Studies on the Extraction of Metal Complexes

XX. The Dissociation Constants and Partition Coefficients of 1-Nitroso-2-naphthol and 2-Nitroso-1-naphthol

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Dissociation constants, partition coefficients, solubilities and absorption spectra have been determined at 25° C for 1-nitroso-2-naphthol and 2-nitroso-1-naphthol. The two compounds have quite different properties, which are discussed. An explanation of these differences is given with reference to the infrared spectra, and to the electron distribution in naphthalene.

In our studies of the extraction of metal ions with organic reagents we have found it important to know the acid dissociation constants and partition coefficients of the organic reagents. As these constants are fundamental properties of the compounds themselves we consider it advisable to present these values separately and not together with the metal extraction data. The present work gives the measurements on 1-nitroso-2-naphthol and 2-nitroso-1-naphthol.

EXPERIMENTAL

Commercially available analytical reagents (B. D. H. and Merck) were recrystallized from alcohol (1-nitroso-2-naphthol) and from chloroform (2-nitroso-1-naphthol). All experiments were carried out at 25° C and in a medium of 0.1 M ionic strength. All chloroform used was alcohol-free and saturated with water. The hexone (methyl *iso*butyl ketone) was shaken with a sodium bicarbonate solution to remove acidic or basic impurities.

The potentiometric titrations on 1-nitroso-2-naphthol were carried out as previously described [1,2] using 0.01 M NaOH + 0.09 M NaClO$_4$ for the titration of 0.50 ml of 0.0991 M HClO$_4$ + 100 ml of 2×10^{-4} M 1-nitroso-2-naphthol in 0.1 M NaClO$_4$. The equivalent points were obtained by Gran's method of plotting $\dfrac{\Delta V/\Delta E}{V}$ against the volume of alkali added [3].

The spectrophotometric measurements of the dissociation constants were made in a thermostated room using a Beckman Model DU spectrophotometer with 1 cm cells. The solutions were made up of 9 ml $1-2 \times 10^{-4}$ M nitrosonaphthol in 0.1 M NaClO$_4$ + 1 ml of 0.1 M sodium acetate-, phosphate-, borate-perchlorate buffers. The hydrogen ion concentration, -log[H$^+$] of the solutions were determined with a 0.01 M HClO$_4$ + 0.09 M NaClO$_4$ buffer.
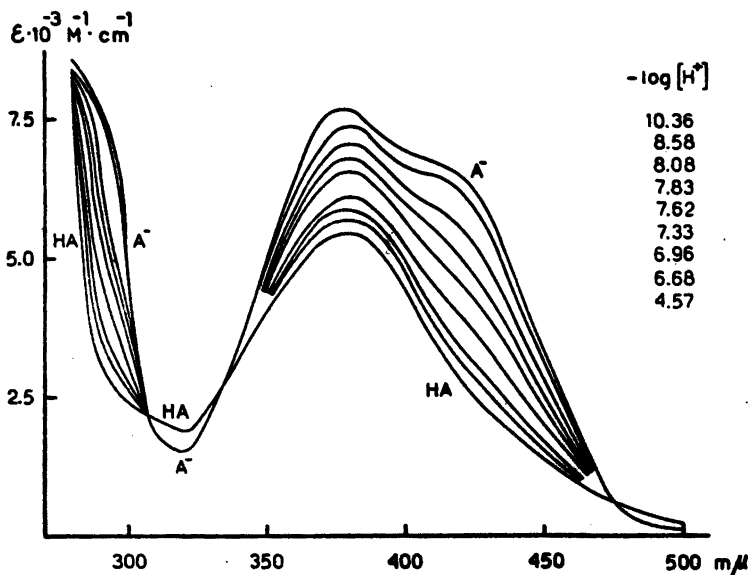
Fig. 1. Variation of the absorption spectra of 1-nitroso-2-naphthol in 0.1 M NaClO₄ with acidity.

The partition coefficients for a 0.1000 M solution of 1-nitroso-2-naphthol in chloroform or hexone and a 0.0500 M solution of 2-nitroso-1-naphthol were determined by shaking 10 ml of the organic phase with 9 ml of 0.1 M NaClO₄ + 1 ml of a 0.1 M sodium acetate-perchlorate buffer. The concentration of reagent in the aqueous phase was determined spectrophotometrically.

