

The Dissociation Constant of 5-Methoxy-2-nitrosophenol in Aqueous Solution and Its Partition Coefficient between Chloroform and Water. A Spectrophotometric Study

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The value $10^{-6.39}$ was obtained spectrophotometrically for the acid dissociation constant, $K_a = [H^+][A^-]/[HA]$, of 5-methoxy-2-nitrosophenol (*o*-nitrosoresorcinol monomethyl ether) in an aqueous solution of ionic strength 0.1 (potassium chloride as neutral salt) at 25°C. The dependence of the dissociation constant on ionic strength was studied and the thermodynamic value at 25°C was found by extrapolation to be $10^{-6.59}$.

The value 26 was obtained for the partition coefficient, $K_d = [HA_{CHCl_3}]/[HA_{H_2O}]$, of the distribution of the acid between chloroform and water at ionic strength 0.1.

The absorption spectra of 5-methoxy-2-nitrosophenol in aqueous and chloroform solutions are presented.

5-Methoxy-2-nitrosophenol (*o*-nitrosoresorcinol monomethyl ether) has been shown by Torii to be a suitable reagent for several metal ions.¹ Peach has reported results of a similar study of 3-methoxy-5-nitrosophenol² prepared from *m*-methoxyphenol by nitrosation.³ The correct structure of the latter reagent, which forms metal chelates, is apparently the structural form of 5-methoxy-2-nitrosophenol where the nitroso and hydroxyl groups are in *ortho* positions.⁴

The *o*-nitrosophenol grouping which forms strong chelates with certain metal ions, particularly cobalt(II), palladium(II), and iron(II) ions, is similar to the chelating groupings in the better known analytical reagents, the *o*-nitrosonaphthols and their water-soluble sulpho derivatives. Nitroso-R acid (1-nitroso-2-naphthol-3,6-disulphonic acid or 1,2-naphthaquinone-1-oxime-3,6-disulphonic acid), for instance, is widely used as a reagent in the analysis of several metal ions. This compound is used in the form of its disodium salt, which is called "Nitroso-R Salt". The author has previously studied the forma-

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tion of metal chelates of Nitroso-R acid ⁵ and 2-nitroso-1-naphthol-4-sulphonic acid (also called 1,2-naphthaquinone-2-oxime-4-sulphonic acid) in aqueous solutions.⁶

5-Methoxy-2-nitrosophenol is more soluble in water than the nitroso-naphthols. It is also soluble in organic solvents. The acid dissociation of the compound and its distribution between chloroform and water were spectrophotometrically studied in this work in order to be able to investigate the formation of metal chelates of the compound in aqueous solution and the extraction of these chelates from water for analytical purposes.

EXPERIMENTAL

Reagents. 5-Methoxy-2-nitrosophenol (a commercial reagent from Eastman Organic Chemicals) was purified by recrystallization from water.

Chloroform („zur Analyse”, from E. Merck AG.) was saturated with water before its use in the experiments.

Potassium dihydrogen phosphate-sodium hydroxide buffer solutions and potassium chloride were used to adjust the pH values and the ionic strengths of the aqueous solutions.

Apparatus. The spectrophotometric measurements were carried out with a Beckman Model DU spectrophotometer using calibrated 10 mm quartz cells.

A Radiometer 4c potentiometer connected to a Beckman glass electrode (type 41262) and an open liquid junction reference calomel electrode containing saturated potassium chloride solution was used to measure the pH values. The hydrogen ion concentrations were calculated by means of apparent activity coefficient values.⁷ The experiments were carried out at 25°C.

Methods. The dissociation constant of 5-methoxy-2-nitrosophenol

$$K_a = [H^+][A^-]/[HA] \quad (1)$$

was determined by the customary spectrophotometric method in which the absorbances of several solutions whose pH values were close to the apparent isoelectric point are measured. The wavelength ranges 280–310 and 330–370 m μ were found suitable for solutions in which the concentration of 5-methoxy-2-nitrosophenol varied from 2.5×10^{-5} to 5.0×10^{-5} M.

The partition coefficient of 5-methoxy-2-nitrosophenol between water and chloroform

$$K_d = [HA_{CHCl_3}]/[HA_{H_2O}] \quad (2)$$

was determined by measuring the concentrations of 5-methoxy-2-nitrosophenol (A^-) in several aqueous phases when about 50 % of the reagent was present in the organic phase. Equal volumes of both solvents and a molar concentration of 4.5×10^{-5} of 5-methoxy-2-nitrosophenol were used. Absorbances in the range from 340 to 355 m μ (near to the absorption peak at 348 m μ) and in the range from 390 to 410 m μ (the shoulder region of the peak) were measured.

