Determination of Nitro Compounds with Titanium(III)-Polyphosphate Solution. (Application of Polyphosphate to Masking Volumetric Analysis)

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The quantitative reduction of nitro compounds by means of standard titanium(III) chloride solution was proposed by Knecht and Hibbert[1] and applied to many compounds by Duin[2], English[3] and Callen[4]. According to their methods, the sample is dissolved in water or alcohol and excess titanium(III) chloride is added. After the reaction mixture has been boiled, the excess of titanium(III) chloride is titrated with standard iron(III) chloride solution, ammonium thiocyanate being used as indicator. Six equivalents of titanium(III) chloride are required for each nitro group; the nitro nitrogen present in the compound is thereby estimated. On the other hand, new quantitative reduction of sulfate by means of metal-polyphosphate system was reported by S. Suzuki[5]. In the present paper we shall describe the determination of mono-, di-, and tri- nitro compounds by reduction with an excess of standard titanium(III)-polyphosphate solution and back-titration with potassium dichromate, cerium(IV) sulfate, or sodium vanadate solution; indicators which were used are methylene blue, diphenylamine and indigocarmine.

TABLE I

MONONITRO COMPOUND
α-nitronaphthalene
o-nitrophenol
p-nitrotoluene
o-nitroaniline
o-chloronitrobenzene
p-chloronitrobenzene
p-bromonitrobenzene
o-nitrobenzenesulfoamide
4-nitrosalisylic acid
2-nitro-*p*-toluidine
4-nitro-*o*-toluidine
m-nitro-*p*-toluidine
2-acetoamino-4-nitro-toluene
2-nitro-4-acetoamino-toluene

TABLE II

DINITRO COMPOUND
m-dinitrobenzene
2, 4-dinitrotoluene
2, 4-dinitrochlorobenzene
2, 6-dinitro-4-toluidine
di-*o*-nitrophenyldisulfide

TABLE III

TRINITRO COMPOUND
2, 4, 6-trinitrophenol (picric acid)
2, 4, 6-trinitrotoluene

Experimental

Equipment.—A sample of nitro compound is dissolved in water or ethanol in a 200-ml. flask, which is warmed under reflux in a current of carbon dioxide after addition of the standard titanium(III) triphosphate solution.

Material.—Mononitro compounds in Table I, dinitro compounds in Table II, and trinitro compounds in Table III, are used as samples for nitro compounds. These nitro compounds are prepared in the authors' laboratory.

Reagents.—Titanium phosphate solution: 5 g. of metallic titanium is dissolved in 100 ml. of concentrated phosphoric acid (sp. gr. 1.82) by heating at 110—150°C. for about 1 hour. In this case, metallic titanium is gradually added within 10 minutes to the hot phosphoric acid, and stirred carefully not to cause overflow through foaming. This titanium(III) phosphate solution is added to 1 liter of about one tenth normal sodium triphosphate solution. The concentration of tervalent titanium is determined by titration with standard potassium permanganate solution.

Reference Standard Solution. — Potassium dichromate: A tenth normal potassium dichlomate solution is prepared.

Cerium(IV) sulfate: Sixty g. of cerium(IV) sulfate is dissolved in 1 liter of 2 N sulfuric acid, and this solution is used after filtration and standardization.

Sodium vanadate: About one tenth normal solution of sodium vanadate is prepared, and standardized by means of liquid amalgam method.

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[1] E. Knecht and E. Hibbert, *Ber.*, **36**, 1549 (1903); **38**, 3318 (1905); **40**, 3819 (1907).

[2] C. F. van Durin, *Chem. Weekblad*, **16**, 1111 (1919); *Chem. Abst.*, **13**, 3113 (1919).

[3] F. L. English, *Anal. Chem.*, **20**, 745 (1948).

[4] T. Callan et al., *J. Soc. Chem. Ind.*, **39**, 86 (1920); **41**, 157 (1922).

[5] S. Suzuki, This Bulletin, **30**, 766 (1957).

