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Studies on Sulfinic Acids

II *. Titrimetric Determination of Aromatic Sulfinic Acids and Sodium Sulfinates

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In connection with a kinetic work on aromatic sodium sulfinates [1], analytical methods were required for controlling the purity of sulfinates as well as a specific method for determination of sulfinate in aqueous solutions containing oxidizable material. For this purpose titrimetric methods were investigated and tested.

This paper deals, from the general analytical point of view, with the oxidimetric titration of sulfinates by potassium permanganate and the potentiometric titration of the sulfinic acid group with nitrous acid. These methods are compared and correlated by various standards; and an automatic potentiometric method for titration with nitrous acid has been elaborated. It is also shown that sodium sulfinates can be titrated with perchloric acid in glacial acetic acid medium.

In many works the sulfinic acids are characterized only by their melting points. As a criterion of purity this is very unsatisfactory, since the melting points are not well defined. As, on heating, sulfinic acids decompose by disproportionation, the observed melting points are not real melting points, but rather, decomposition points [2] which depend on how the decomposition reaction proceeds:

$$3\ RSO_2H \longrightarrow RSO_2SR + RSO_3H + H_2O$$

Elementary analysis alone is not of much value, since a mixture of disproportionation products can have the same elementary composition as the original substance. In the case of the aromatic sulfinic acids or sulfinates, a slight partial oxidation does not affect the elementary analysis in any considerable degree, except for oxygen, because of the relatively high molecular weight compared with the atomic weight of oxygen.

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Therefore as a criterion of purity, some form of specific functional group analysis is desirable. For titrimetry several oxidimetric methods have been used. Ramberg [3] determined ethyl sulfinic acid with potassium bromate in hydrochloric acid medium, but found that induced oxidation with air oxygen occurred. The same was the case when potassium permanganate in acid solution was used. The effect of autoxidation can be avoided if titration is made in a slightly alkaline or neutral solution; and, in this way, Allen [4] titrated salts of aliphatic sulfinic acid with permanganate. Krishna and Das [5] determined 19 aromatic sulfinic acids by a gas volumetric method, using potassium iodide-potassium iodate in the presence of hydrogen peroxide, but this method is too complicated and sensitive to impurities to be of practical value. Ackerman [6] used sodium hypochlorite for titration of sodium benzene sulfinate, but a disadvantage is the instability of the hypochlorite solution.

Of the oxidimetric methods, the potassium permanganate method proved to be the best and was adopted in this work. Oxidation with free bromine and iodine was also tried, but proved to be unreliable, owing to side reactions resulting in the formation of sulfonyl halogenide or disulfone [4,7,8]. Nor were attempts to use ceric sulfate in sulfuric acid successful, since the mole ratio ceric sulfate/sulfinate was not an integer. Gringras and Sjöstedt, however, have shown that it is possible to obtain the ratio 1.5 under certain conditions [9].

The oxidimetric method suffers from the same disadvantage as elementary analysis. Disproportionation does not alter the total of redox equivalents. For solutions containing other oxidizable material oxidimetric methods are useless. Consequently, a more specific method was needed. The only one that could be found is based on the reaction between sulfinic acid and nitrous acid:

$$2\ RSO_2H + HNO_2 \longrightarrow (RSO_2)_2NOH + H_2O$$

In a few cases this method has previously been used for the determination of benzenesulfinic acid [10,11] and *p*-toluenesulfinic acid [10–12]. Marvel *et al.*[13,14], who applied it for the titration of dodecane sulfinic acid, demonstrated a tendency to the formation of $(RSO_2)_3NO$ as a side reaction.

When the oxidimetric and the potentiometric nitrous acid titrations are compared for the same sodium sulfinates, the nitrous acid titration gives an equivalent weight which is 1—2 % too high. The reproducibility of the nitrous acid titrations is, however, as good as that of the permanganate titration. If the nitrite solution used for the nitrous acid titration is standardized against a pure sample of the sulfinate which is to be determined, then this titration can be employed for determining, with ordinary analytical accuracy, the sulfinate concentration in other solutions, provided the titrations are performed under conditions comparable with those of the standardization.