RESULTS AND DISCUSSION

The spectra of 5-methoxy-2-nitrosophenol in aqueous solutions are shown in Figs. 1 and 2. Data illustrating the determination of the dissociation constant from absorbances in two wavelength regions separated from each other by a relative sharp isosbestic point at 320 m μ are given in Table 1.

The determined values of the acid dissociation constant at different ionic strengths are listed in Table 2. These data can be represented by the Debye-Hückel equation

$$6.59 = pK + 1.018\sqrt{I}/(1 + 0.99\sqrt{I}) - 0.41I \quad (3)$$

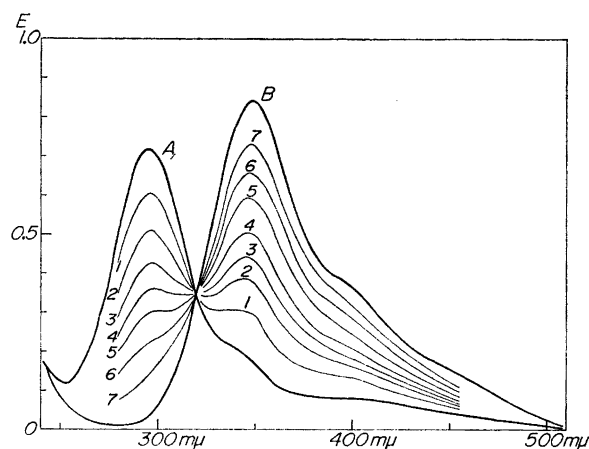


Fig. 1. Absorption spectra of 5-methoxy-2-nitrosophenol ($c=5.0 \times 10^{-5}$ mole/l) in aqueous solutions of different hydrogen ion concentration. Curves: A, in 0.01 M HCl; B, in 0.01 M NaOH; 1, $-\log[\text{H}^+]=5.85$; 2, 6.18; 3, 6.39; 4, 6.56; 5, 6.77; 6, 6.98; 7, 7.34. Solutions 1–7 were buffered; $c_{\text{buff}}=10^{-3}$, $\sqrt{I}=0.085$.

Table 1. Evaluation of the dissociation constant of 5-methoxy-2-nitrosophenol in aqueous solution from absorbances measured at different wavelengths (25°C).

$c = 5.0 \times 10^{-5}$, $I = 0.0042$

$m\mu$			E at $-\log[\text{H}^+]$ values					pK_a
	HL	L^-	6.18	6.39	6.56	6.77	6.98	
285	0.611	0.009	0.421	0.347	0.288	0.221	0.172	6.52
290	0.683	0.018	0.474	0.394	0.329	0.272	0.197	6.53
295	0.715	0.034	0.502	0.420	0.357	0.295	0.218	6.53
300	0.698	0.061	0.497	0.418	0.359	0.303	0.233	6.53
305	0.631	0.104	0.466	0.397	0.350	0.303	0.247	6.53
$pK_a =$			6.52	6.50	6.50	6.55	6.56	

$c = 2.5 \times 10^{-5}$, $I = 0.0017$

$m\mu$			E at $-\log[\text{H}^+]$ values					pK_a
	HL	L^-	6.18	6.40	6.57	6.78	7.00	
335	0.109	0.345	0.183	0.201	0.226	0.260	0.281	6.56
340	0.099	0.386	0.191	0.215	0.243	0.284	0.310	6.54
345	0.089	0.413	0.194	0.222	0.252	0.297	0.325	6.54
350	0.080	0.419	0.187	0.216	0.249	0.294	0.326	6.55
355	0.068	0.399	0.169	0.197	0.230	0.275	0.307	6.57
$pK_a =$			6.52	6.57	6.57	6.54	6.57	

Table 2. pK_a -values of 5-methoxy-2-nitrosophenol in aqueous solution of different ionic strengths (KCl as neutral salt).

\sqrt{I}	$c \times 10^6$, mole/l	Wavelength range, $m\mu$	pK_a	pK_a°
0.041	2.5	335–355	6.553	6.592
0.065	5.0	285–305	6.526	
0.179	2.5	285–305	6.464	
0.179	2.5	335–355	6.447	
0.316	5.0	285–305	6.385	
0.316	5.0	335–355	6.372	
0.522	5.0	285–305	6.359	
0.522	5.0	335–355	6.350	
0.745	5.0	285–305	6.398	
0.745	5.0	335–355	6.383	
			6.456	
			6.379	
			6.355	
			6.391	

The parameter values in this equation were evaluated from the collected data.