CALCULATION OF THE DISSOCIATION CONSTANTS FROM THE SPECTRO-PHOTOMETRIC DATA

Both 1-nitroso-2-naphthol and 2-nitroso-1-naphthol showed measurable shifts in their spectra in the pH range of 5—10 as may be seen in Figs. 1 and 2. These shifts are due to the dissociation of the nitrosonaphthols and to the fact that the acidic and basic forms have different absorption spectra. At some wavelengths the molar absorptivities of the two forms are the same, *i. e.* the two extinction curves intersect. These points of intersection are called isobestic points and are useful for the indication of solvent effects (*e. g.* a shift in the extinction curve of acidic form when the ionic medium is changed). By keeping the ionic medium constant at 0.1 M with mainly NaClO₄ we obtained very sharp isobestic points (Figs. 1 and 2).

In the case of the nitrosonaphthols we could determine both the absorption of the acidic from A_0 at pH<5 and the absorption of the basic form A_- at pH>10. For a constant total concentration of the nitrosonaphthol the dissociation constant k_a was then obtained from the following equation:

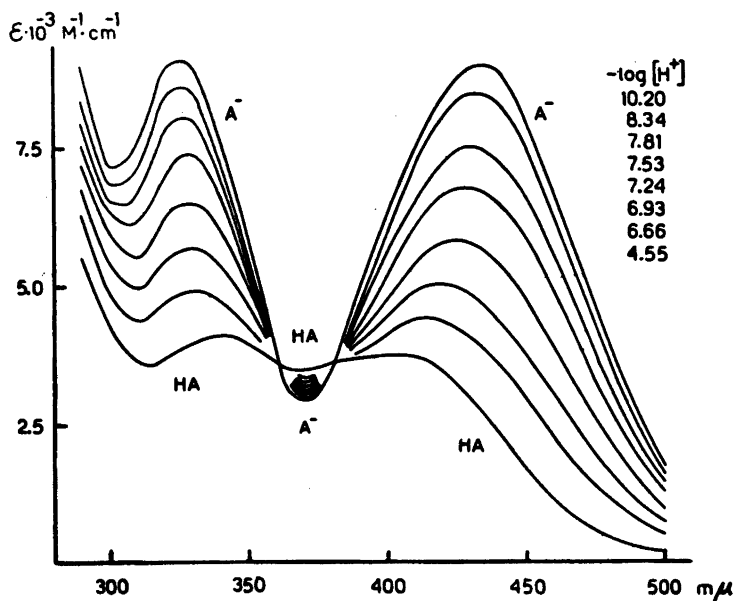$$k_a = [\text{H}^+] \cdot \frac{(A - A_0)}{(A_- - A)}.$$

Fig. 2. Variation of the absorption spectra of 2-nitroso-1-naphthol in 0.1 M NaClO₄ with acidity.

Data for several wavelengths (Tables 1 and 2) were used for the calculation of log $(A—A_o)/(A_-—A)$. These values were then plotted against $— \log[H^+]$. The best line with a slope equal to 1 gave pk_a at log $(A—A_o)/(A_-—A) = 0$.

The following values were obtained for the dissociation constants in 0.1 M NaClO₄:

Table 1. Spectrophotometric determination of pk_a for 1-nitroso-2-naphthol in 0.1 M NaClO₄. The absorption A of 10^{-4} M solutions at different values of $— \log [H^+]$ for wavelengths used in the calculation of pk_a.

λ mμ	$— \log [H^+]$										
	1.80	3.03	4.57	6.68	6.96	7.33	7.62	7.83	8.08	8.58	10.46
290	0.322	0.322	0.317	0.363	0.400	0.470	0.567	0.612	0.667	0.767	0.778
370	0.531	0.534	0.528	0.556	0.573	0.584	0.628	0.651	0.673	0.701	0.751
380	0.550	0.548	0.545	0.567	0.584	0.612	0.656	0.678	0.706	0.739	0.767
390	0.528	0.534	0.520	0.548	0.567	0.584	0.628	0.651	0.678	0.706	0.728
400	0.446	0.445	0.448	0.478	0.500	0.528	0.573	0.600	0.628	0.667	0.695
410	0.355	0.353	0.356	0.384	0.409	0.456	0.512	0.556	0.595	0.651	0.678
420	0.281	0.281	0.279	0.317	0.341	0.400	0.461	0.503	0.556	0.617	0.651
430	0.224	0.225	0.224	0.259	0.284	0.339	0.400	0.442	0.489	0.550	0.584
440	0.176	0.178	0.183	0.203	0.222	0.270	0.316	0.348	0.384	0.431	0.459
450	0.136	0.137	0.140	0.156	0.168	0.203	0.235	0.257	0.284	0.316	0.338

Table 2. Spectrophotometric determination of pk_a *for 2-nitroso-1-naphthol in 0.1 M NaClO$_4$. The absorption* A *of* 10^{-4} M *solutions at different values of* $-\log [H^+]$ *for wavelengths used in the calculation of* pk_a.