Indicator: 0.1% methylene blue, 0.1% indigo carmine and 0.2% diphenylamine solutions are used as indicators.

Recommended Procedure

Place each sample of accurately measured 0.0300 g. of air dry nitro compounds in a 200-ml. three necksed flask, add 5 ml. of ethanol to dissolve it, and then 25 ml. of a standard titanium polyphosphate solution. Connect a reflux condenser with the flask and a tube into which carbon dioxide has been introduced. Boil the solution well for 5 minutes on a hot plate. Cool the flask in ice water and titrate the solution with a standard oxidizing solution, in a current of carbon dioxide. The indicator is added near the end point, where methylene blue changes color from colorless to blue, indigo carmine also from colorless to blue, while diphenylamine from chocolate violet to pink.

Results and Discussion

Mononitro Compounds: *α-Nitronaphthalene* prepared within 80% yield by means of nitration of naphthalene and recrystallization from ethyl alcohol is estimated with titanium(III) polyphosphate as shown in Table IV. When the sample solution is titrated using methylene blue as indicator, the end point is given a little earlier than the theoretical end point. This is due to the fact that colorless leuco compound of methylene blue produced by reduction of the indicator with titanium (III) salt, is oxidized by standard oxidizing solution before complete oxidation of titanium(III) in solution, which should be oxidized in advance, is achieved. Accordingly it appears as if excess of titanium is consumed by the sample solution and the result shows a higher value. In order to avoid this effect of indicator, iron(II) sulfate is added to the sample solution, in the presence of which methylene blue is not affected till all titanium remaining there has been completely oxidized with the standard solution; then the results show real values as given in the iron(II) sulfate column of Table IV. These facts will also be described hereafter. The result of the estimation of nitronaphthalene by this method is unsatisfactory, the experimental value being 75% of the theoretical one. When indigo carmine is used as indicator, it is oxidized simultaneously with titanium, because of its lower oxidation potential than methylene blue. The end point is determined at the point of decoloration of indigo carmine which is oxidized to colorless leuco compound. In the titration of the solution to which the standard iron(II) sulfate is added, excess of titanium(III) and iron(II) as well as the indicator are all oxidized at the end point. Here lies the difference between methylene blue and indigo carmine. In the presence of triphosphate, in nearly neutral solution, the dichromate ion is changed to the chlomate, whose oxidizing force becomes so weak that it can not oxidize diphenylamine indicator completely; consequently the end point is indistinct. *o-Nitrophenol* is prepared by means of nitration of phenol and separation from *p*-nitrophenol by steam distillation. This nitro compound is determined satisfactorily as shown in Table IV. After nitration of toluene in sulfuric acid medium, *p-nitrotoluene* is separated by means of vacuum distillation and recrystallized from ethyl alcohol; it melts at 56°C. The result of the estimation of *p*-nitrotoluene by the present reduction method corresponds to 72% of nitro group present in the sample. Addition of iron solution to the sample is unsuitable for this compound, except in the case of methylene blue indicator. *o-Nitroaniline* is obtained by nitration of acetanilide in acetic acid anhydride. When methylene blue is used as indicator and iron(II) sulfate is added to the sample solution of *o*-nitroaniline, the titre of cerium(IV) sulfate or sodium vanadate enormously increases, and the estimated value of nitro group correspondingly falls away. A similar fact is also recognized in the determination of 2-nitro-*p*-toluidine described below; it appears as if the resultant diamine compound comes to interfere with the titration. *p-Chloronitrobenzene* is prepared by means of nitration of chlorobenzene in sulfuric acid and recrystallization from ethyl alcohol. The result of determination of this compound is accurate when a sample solution is titrated in the presence of iron(II) sulfate and methylene blue indicator. In the determination of *p-bromonitrobenzene*, diphenylamine shows a pseduo-end point giving rise to a higher result. This compound is prepared by means of nitration of bromobenzene in sulfuric acid, and recrystallization from ethyl alcohol. *o*-Nitrobenzenesulfonylchloride is obtained by oxidation of di-*o*-nitrodiphenylsulfide with chlorine in a mixture of nitric and hydrochloric acid. By means of ammoniation of sulfochloride radical to sulfoamid radical, *o-nitrobenzenesulfoamide* is prepared from *o*-nitrobenzenesulfonylchloride. The determination of this