Tables 1 and 2 show the oxidimetric and nitrous acid titrations. For comparison, sulfinates were used that crystallized well, and could therefore be easily purified by repeated recrystallization. They were chosen from a series of sulfinates, the preparation of which was described in an earlier paper [15]. The sodium sulfinates crystallize with two molecules of crystal water or with crystal alcohol. They lose crystal solvent in the air and must be carefully dried at an elevated temperature under vacuum, before titration. The titrations were performed on samples purified and dried in different ways, and

Table 1. Oxidimetric titration of aromatic sulfinates.

Sodium sulfinate or sulfinic acid	Sample origin and treatment		Method	Sample wt mg	Equiv. wt	
					Found	Mean
p-$CH_3CONHC_6H_4SO_2H$	Recrystallized from water		Bromate	28.4	198.8	
			»	46.96	198.7	198.8
M = 199.2			NaOH	229.8	198.4	
p-$CH_3C_6H_4SO_2Na$	Synthetized by reduction with Zn	Recrystallized once	$KMnO_4$Diff.	47.9	178.3	
			» Pot	47.9	178.9	
			» Diff.	38.8	178.0	
			» Pot.	38.8	179.5	178 8
M = 178.2			Bromate	38.2	178.6	
			»	46.1	178.9	
		Recrystallized twice	$KMnO_4$Diff.	49.0	179.0	
$C_6H_5SO_2Na$	Acidified after 1 min.		$KMnO_4$Diff.	77.6	164.2	
	» » 10 »		» »	90.5	163.5	
	Recrystallized	Dried 2 h at 100°	» »	90.8	164.0	164.3
M = 164.1		Additional drying 1 h 140°	» »	93.4	164.8	
			» »	87.1	165.2	
o-$ClC_4H_4SO_2H$	Recrystallized once from chloroform		$KMnO_4$Diff.	90.0	178.2	
			» Pot.	90.0	179.5	
			NaOH	90.0	176.2	
M = 176.6			$KMnO_4$Diff.	103.6	177.9	
			» Pot.	103.6	179.4	
			NaOH	103.6	176.9	
	Recrystallized twice from chloroform		$KMnO_4$Diff.	101.2	177.4	
			» Pot.	101.2	177.0	177.0
			NaOH	101.2	176.7	
o-$ClC_6H_4SO_2Na$			$KMnO_4$Diff.	103.2	199.5	
			» »	102.2	198.4	199.0
M = 198.6			» »	100.2	199.0	
p-$ClC_6H_4SO_2Na$	Recryst. thrice	Dried 3 h at 80° and 1 h at 140°	$KMnO_4$Diff.	85.7	198.2	
			» »	87.6	199.4	198.6
M = 198.6		Dried 1 h at 100°	» »	118.9	198.2	
m-$NO_2C_6H_4SO_2Na$	Recryst. once from ethanol-water		$KMnO_4$Diff.	146.5	210.3	
			» »	99.4	210.2	
			» Pot.	99.4	210.0	210.1
M = 209.1	Recryst. twice from ethanol-water		» Diff.	107.1	210.0	
	Recryst. thrice from ethanol-water		» Pot.	144.8	210.2	

