

Use of Cumene Hydroperoxide as an End-point Indicator in the Titration of Bases by Catalytic Thermometric Titrimetry*

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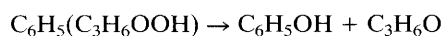
The use of the decomposition reaction of cumene hydroperoxide for indication of the end-point of the titration of organic bases with perchloric acid was investigated. The rise in temperature at the end-point is of the order of 25 °C. Only strong bases can be determined when the titrand solvent is acetic acid - acetic anhydride (92 + 8 v/v), but even weak bases such as caffeine can be determined in 1,2-dichloroethane. Some titration curves resulting from titration of bases with boron trifluoride (a Lewis acid) are presented.

Keywords: Catalytic titrimetry; thermometric titrimetry; cumene hydroperoxide

In catalytic thermometric titrimetry, the excess of titrant catalyses an exothermic reaction and the rise in temperature is employed to locate the end-point of the titration. The substance that undergoes such an indicative reaction is called a thermometric indicator.

Different indicative reactions for the titration of organic bases with acids have been reported, e.g., the reactions between acetic anhydride and water¹⁻⁴ or organic hydroxy compounds,^{2,5,6} the polymerisation of 2-phenylpropene⁷⁻¹⁰ and the polymerisation of 2-methylpropyl vinyl ether.⁸ More recently, Greenhow and Vinas¹¹ carried out a systematic study in which methods based on the reaction of acetic anhydride and hydroxy compounds and on the polymerisation of 2-phenylpropene were compared.

In this paper, the acid-catalysed decomposition of cumene hydroperoxide in accordance with the reaction



is proposed as the indicative reaction for the titration of bases with acids.

Experimental

Reagents

Acetic acid, acetic anhydride, perchloric acid and potassium hydrogen phthalate were of analytical-reagent grade. Amines and potassium benzoate were of laboratory-reagent grade. 1,2-Dichloroethane and 1,4-dioxane were dried with 4A molecular sieves before use.

Cumene hydroperoxide as a solution in cumene was employed as indicator. The nominal titre of the cumene hydroperoxide was 80% and that determined iodimetrically was 82.5%.

A 0.1 M solution of perchloric acid in acetic acid was prepared and standardised with potassium hydrogen phthalate according to Kolthoff *et al.*¹² A 0.1 M boron trifluoride etherate solution was prepared by dissolution of the required amount of the compound in 1,2-dichloroethane.

Apparatus

A motor-driven micrometer syringe as described by Greenhow and Spencer¹⁰ was employed to introduce the titrant at a constant delivery rate. The temperature change was detected by means of a thermistor in one arm of a Wheatstone bridge and recorded on a strip-chart recorder as described else-

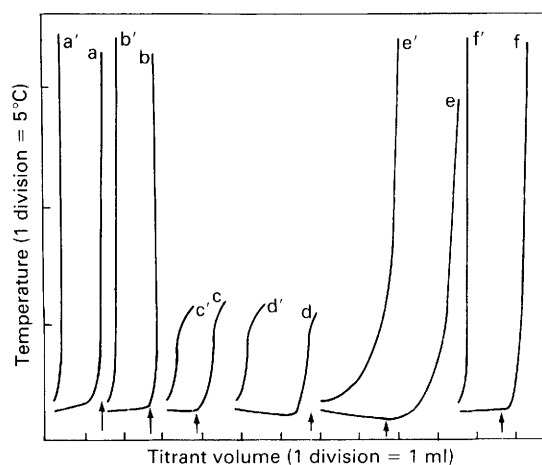


Fig. 1. Catalytic thermometric titration of bases in acetic acid - acetic anhydride (92 + 8 v/v) with perchloric acid in acetic acid. Base, mass of base (mg), volume of acetic acid - acetic anhydride (ml), volume of cumene hydroperoxide 82.5% v/v in cumene (ml), concentration of titrant (M): a, caffeine: 19.64, 10.0, 0.5, 0.1; b, potassium hydrogen phthalate: 29.62, 10.0, 0.5, 0.1; c, caffeine: 15.37, 10.0, 0.1, 0.1; d, potassium hydrogen phthalate: 27.90, 10.0, 0.1, 0.1; e, potassium hydrogen phthalate: 3.09, 10.0, 0.5, 0.01; f, triethylamine: 11.21, 10.0, 0.5, 0.1. a'-f', blanks of a-f. Arrows indicate expected end-points