TABLE IV

DETERMINATION OF MONONITRO COMPOUNDS

Sample	Indicator	Oxidizing agent	Estimated %	
			H_3PO_4—$Na_5P_3O_{10}$	$FeSO_4$ added
α-nitronaphthalene	M. B.	Cr	83.01	74.40
		Ce	86.58	65.01
		V	84.34	77.01
	I. C.	Cr	82.34	88.42
		Ce	83.46	78.42
	D. A.	Cr	94.32	excess
		Ce	85.56	76.34
o-nitrophenol	M. B.	Cr	105.82	103.21
		Ce	107.23	101.34
		V	99.68	99.25
	D. A.	Cr	106.35	102.54
		Ce	106.46	97.34
		V	105.99	98.87
p-nitrotoluene	M. B.	Cr	67.44	71.70
		Ce	84.69	67.31
		V	88.64	72.45
	I. C.	Cr	71.32	excess
		Ce	72.32	72.48
		V	72.85	71.63
	D. A.	Cr	70.11	excess
		Ce	73.93	73.34
		V	83.58	73.34
o-nitroaniline	M. B.	Cr	102.23	99.54
		Ce	103.56	trace
		V	101.36	〃
	D. A.	Cr	101.73	excess
		Ce	100.53	99.32
		V	89.79	97.35
p-chloronitrobenzene	M. B.	Cr	100.96	97.35
		Ce	102.35	99.23
		V	102.52	98.32
	I. C.	Ce	97.38	99.01
	D. A.	Ce	excess	101.56
p-bromonitrobenzene	M. B.	Cr	113.34	105.31
		Ce	111.86	102.33
		V	112.81	104.01
	D. A.	Cr	excess	excess
		V	〃	〃
o-nitrobenzenesulfoamide	M. B.	Cr	109.56	104.61
		Ce	105.15	107.07
		V	excess	105.34
	I. C.	Ce	106.36	105.84
	D. A.	Cr	105.41	excess
4-nitrosalisylic acid	M. B.	Cr	114.16	〃
		Ce	100.21	trace
		V	103.56	〃
	I. C.	Ce	101.43	101.32
	D. A.	Ce	101.02	98.72
2-nitro-*p*-toluidine	M. B.	Ce	93.21	trace
		V	94.62	95.55
	I. C.	Ce	96.30	excess
	D. A.	Cr	excess	〃
		Ce	97.89	95.64
2-acetoamino-4-nitrotoluene	M. B.	Ce	100.85	96.28
		V	102.13	96.51
	I. C.	Ce	113.54	95.86
	D. A.	Ce	96.46	97.37
4-acetoamino-2-nitrotoluene	M. B.	Cr	112.45	98.43
		Ce	108.23	96.58
		V	90.57	96.65
	D. A.	V	90.57	97.78
o-chloronitrobenzene	M. B.	Cr	98.66	trace
		Ce	112.45	〃
		V	98.21	〃
	I. C.	Ce	97.89	97.60
	D. A.	Ce	98.44	97.53
		V	83.05	99.32

