SELECTIVE DETERMINATION OF AROMATIC NITROSO COMPOUNDS

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Received February 7th, 1979

A method is suggested for selective determination of aromatic nitroso compounds based on titration with tin dichloride solution in glycerol, the substance to be determined being dissolved in absolute ethanol saturated with dry hydrogen chloride. The titration end point was determined potentiometrically, amperometrically, or visually using phenoxazine type redox indicators.

Nitroso compounds enter a number of colour reactions[1,2], which can be utilized for their identification and determination. They can also be reduced as far as amines by using appropriate reductants. Quantitative reductions were usually carried out indirectly in various media, with retitration of the excess reductant[3–7]. Among suitable reductants is tin dichloride, whose solutions in glycerol can be stored on air for several months without changes in the titre[8,9]. Arribas and coworkers[8–11] suggested the application of this stabilized Sn(II) solution to the determination of some ions in solutions of Na_2CO_3 or in other media. A polarographic method of determination of nitroso compounds in the presence of nitro compounds has been proposed by Gawargious and coworkers[12]. In acidic medium, nitroso compounds can be reduced with ferrous ions in the presence of thiocyanates as far as amines, and the ferric ions created are retitrated[13]. A considerably more convenient method using ferrous ions has been suggested by Katalin and coworkers[14]. Tin dichloride has been applied to the determination of 1-nitroso-2-naphthol in 50% hydrochloric acid[15] according to the scheme

$$\mathrm{R{-}NO + 2\,Sn^{2+} + 4\,H^{+} \rightarrow R.NH_2 + 2\,Sn^{4+} + H_2O}\,. \qquad (A)$$

In the present work, use is made of the good solubility of aromatic nitroso compounds in organic solvents to demonstrate that on titration with glycerol solution of $SnCl_2$ in absolute ethanol saturated with hydrogen chloride, some nitroso compounds are reduced according to the scheme (*A*), often, however, the reaction follows the scheme (*B*):

$$\mathrm{R{-}NO + Sn^{2+} + 2\,H^{+} \rightarrow R\text{-}NHOH + Sn^{4+}}\,. \qquad (B)$$

The reduction in ethanol saturated with HCl was monitored potentiometrically or amperometrically, and the titration end point was also indicated using some phenoxazine type indicators.

EXPERIMENTAL

Solutions and Apparatus

Stock solution of 0·05M-Sn(II) was prepared by dissolving 5·04 g of $SnCl_2 . 2H_2O$ *p.a.* in 375 ml of glycerol *p.a.* and diluting to 500 ml with absolute ethanol. The titre of the solution was checked by using $K_3[Fe(CN)_6]$ standard solution[16].

Solutions of nitroso compounds were prepared by dissolving weighed amounts of the substances always in 100 ml of absolute ethanol saturated with dry hydrogen chloride. The following concentrations were used: 0·005M 1-nitroso-2-naphthol *p.a.* (Lachema), 2-nitroso-1-naphthol *p.a.* (Lachema), 4-nitrosophenol, 4-nitrosoresorcinol, and 2,4-dinitroresorcinol; 0·0025M 4-nitroso-N,N-dimethylaniline *p.a.* (Lachema), 3-methyl-4-nitrosophenol *p.a.* (Lachema), 2-nitroso-1-naphthol-4-sulphonic acid *p.a.* (Lachema), 1-nitroso-2-naphthol-3-carboxylic acid, and uracil (Farmakon). Solutions of nitro compounds for examination of the interfering effects were prepared by dissolving the substances in 100 ml of the solvent so that 0·5M 2-nitro-1-naphthol (Lachema) and 2-nitro-3,4-dimethylaniline (Lachema) solutions emerged. The indicators were dissolved in absolute ethanol so that 0·25% 2-amino-3-phenoxazone, 0·5% 4-methyl-7-amino-3-phenoxazone, and 0·5% gallocyanine solutions were obtained. All chemicals were recrystallized and the purity of the substances studied was checked by elemental analysis (C, H, N).

A pH-meter MV 87 (Präcitronic, Dresden, GDR) with platinum indicating electrode and saturated calomel reference electrode was employed for the potentiometric titrations. The titrant was added by means of a microburette with 0·01 ml divisions. The same microburette was used for the amperometric titrations, carried out by employing a universal building-block system of operational amplifiers[17,18].

In the potentiostatic system for amperometric titrations in the non-aqueous medium Pt foil electrodes as indicating and subsidiary electrodes were used. The same S.C.E. was used as a reference electrode.