The dependence of the acid dissociation constant of 5-methoxy-2-nitrosophenol on ionic strength, which was adjusted with potassium chloride, is shown in Fig. 3.

5-Methoxy-2-nitrosophenol is a much stronger acid than phenol and it is also a stronger acid than the nitrosophenols.⁸ The interpolated value 6.39 for pK_a of this acid represents the equilibrium constant in aqueous solution at ionic strength 0.1.

Table 3 shows values of the partition coefficient of 5-methoxy-2-nitrosophenol between chloroform and water. When the ionic strength of the aqueous phase is 0.1, the value of $\log K$ is 1.42. The values of $\log K$ at ionic strengths

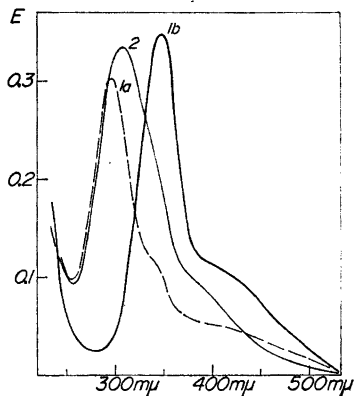


Fig. 2. Absorption spectra. 1a, 5-methoxy-2-nitrosophenol ($c=2.1 \times 10^{-5}$ M) in acid aqueous solution; 1b, in alkaline aqueous solution ($c=2.1 \times 10^{-5}$ M); 2, in chloroform ($c=3.2 \times 10^{-5}$ M) at 25°C.

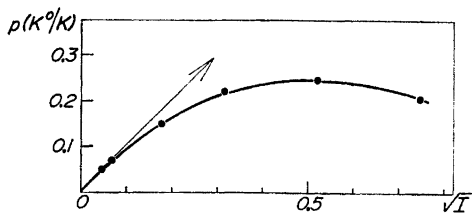


Fig. 3. $p(K^\circ/K)$ as a function of the ionic strength of the aqueous solution (adjusted with potassium chloride).

Table 3. Spectrophotometric data for the determination of the partition coefficient of 5-methoxy-2-nitrosophenol between chloroform and water. $c=4.5 \times 10^{-5}$ mole/l, $I=0.100$, 25°C .

$-\log[\text{H}^+]$	E at		$\log K_d$ at $350 \text{ m}\mu$	$\log K_d$ at $400 \text{ m}\mu$
	$350 \text{ m}\mu$	$400 \text{ m}\mu$		
9.92	0.756	0.357		
8.46	0.612	0.288	1.44	1.44
8.13	0.506	0.240	1.43	1.43
7.89	0.411	0.198	1.42	1.40
7.69	0.327	0.160	1.41	1.39
7.48	0.239	0.118	1.43	1.40
7.25	0.159	0.080	1.43	1.40
			1.43	1.41

0.090 and 0.782 are 1.48 and 1.45, respectively; the aqueous phases in these experiments were buffered, but the same amount of the reagent was used. These values are slightly higher than the value at ionic strength 0.1 (aqueous phase). The latter value of the partition coefficient of 5-methoxy-2-nitrosophenol between chloroform and water is, however, lower than the values reported for other *o*-nitrosophenols, such as the nitrosonaphthols,⁸ which have been employed as metal extraction reagents.

Spectral characteristics of 5-methoxy-2-nitrosophenol are given in Table 4. The peaks in the absorption spectra of acid and alkaline solutions in water at 295 and 348 $\text{m}\mu$, respectively, are typical for the *o*-nitroso grouping. However, the peaks are located at lower wavelengths in these absorption spectra, than in the spectra of nitrosonaphthols and nitrosonaphtholsulphonates.⁵ The occurrence of the shoulder at about 400 $\text{m}\mu$ in the spectrum of the anionic form of 5-methoxy-2-nitrosophenol is somewhat strange; this shoulder, like the peak at 348 $\text{m}\mu$, is, however, regularly observed in the spectrum of the dissociated form of the compound.

5-Methoxy-2-nitrosophenol is similar in its properties to *o*-nitrosophenol and *o*-nitrosocresol which form metal chelates of similar type and stability and which have been used as analytical reagents for metal ions.^{9,10}

Table 4. Characteristics of the absorption spectra of 5-methoxy-2-nitrosophenol in chloroform and water (25°C).

Solvent	λ_{max} $\text{m}\mu$	$\epsilon \times 10^{-4}$
CHCl_3 ; (HL)	310	1.04
H_2O ; (HL)	295	1.44
(L ⁻)	348	1.65
isobestic points	242	
	320	

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