λ mμ	$-\log [H^+]$									
	2.01	3.02	4.55	6.66	6.93	7.24	7.53	7.81	8.34	10.20
310	0.361	0.367	0.367	0.442	0.500	0.556	0.617	0.662	0.706	0.751
320	0.370	0.370	0.367	0.473	0.545	0.623	0.695	0.778	0.840	0.890
330	0.389	0.394	0.395	0.495	0.573	0.651	0.739	0.801	0.851	0.901
340	0.403	0.408	0.411	0.481	0.539	0.606	0.667	0.701	0.723	0.762
410	0.374	0.374	0.375	0.442	0.495	0.545	0.612	0.662	0.723	0.751
420	0.344	0.346	0.346	0.436	0.503	0.584	0.667	0.723	0.806	0.845
430	0.297	0.296	0.299	0.409	0.489	0.578	0.678	0.751	0.845	0.890
440	0.235	0.234	0.235	0.359	0.442	0.545	0.651	0.723	0.834	0.890
450	0.171	0.170	0.170	0.295	0.378	0.475	0.589	0.662	0.751	0.795
460	0.112	0.111	0.113	0.228	0.303	0.394	0.492	0.556	0.634	0.667
470	0.071	0.070	0.072	0.167	0.232	0.305	0.388	0.442	0.500	0.537
480	0.044	0.045	0.046	0.118	0.164	0.222	0.280	0.322	0.363	0.392
490	0.028	0.028	0.029	0.083	0.112	0.151	0.195	0.223	0.251	0.270

1-nitroso-2-naphthol: $pk_a = 7.63 \pm 0.02$ ($pK_a = 7.77$ *)
2-nitroso-1-naphthol: $pk_a = 7.24 \pm 0.02$ ($pK_a = 7.38$ *)

A potentiometric determination for 1-nitroso-2-naphthol gave $pk_a = 7.59 \pm$ 0.02 in close agreement of the spectrophotometric value.

The dissociation constants have previously been determined by Trübsbach[5] at 25°C by conductometric measurements of dilute solutions. He obtained $K_a = 26 \times 10^{-9}$ ($pK_a = 7.59$) for both 1-nitroso-2-naphthol and 2-nitroso-1-naphthol. A result given by Wenger, Monnier and Jaccard[6] seems to be based on an erronous interpretation of a potentiometric titration.

DISCUSSION

It is quite clear from the data collected in Table 3 and from Fig. 3 that 1-nitroso-2-naphthol and 2-nitroso-1-naphthol have quite different properties.

The question arises whether these differences can be explained by a tautomeric equilibrium:

(A)   (B)

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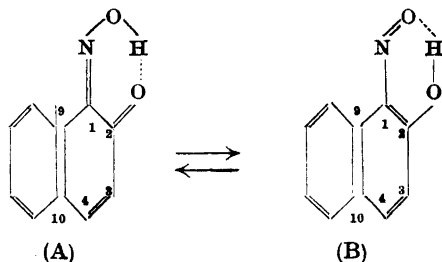
* Thermodynamic values. The activity coefficients were taken from Conway[4], p. 102—3.
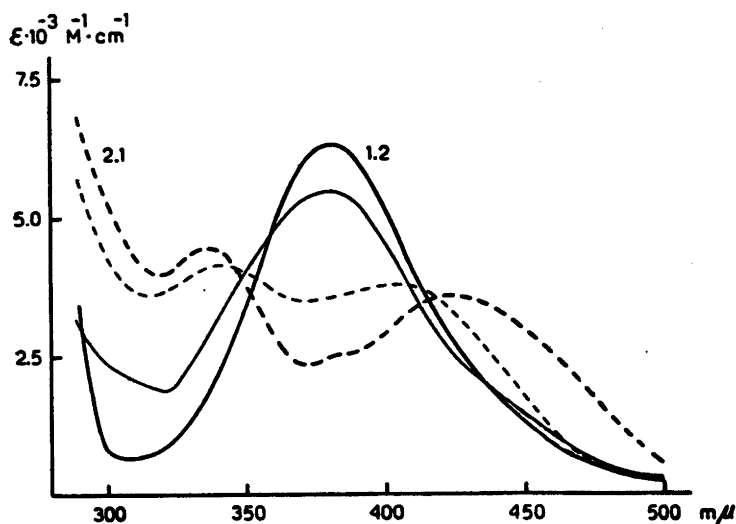
Fig. 3. Absorption spectra of the nitrosonaphthols in chloroform (thick lines) and in water (thin lines). The full curves represent 1-nitroso-2-naphthol; the dashed curves 2-nitroso-1-naphthol.