Sulfinate	Sample origin and treatment		Sample wt mg	Nitrite conc. N	Equiv. wt Found	Equiv. wt Mean	Correction E_{HNO_2}/E_{KMnO_4}
p-$CH_3C_6H_4SO_2Na$ M = 178.2	Synth. by Zn reduction	Recrystallized once	114.0	0.1009	180.6	180.5	1.010
			338.4	0.1009	179.7		
		Recrystallized twice	557.2	0.0992	180.3		
			551.2	0.0992	181.2		
	Synth. by Na_2SO_3 reduction	Recrystallized once	116.0	0.1004	181.0		
		Recryst. twice	116.5	0.1004	179.9		
		Recryst. twice, Additional drying 2 h	133.9	0.1004	180.7		
		Recryst. 4 times	114.6	0.1004	180.3		
		Recryst. 4 times, Oxygen-free titration	120.8	0.1004	180.9		
		Recryst. 4 times	124.8	0.1004	181.1		
		Recryst. 4 times, Extracted with benzene [a]	138.2	0.1004	180.5		
		Recryst. from DMSO [b]	146.4	0.1004	181.7		
$(p\text{-}CH_3C_6H_4SO_2)_2Ba$	M/2 = 223.9. Recryst. from ethanol		304.8	0.0992	[226.2]		
$C_6H_5SO_2Na$ M = 164.1	Dried 1 hour 80°		216.8	0.1000	166.1	167.1	1.016
			98.4	0.05040	167.6		
	Recrystal. Dried 2 h 100°		102.2	0.05040	167.6		
p-$ClC_6H_4SO_2Na$ M = 198.6	Recryst. twice	Dried 1 h 80°	103.9	0.05040	201.1	201.4	1.014
		Additional drying 1 h 100°	98.6	0.05040	200.7		
	Recryst. thrice	Dried 2 h 80°	99.4	0.05040	201.1		
		Dried 1 h 80° + 1 h 140°	101.9	0.05040	201.2		
		Treated with benzene [c]	99.5	0.05040	202.0		
		Titration in glac.acet. acid [d]	101.6	0.05040	201.6		
		Automatic diff. titr.	102.1	0.0514	201.3		
			104.3	0.0514	201.5		
			103.3	0.0514	201.5		
			149.9	0.0514	201.2		
			202.8	0.0514	201.0		
			746.4	0.0514	200.4		
		Under nitrogen	102.1	0.0514	202.4		
		Air dry M = 234.6	103.6	0.05040	[237.1]		
	Purified *via* Ag salt [e]		101.2	0.05040	201.8		
			93.8	0.05040	201.9		

a To remove any neutral disproportionation products. *b* Followed by recrystallization from ethanol. *c* Benzene was distilled from the sulfinate to remove water azeotropically. *d* The acetic acid was destilled from sulfinate. *e* Precipitated as silver salt. Decomposed with sodium bromide and recrystallized.

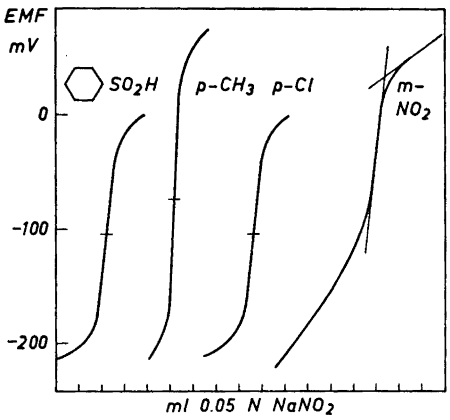

Fig. 1. Potentiometric titration of sulfinic acids with nitrous acid.

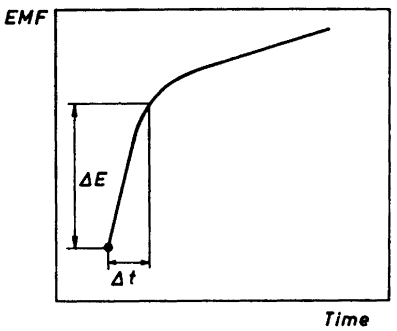

Fig. 2. Electrode response by addition of an increment of titrant near the equivalence point.

with different solutions that were independently prepared and standardized. Repeated purification or crystallization and different conditions for drying the salts do not alter the difference between the two methods, and from the tables it is clear that a significant discrepancy exists between the results. Evidently, the permanganate titration gives the correct result.

Permanganate titration. Since oxidation in an acid medium gives side reactions, the potassium permanganate titration was performed in a neutral medium by adding an excess of permanganate solution large enough to permit of the sulfinate being completely oxidized by the manganese dioxide step. The determination was completed by acidification, addition of potassium iodide and back titration with thiosulfate in the usual manner, with dead stop point indication (designated as $KMnO_4$ Diff. in the tables). As a check, the titration was performed also by direct potentiometric titration with a platinum indicator electrode (designated as $KMnO_4$ Pot. in the tables). With this method the indication was less sharp, but it gave essentially the same result.