Determination Procedure

10 ml of the nitroso compound of interest in absolute ethanol saturated with hydrogen chloride was placed in a titration flask and after stirring, titrated with glycerol solution of tin dichloride until the potential jump; the solution was stirred after each titrant addition. The results of determination along with the indicator colour changes are given in Table I. The formal oxidation-reduction potentials were then read graphically from the titration curves (Table II). In the case of 2-nitroso-1-naphthol-4-sulphonic acid, the titrations were conducted at 50—60°C in argon atmosphere; the same conditions were applied to the determination of 4-nitroso-1-naphthol-2-carboxylic acid, where quantitative results were only obtained in the presence of 50 mg of zinc acetate.

The polarization curves of the substance examined were measured in conditions used for the subsequent amperometric determination, employing the device shown in Fig. 1. The polarizing voltage was applied to the electrodes in 15 mV steps by means of the voltage divider from the potentiometer AO-76. The corresponding current values were recorded after conversion to voltage, the polarization curve was plotted from the points, and the voltage to be used for the amperometric titrations was read off.

The amperometric titration of 10 ml of the nitroso compound solution in ethanol was carried out by using the same device. As can be seen from Fig. 1, the arrangement is different from a conventional one in that a potentiostat is employed to maintain the desired potential of the

indicating electrode. This was necessary, because otherwise the potential of the indicating electrode would change during the titration owing to the IR voltage drop in the low-conducting solution. The course of the amperometric determination was in accordance with that of the potentiometric titration. The determinations of 4-nitrosophenol and 4-nitrosoresorcinol were performed in nitrogen inert atmosphere.

When direct volumetric determination was performed using visual indicators, one drop of the indicator solution was added to the solution titrated and the latter was stirred vigorously during the titration to the colour change. The results are also given in Table I.

RESULTS AND DISCUSSION

The solutions of the model aromatic nitroso compounds in absolute ethanol saturated with HCl were reduced with solution of glycerol complex of Sn(II) (ref.[19]) in ethanol–glycerol mixture. The course of the reduction was monitored potentiometrically and amperometrically, and in some cases the reaction end point was visualized by using oxazine type indicators. The formal oxidation–reduction potentials of the substances were read from the potentiometric curves and used to find the number of the exchanged electrons according to the relation

$$n_B = n_A(E_A^{o,f} - E)/(E - E_B^{o,f}), \qquad (1)$$

where n_A and n_B are the numbers of exchanged electrons of the titrating agent and of the substance titrated, respectively, E is the (graphically determined) potential of the equivalence point, and $E_A^{o,f}$ and $E_B^{o,f}$ are the formal potentials of the titrating agent and of the substance titrated, respectively.

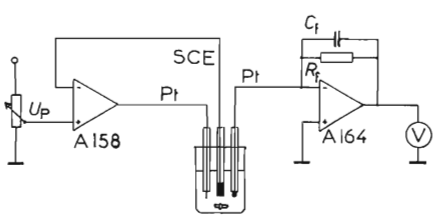

FIG. 1

Potentiometer AO-76 as Source of Polarizing Voltage U_p, Operational Amplifier AI-58 as Potentiostat, Operational Amplifier AI-64 as Current-Voltage Converter, $f_F = 10\ k\Omega$, $C_f = 4\ \mu F$

TABLE I

Volumetric Determination of Some Aromatic Nitroso Compounds in Absolute Ethanol Saturated with Dry Hydrogen Chloride by Titration with Glycerol Solution of Tin Dichloride

Substance prepared mg	End point indication[a]	Found[b] mg	s_r %	Colour change
1-Nitroso-2-naphthol	Pot	8·666	0·047	
8·659	Amp, 240 mV	8·657	0·017	
	Gall	8·670	0·006	violet — colourless
	MAP	8·590	0·364	red-brown — colourless
	AP	8·693	0·686	red — yellow
2-Nitroso-1-naphthol	Pot	8·684	1·135	
8·659	Amp, 660 mV	8·644	0·663	
	Gall	8·623	0·747	blue-violet — yellowish
	MAP	8·658	0·354	red-brown — colourless
	AP	8·594	0·055	red — yellow
4-Nitroso-N,N-dimethyl-aniline	Pot	3·761	0·659	
3·755	Amp, 150 mV	3·742	0·485	
	Gall	3·755	0·031	blue-violet — colourless
	MAP	3·754	0·188	red-brown — light yellow
	AP	3·756	0·047	red-brown — light yellow
3-Methyl-4-nitrosophenol	Pot	3·400	0·990	
3·428	Amp, 420 mV	3·404	2·430	
	Gall	3·432	0·361	violet — colourless
	MAP	3·424	0·293	red-brown — colourless
	AP	3·427	0·137	red — yellow
2-Nitroso-1-naphthol-4-sulphonic acid	Pot[c]	6·321	0·860	
6·331	Amp, 630 mV	6·346	0·879	
	Gall	6·323	0·317	violet — light yellow
	MAP	6·332	0·196	red-orange — yellow
	AP	6·333	0·027	red — light yellow
1-Nitroso-2-naphthol-3-carboxylic acid	Pot[c,d]	5·173	3·130	
5·129	Amp, 600 mV	5·087	2·149	
4-Nitrosophenol	Amp, 840 mV	6·107	2·419	
6·155				
4-Nitrosoresorcinol	Amp, 620 mV	6·915	2·632	
6·955				