Table 1. Results for stoichiometries of titration of bases in acetic acid - acetic anhydride and in 1,2-dichloroethane (DCE). Titrant: 0.1 M perchloric acid

Base	No. of moles titrated/No. of moles present	
	Acetic acid - acetic anhydride (RSD, %)*	DCE (RSD, %)*
Potassium hydrogen phthalate ..	1.01 (1.3)	—
..	1.02 (0.7)†	—
Potassium benzoate ..	0.96 (0.7)	1.02 (1.0)
Morpholine	—	0.96 (0.5)
Triethylamine	1.08 (0.9)	1.14 (0.7)
Diethanolamine	0.69 (8.2)	1.06 (1.3)
Caffeine	0.60 (1.2)	1.01 (1.3)
Dimethylformamide ..	0.06 (1.1)	0.37 (0.4)
Dimethyl sulphoxide ..	0.04 (1.4)	0.30 (1.9)

* Relative standard deviation ($n = 3$) in parentheses.

† Titrant 0.01 M perchloric acid.

* Presented at the 3rd International Symposium on Kinetics in Analytical Chemistry, Dubrovnik—Cavtat, Yugoslavia, 25-28 September, 1989.

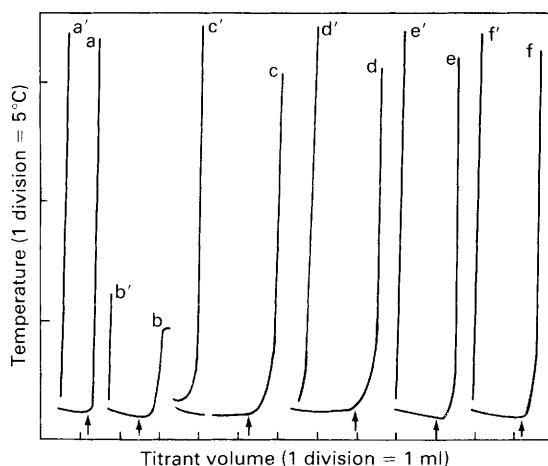


Fig. 2. Titration of bases in 1,2-dichloroethane (DCE) with perchloric acid in acetic acid. Base, mass of base (mg), volume of DCE (ml), volume of cumene hydroperoxide 82.5% v/v in cumene (ml), concentration of titrant (M): a, caffeine: 14.50, 10.0, 0.5, 0.1; b, caffeine: 16.47, 10.0, 0.1, 0.1; c, caffeine: 2.92, 10.0, 0.5, 0.01; d, caffeine: 2.77, 9.5, 1.0, 0.01; e, triethylamine: 11.50, 10.0, 0.5, 0.1; f, potassium benzoate: 18.12, 10.0, 0.5, 0.1. a'–f', blanks of a–f, respectively. Arrows indicate expected end-points

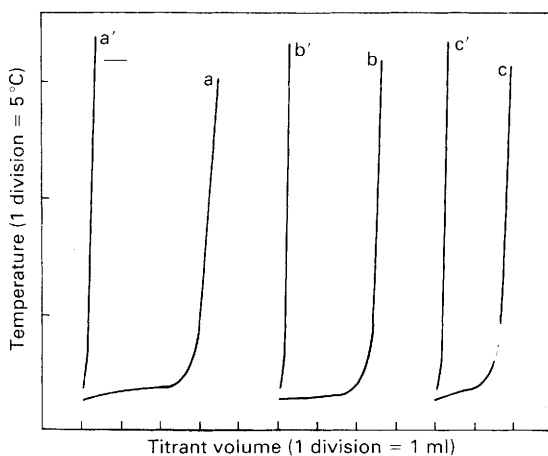


Fig. 3. Titration of bases in 1,2-dichloroethane (DCE) with 0.1 M boron trifluoride etherate in DCE. Base, mass of base (mg), volume of DCE (ml), volume of cumene hydroperoxide 82.5% v/v in cumene (ml): a, morpholine: 16.42, 10.0, 0.5; b, dicyclohexano-18-crown-6: 31.84, 10.0, 0.5; c, caffeine: 12.10, 10.0, 0.5. a'–c', blanks of a–c

where.¹³ The titrations were performed in an unsilvered 25-ml Dewar flask and the solutions were stirred with a magnetic stirrer.