Nitrous acid titration. The nitrous acid titration was performed at room temperature with sodium nitrite; sulfuric acid medium was employed for liberating the nitrous acid. Potassium bromide was used as a catalyst. Typical titration curves, which were obtained with a platinum indicator electrode, are shown in Fig. 1. Their slope is dependent on the speed of titration, as the electrode response is not instantaneous, Fig. 2.

During titration the sulfonyl hydroxylamine is precipitated in the aqueous medium. Precipitation can be avoided by using glacial acetic acid medium, but this does not alter the shape of the curves. Elevation of temperature is reported to have a good effect on the titration curve by diazotization [16], but cannot be applied because of the instability of the sulfinic acid and the sulfonyl hydroxylamine. The use of oxygen-free water and titration in nitrogen atmosphere did not improve the results.

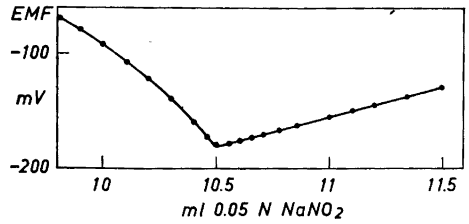

Fig. 3. Titration of *p*-chlorobenzenesulfinic acid with polarized Pt-electrodes.

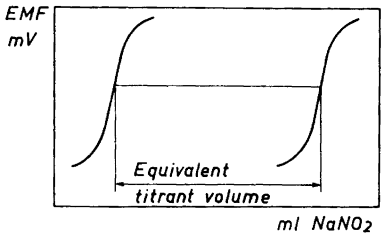

Fig. 4. Automatic differential titration.

The slope of the curves introduces an uncertainty in the determination of the equivalence point, since *a priori* it is not certain that it coincides with the inflection point. When using potentiometric indication by diazotization, Müller and Dachselt obtained the equivalence point as a break at the end of the potential jump [17]. For *m*-nitrobenzenesulfinate an equivalence point is obtained which is consistent with the permanganate value, if the intersection of the lines shown in Fig. 1 is taken as the equivalence point.

The potentiometric indication was therefore checked by some other methods. Iodide-starch paper did not give a sharp enough indication to be useful. Spot test indication by diazotization and coupling according to Feigl [18] was sharper and gave the same result as the potentiometric titration. Potentiometric indication, with identical, polarized platinum electrodes according to Lingane [19], gave a better result, but was very inconvenient as the electrode response was extremely slow. Fig. 3 shows an example with this method.

As the shape of the titration curves is dependent on the speed of titration it was necessary to reproduce the titrations in exactly the same way. For this purpose an automatic titration device was used that allowed of a very slow titration in the neighbourbood of the equivalence point. The uncertainty in the indication is easily eliminated by running a titration curve for an arbitrary amount of sulfinate and, after adding the sample, continuing the titration, which now automatically repeats the curve in exactly the same manner. The distance between the curves represents the nitrite equivalent used, and is independent of the equivalence potential, Fig. 4. This method, here referred to as automatic differential titration, gave the same result as the manual titration performed in the conventional manner, and was used for routine work. Because of the controlled speed of titration a high degree of precision is obtained.

The results of the different indication methods are shown in Table 3. They prove that the discrepancy between oxidimetric and nitrous acid titration cannot be due to the method of indication. It must therefore be due either to decomposition of the sulfinic acid in the acid medium or to a side reaction.

As is seen from Table 4, the acid concentration has an influence on the result of the nitrous acid titration. Hydrochloric acid in larger concentrations, in which case potassium bromide was excluded, yielded very poor results with *p*-chlorobenzenesulfinate; and during titration a smell of sulfonyl chloride

Table 3. Influence of indication method on nitrous acid titration of p-$ClC_6H_4SO_2Na$.