TABLE I
(*Continued*)

Substance prepared mg	End point indication[a]	Found[b] mg	s_r %	Colour change
2,4-Dinitrosoresorcinol 8·404	Amp, 540 mV	8·383	1·346	
Nitrosouracil 3·527	Amp, 630 mV	3·519	0·706	
	Gall	3·525	0·100	violet — colourless
	MAP	3·531	0·066	red-brown — yellow
	AP	3·529	0·050	red — colourless

[a] Pot — potentiometric, Amp — amperometric, the polarization voltage (mV) is given for the amperometric method; indicators: Gall — gallocyanine, MAP — 4-methyl-7-amino-3-phenoxazone, AP — 2-amino-3-phenoxazone; [b] average from three determinations; [c] at 50—60°C; [d] zinc acetate added.

The results are given in Table II. Obviously, the reductions proceed largely according to the scheme (*B*) by two-electron exchange to hydroxylamine derivatives, in the case of 4-nitroso-N,N-dimethylaniline, 3-methyl-4-nitrosophenol, and uracil according to the scheme (*A*) by four-electron exchange as far as the corresponding amines.

Owing to the presence of a sufficient quantity of ethoxonium ions, the solutions were acidic enough for the hydrolysis of Sn(II) to be prevented, and the polarity of

TABLE II
Formal Oxidation-Reduction Potentials ($E^{0,f}$), Potential Change in the Equivalence Point per 0·1 ml Volume (ΔE), and Number of Exchanged Electrons (n)

Substance	$E^{0,f}_A$ mV	$E^{0,f}_B$ mV	ΔE mV	n_B calc.
1-Nitroso-2-naphthol	80	355	210	1·79
2-Nitroso-1-naphthol	39	401	213	1·85
4-Nitroso-N,N-dimethylaniline	101	404	303	3·88
3-Methyl-4-nitrosophenol	60	505	354	3·91
2-Nitroso-1-naphthol-4-sulphonic acid	14	273	145	2·04
1-Nitroso-2-naphthol-3-carboxylic acid	26	244	137	2·07

the medium made possible solute–solvent interaction. The results of the potentiometric and amperometric titrations as well as those obtained by using indicators are given in Table I.

Exceptional was the behaviour of 3-methyl-4-nitrosophenol in that it dissolved very slowly in the HCl-saturated ethanol; only after 2 days' standing of the solution the reduction proceeded sufficiently quickly and quantitatively. The reduction of 2-nitroso-1-naphthol-4-sulphonic acid and 1-nitroso-2-naphthol-3-carboxylic acid proceeded reluctantly at normal temperature, only at 50–60°C it was fast enough and afforded satisfactory results. In the case of the latter substance, it is advisable to add a small amount of zinc acetate to the solution titrated, in order to obtain more precise results.

Amperometric titration proved to be more suitable for stannometric determination of nitroso compounds in the nonaqueous solvent, with regard to the better establishing of potentials. The method proposed is suited to determination of organic substances possessing the $\geqslant C—N=O$ grouping. Substances involving the $—N—N=O$ grouping cannot be determined stannometrically in the solvent used; the polarization curves could not be obtained either. The $—O—N=O$ and $\geqslant C=N—OH$ groups behaved likewise; it can be thus inferred that the reduction of nitroso substances, possessing the $—C—N=O$ grouping, with glycerol complex of Sn(II) in ethanolic solution saturated with hydrogen chloride is selective. The effect of nitro compounds, which themselves are not reduced in this medium, on the reduction of nitroso compounds was also investigated. The results indicate that nitro compounds do not affect the determination if present in ratio 1 : 1, in a higher excess (up to 100-fold) they raise the results slightly. The relative error of determination never exceeded $\pm 3\%$ in the analyses performed. Aldehydes, ketones, and other reducible substances did not affect the course of the reduction either; the determination of aromatic nitroso compounds in absolute ethanol saturated with dry hydrogen chloride with solution of Sn(II) in glycerol can be thus considered to be selective. Very rapid is the determination using some oxidation-reduction indicators of the phenoxazine type, whose oxidation–reduction properties have been studied[20–24].

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Translated by P. Adámek.