TABLE V

DETERMINATION OF DINITRO COMPOUNDS

Sample	Indicator	Oxidizing agent	Estimated %	
			H_3PO_4—$Na_5P_3O_{10}$	$FeSO_4$ added
di-*o*-nitrophenyldisulfide	M. B.	Cr	32.56	28.41
		Ce	54.29	36.78
		V	48.62	30.41
	D. A.	Ce	46.31	trace
2, 4-dinitrochlorobenzene	M. B.	Cr	102.56	100.76
		Ce	114.63	trace
	I. C.	Ce	103.52	102.43
	D. A.	Ce	101.01	102.08
		V	103.73	99.60
2, 6-dinitro-4-toluidine	M. B.	Cr	excess	98.31
		Ce	97.46	96.53
		V	97.34	95.53
	I. C.	Ce	excess	96.58
	D. A.	Ce	98.13	excess
m-dinitrobenzene	M. B.	Cr	115.38	98.73
		Ce	104.59	98.82
		V	101.10	97.30
	D. A.	Cr	104.12	excess
		Ce	98.02	96.13
		V	99.02	98.34
2, 4-dinitrotoluene	M. B.	Cr	101.34	99.47
		Ce	111.22	trace
		V	114.32	〃
	I. C.	Ce	106.35	103.83
		V	99.05	99.43
	D. A.	Ce	100.87	100.51

nitroamide gives a higher result in the similar titration. 4-*Nitro-2-aminobenzoic acid* is diazoated at a low temperature, and hydrolyzed by heating the solution to 4-nitrosalisylic acid; the nitrosalisylic acid is recrystallized from the mixture of equal parts of ethyl alcohol and acetic acid. The determination of this compound, using methylene blue as indicator in the presence of iron(II) sulfate, gives a lower result. *p*-Toluidine is nitrated to 2-*nitro-p-toluidine* in an excess of sulfuric acid. On the other hand, 2-nitro-*p*-toluidine is also prepared through reduction of dinitrotoluene. The titration of the solution using methylene blue and iron(II) sulfate also gives a lower result. 2-Nitro-4-aminotoluene is acetylated to 2-*nitro*-4-*acetoamino-toluene* and 4-nitro-*o*-toluidine to 2-acetoamino-4-nitrotoluene in acetic acid anhydride, and these acetoaminoes are estimated satisfactorily with iron(II) sulfate-titanium(III)-polyphosphate system.

Dinitro Compounds.—*m-Dinitrobenzene* is prepared by nitration of nitrobenzene and determined as shown in Table V. Although English pointed out that the estimation of dinitro compound gave a higher result, no such discrepancy is observed in the present investigation. *p*-Nitrotoluene is oxidized to 2,4-*dinitrotoluene* by nitration in a large amount of sulfuric acid, and it is purified by recrystallization from ethanolic solution. The dinitro compound is determined by the above-mentioned procedure, but methylene blue-iron(II) sulfate system gives lower results for it. 2,4-*Dinitrochlorobenzene* prepared by nitration of *p*-nitrochlorobenzene, is estimated as in Table V and gives a slightly higher value. When treated with ammonium sulfide in an ethanolic solution, trinitrotoluene, TNT, is subject to partial reduction in *p*-nitro position and changes to 2,6-*dinitro*-4-*toluidine*. This amino compound is satisfactorily determined as shown in Table V. When *o*-chloronitrobenzene is boiled with sodium sulfide in an ethanolic solution, it begins to change into *di-o-nitrophenyldisulfide*. The derivatives can not be estimated by means of the metal-polyphosphate reduction systems.

Trinitro Compound.—*Commercial picric acid* can not be determined in this way, because its solution containing titanium (III) polyphosphate is of a greenish brown color, and so it is impossible to observed the end point. *Trinitro toluene*, TNT, prepared through nitration of dinitrotoluene is determined; the obtained values, though in good agreement with one another, are somewhat lower corresponding to only 96% of theory (Table VI).

TABLE VI

DETERMINATION OF TRINITRO COMPOUNDS

Sample	Indicator	Oxidizing agent	Estimated %	
			H_3PO_4—$Na_5P_3O_{10}$	$FeSO_4$ added
picric acid	M. B.	Cr	96.34	86.42
	I. C.	Ce	107.48	102.45
	D. A.	V	101.35	98.54
2,4,6-trinitrotoluene	M. B.	Cr	excess	98.31
		Ce	97.46	96.53
		V	97.34	95.23
	I. C.	Cr	excess	96.58
	D. A.	Cr	98.13	excess
		V	excess	〃

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