Indication method	Sample wt mg	Nitrite conc. N	Equiv. wt.
Spot test	101.5	0.05040	201.6
Polarized electrodes	101.0	0.05040	199.8
	102.0	0.05040	200.8
	87.8	0.05040	200.2
	104.8	0.05040	200.1
Manual potentiometric	99.8	0.05040	201.7
	101.7	0.05040	201.6
Manual differential	104.9	0.05040	202.2
	103.9	0.05040	201.5
Automatic differential	105.6	0.0519	202.2
	105.3	0.0519	201.5
	101.9	0.0519	202.0

developed. This points to decomposition of the sulfinic acid. As halide ions catalyze the decomposition of sulfinic acids by disproportionation in the absence of oxygen [20–22] as well as the autoxidation by oxygen [23,24], whereas the salts are stable, the increase of hydrochloric acid concentration should have a greater effect than increase of the sulfuric acid concentration. Both increase the sulfinic acid concentration by depressing dissociation, whereas in the case of hydrochloric acid, the catalyst concentration is simultaneously increased.

A small influence of sample size could be detected, when the sample size was increased in order to diminish the importance of indication errors. The influence of sample size over a larger range is shown in Table 5. The deviation from the theoretical value increases with smaller samples. A possible explanation for this effect may be the side reaction described by Marvel *et al.*[14], which is probably influenced by the ratio sulfinic acid-nitrous acid concentration. It may also be attributed, however, to oxygen disturbance. If, during a titration a certain amount of oxygen is available in the system, a relatively larger proportion of the sample may be oxidized if the sample is small.

Table 4. Influence of acid concentration on nitrous acid titration of p-$ClC_6H_4SO_2Na$. 0.0514 N $NaNO_2$. Automatic differential titration.

Acid	Conc. N	Sample wt. mg	Equiv. wt.
HCl	7	102.4	233.0
»	4	102.4	211.8
»	2	104.2	208.8
H_2SO_4	5	101.2	205.2
»	1	Mean from Tab. 2	201.4

Table 5. Influence of sample size on nitrous acid titration of p-$ClC_6H_4SO_2Na$ in 1 N H_2SO_4 by automatic differential titration.

Sample wt. mg	746	202	100	76	52
Deviation from $E_{Calc.}$	1.8	2.4	2.8	7.4	14.1
Per cent error	0.9	1.2	1.4	3.8	7.1

With the present material, it is not possible to decide on the cause of the discrepancy without further investigation. The exclusion of oxygen, by titration with degassed water under a nitrogen stream passed over the surface in the open titration vessel, did not eliminate the discrepancy, but the measures taken may not have been sufficiently efficient.

As the comparison with the oxidimetric titration made it possible to calculate reliable correction factors for the discrepancy (true normality of $NaNO_2$ solution $\times$ E_{NaNO_2}/E_{KMnO_4} = corrected normality for nitrous acid titration), further investigation was not regarded as necessary for the present purpose. The complications described require that the titration of sulfinic acids with nitrous acid according to the present method is carried out under carefully controlled conditions with sample sizes not too small and not differing too much from each other.

Examination of the nitrous acid titration of the series of sulfinates, from which the members used for this investigation were chosen[15], reveals that the reactivity by the nitrous acid titratio nis parallel with the nucleophilicity[1] of the sulfinates. The *ortho*-substituted members, which show a hindering *ortho*-effect, reacted too slowly; and some hardly reacted at all. Some *meta*-substituted members did not react satisfactorily.

Perchloric acid titration. Sodium sulfinates may also be determined by titration with perchloric acid in acetic acid medium according to Fritz[25]. Table 1 in Ref.[15] shows the results obtained with potentiometric indication. The equivalent weight obtained by titration of the salt agrees well with the result from permanganate titration and is readily reproducible. In a mixture with the corresponding sulfonates, only the sulfinates are titrated. With perchloric acid in dioxane, however, the sulfonate could also be distinguished on the automatically recorded titration curve, but not with sufficient accuracy for determination, when the solvent was either methyl isobutyl ketone, or acetic anhydride; the methyl isobutyl ketone and the anhydride, respectively, being mixed with a small amount of methanol, which is necessary to obtain a reasonable solubility of the salts.

