalic anhydride (Method-III)

Chemicals required: (a) Standard aq. HCl, (b) Standard aq. KOH, (c) Phenolphthalein indicator, (d) Aq. Na_2CO_3 (primary standard), (e) Methyl orange indicator.

Procedure: 25 mL of standardised aq. KOH solution was pipetted out into a 250 mL conical flask and titrated against standardised aq. HCl from the burette in the presence of phenolphthalein indicator till a colourless end point was obtained. At this stage, the reading was noted. This was the blank reading (B).

1.0105 gms. of phthalic anhydride was taken in a 250 mL conical flask. To this was added, with a pipette, 25 mL of aq. KOH solution and the mixture warmed for a few min. The clear solution was cooled to room temperature and titrated against standard aq. HCl from the burette using phenolphthalein as indicator till colourless end point was obtained. At this stage, the reading was noted. This was the sample reading (S).

20 mL of primary standard (0.9125 N) aq. Na_2CO_3 solution was pipetted out into a conical flask and titrated against aq. HCl (volume consumed = 16.1 mL) from the burette using methyl orange as indicator.

Calculations:

Normality of aq. HCl solution $= \dfrac{20 \times 0.9125}{16.1} = 1.1325$ N

Weight of the sample of anhydride taken $(W_3) = 1.0105$ gms.

Blank reading (B) = 17.7 mL

Sample reading (S) = 5.5 mL

Volume of aq. HCl consumed for the anhydride $(V_3) = 17.7 - 5.5$ mL
$$= 12.2 \text{ mL}$$

Molecular weight of the anhydride = 148

Purity of the sample or assay of anhydride $= \dfrac{1.1325 \times 12.2 \times 148 \times 100}{2 \times 1000 \times 1.0105}$

$$= 101.1\%$$

The titrations with acetic anhydride, succinic anhydride, phthalic acid and terephthalic acid were done exactly as above except that their molecular weights (for calculation purposes) were taken as shown in Table-1.

ACKNOWLEDGEMENTS

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