Procedure

After the dissolution of the sample of base in 1,2-dichloroethane or in acetic acid - acetic anhydride in the Dewar flask, the desired amount of indicator is added, then the titrant is added at constant delivery rate of 0.4 ml min⁻¹.

Results and Discussion

In preliminary experiments it was observed that glacial acetic acid cannot be employed as the titrand solvent because the indicative reaction does not occur in this medium. On the other hand, if the base to be titrated is dissolved in acetic anhydride, the decomposition of cumene hydroperoxide occurs before the neutralisation of bases is started. However, either the ineffectiveness of the catalyst in acetic acid or the premature catalytic effect in acetic anhydride can be avoided

by employing a suitable mixture of these two solvents. As is shown in Fig. 1, acetic acid - acetic anhydride (92 + 8 v/v) is suitable for the titration of bases with perchloric acid in acetic acid. It is observed that the rise in temperature and the shape of the titration curves are influenced by the content of cumene hydroperoxide.

The results in Table 1 show that this titrand solvent is adequate for the titration of stronger bases. With weaker bases, substoichiometric amounts of bases tend to be obtained. This may be explained by considering that the hydrogen ion concentration necessary to initiate the decomposition of cumene hydroperoxide is reached before the equivalence point with the weaker bases. In fact, in accordance with Kolthoff and Bruckenstein,¹⁴ the hydrogen ion concentration at the equivalence point of the titration of bases with perchloric acid in acetic acid is inversely proportional to the square root of the dissociation constant of the base.

In Fig. 2 the titration curves corresponding to the titration of some organic bases in 1,2-dichloroethane with perchloric acid in acetic acid are presented. Well shaped titration curves were obtained with 0.1 and 0.01 M perchloric acid. However, when the concentration of the titrant was 0.001 M the titration curves were unsuitable for end-point detection.

It should be noted that in 1,2-dichloroethane, in contrast to acetic acid - acetic anhydride, even weaker bases such as caffeine can be titrated. However, very weak bases such as dimethylformamide and dimethyl sulphoxide are only partially titrated in 1,2-dichloroethane.

Greenhow⁷ employed the results of the stoichiometry of the titration of organic bases for the evaluation of the basicity of the bases. The present results may also be employed for this purpose. For example, in 1,2-dichloroethane it is possible to distinguish between weak bases, such as caffeine, and very weak bases, such as dimethylformamide, where the fractions titrated at the end-point of titration are 1.0 and 0.4, respectively. By comparing the fraction titrated in acetic acid - acetic anhydride it is possible to conclude, for example, that the basicity increases in the order dimethylformamide, caffeine, triethylamine. However, as pointed out by Greenhow and Vinas,¹¹ in the titration of primary and secondary amines acetylation of amines may occur. This explains the substoichiometric amounts found for diethanolamine and morpholine with acetic acid - acetic anhydride.

Some preliminary titration curves from the titration of bases with boron trifluoride etherate in 1,2-dichloroethane are presented in Fig. 3. It was also observed that if the titrand solvent is 1,4-dioxane no catalytic effect is observed, probably owing to the Lewis base properties of this solvent.

It is usual in existing methods of catalytic thermometric titrimetry in non-aqueous solvents for the indicator to be the titrand solvent or a mixture of solvents. However, in the present method, the indicator is present in relatively small amounts (about 4%), which may be of interest when it is desirable that the properties of the main solvent are not significantly affected.

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo for financial support.

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Paper 9/04565A

Received October 24th, 1989

Accepted December 18th, 1989