EXPERIMENTAL

All samples were dried in a drying pistol for at least 1 hour at 60—80° under vacuum in the presence of phosphorus pentoxide.

Bromine titration. The sample was dissolved in 20 ml glacial acetic acid. To this were added 25 ml 1 N KBr, 50 ml 1 N HCl and 25 ml 0.05 N $KBrO_3$. After 15 min 1 g KI

was added and the liberated iodine titrated with 0.1 N sodium thiosulfate with dead stop point indication.

Permanganate titration. If the sample was sulfinic acid, it was neutralized. When direct potentiometric titration with a Pt indicator electrode was used, excess of the 0.1 N (= 0.02 M) potassium permanganate solution was added and, as a check, back titration with thiosulfate was made after acidifying with 10 ml 5 N H_2SO_4 and adding 1 g KI. The total sample volume was usually about 50 ml. When the excess method alone was used, a 5—10 min interval was allowed to elapse before acidification, and care was taken that the acidified solution was titrated immediately.

Nitrous acid titration. The sample was dissolved in 20 ml of water. If the sample is in the form of acid, neutralization facilitates dissolution. Then 10 ml of 5 N H_2SO_4 and 1 g of KBr were added. The volume was made up to 50 ml and titrated with 0.1 or 0.05 N sodium nitrite with the buret point under the surface. Potentiometric indication with a Pt indicator electrode was used. The titration curve was drawn in the neighbourhood of the equivalence point by adding small portions of titrant and waiting, during equal intervals, for the potential increase to approach a practically acceptable degree of steadiness before reading the potential. The electrode response to an addition of titrant has the form shown in Fig. 2. Platinum black or gold electrodes did not improve the result.

Automatic differential titration. On an automatic precision infusion apparatus [26], with a wide range speed gear, the syringe operating axis was provided with a toothed wheel with 100 teeth operating a micro-switch connected to an electric counter. In this way an electric micrometer syringe was obtained. The same axis was mechanically connected to a recorder, which was fed from the indicator circuit potentiometer. A Pt wire in the titrant stream was used as a reference electrode. The speed range was determined within which direct titration gave results independent of speed; and the differential titration was always made within this speed range. In the neighbourhood of the equivalence point the speed was diminished to a value corresponding to the sum of Δt's in Fig. 2, required for the manual recording of the titration curve. The nitrite titrant was standardized directly to the readings of the counter operating at the same speed as that which was used for titration. 100 counts corresponded to about 1 ml. The reference curve of the difference titration was recorded with a small sample in a volume of 50 ml. This volume was added to the sample to be analyzed, which had been dissolved in a few millilitres of water, and titration was then continued. The volume difference between the curves was obtained by the automatic operation of the counter at preselected potentials by the indication potentiometer unit. This unit was a commercial type of automatic titrator, Radiometer, type TTT 1.

Perchloric acid titration. Titration was performed in glacial acetic acid with 0.05 N perchloric acid in acetic acid medium standardized against potassium biphthalate. The solvent was controlled for blank. Indication was made with a Pt indicator electrode and an asbestos plugged saturated calomel electrode as reference. The *p*-methoxybenzenesulfinate could not be titrated in acetic acid, but gave better results in mixtures of acetone-methanol or methyl isobutyl ketone-methanol, with perchloric acid in dioxane.

Standardization. The permanganate solution was standardized with sodium oxalate in the conventional manner. The sodium nitrite was standardized with ceric sulfate in 2 N sulfuric acid of 50° according to Furman [27] by potentiometric titration with a Pt indicator electrode. The ceric sulfate was standardized with sodium oxalate by potentiometric titration in 2 N sulfuric acid at 90° with a Pt indicator electrode. The nitrite standardization was also checked against permanganate according to Kolthoff and Sandell [28], and against sulfanilic acid according to Scholten and Stone [29].

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