the two nitrosonaphthols having different equilibrium constants. However, evidence has been given by Sluiter [7], as well as by French and Perkins [8] and by Baltazzi [9] that the quinonoid modification (A) predominates. Infrared studies in our laboratory [10] showed that a strong intramolecular hydrogen bond is present in 1-nitroso-2-naphthol (Fig. 4). The strength of this bond is comparable with the one in acetylacetone [11], and stronger than the one in oxine and 2-nitrophenol (Fig. 4) or tropolone [11]. Furthermore the infrared spectrum showed the presence of a broad carbonyl band at 1 625 cm^{-1}. This carbonyl band is also observed in β-diketones and tropolone (cf. Bellamy [11], p. 123, 130). The infrared data therefore support the view that the quinonoid form (A) predominates, the length of the OH-bond being 1.10 Å. The distance from the hydrogen atom to the quinone oxygen can be estimated at 1.5 Å, which is much less than the sum of the van der Waals radii (2.6 Å).

The hydrogen bridging and chelate ring stabilisation is also supported by the fact that, according to Trübsbach [5], 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are not much stronger but weaker acids than 4-nitroso-1-naphthol ($pK_a = 6.59$). The same order of acidity has been found for 2-nitro-1-naphthol and 4-nitro-1-naphthol [12]. Against this Havinga and Schors [13] have reported $pK = 8.01 \pm 0.04$ ($pK_a = 8.05$) for 4-nitroso-1-naphthol.

It is now clear from experimental data of Abrahams, Robertson and White [14] as well as from π-electron calculations of Jaffé [15] and of Klement [16] that in naphthalene the carbon atoms in positions 9 and 10 have an inductive effect which of course acts more strongly on the 1-positions than on the 2-positions. Thus the electron densities at the carbon atoms in naphthalene decrease in the order $C_9 > C_1 > C_2$.
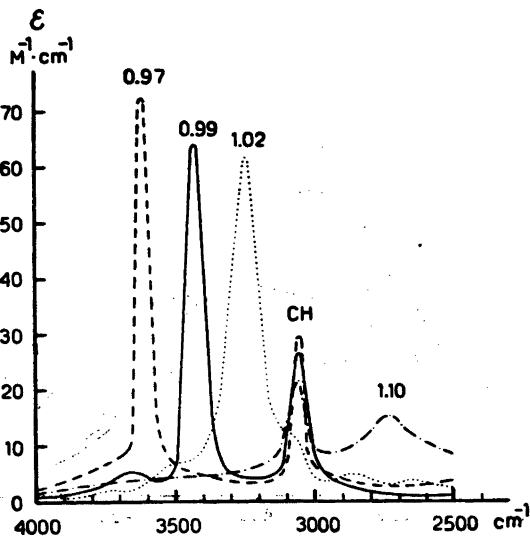
Fig. 4. Infrared absorption spectra of 1-naphthol — — — —, 8-quinolinol (oxine) ————, 2-nitrophenol . . . . . ., and 1-nitroso-2-naphthol — · — · — · — in CCl₄ at 25 °C. The OH peaks correspond to different lengths of the OH bonds (in Å).

It is also clear that the bond between the 1 and 2 carbons has a higher electron density than other bonds; this would favor the contribution of structure (A') to a mesomeric state, or the tautomeric form (B).

(A)   (A')
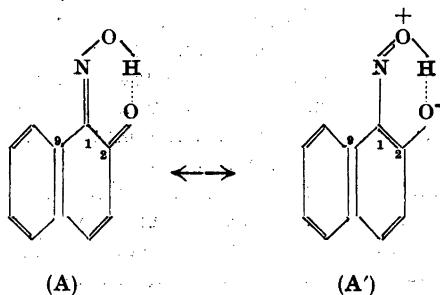
The difference in acidities of the two nitrosonaphthols may be explained by a higher inductive effect acting on the quinonoid oxygen in position 1 thus weakening the hydrogen bond and giving a stronger acid. Thus 2-nitroso-1-naphthol would be expected to be a stronger acid than 1-nitroso-2-naphthol, and this in fact is the case. Lauer [17] has shown that 1-naphthol (pk_a = 9.85) is a stronger acid than 2-naphthol (pk_a = 9.93), however, the colorimetric method with phenolphthalein used for the determination of the dissociation constants is not very accurate. In fact Kieffer and Rumpf [18] have recently obtained pK_a = 9.23 for 1-naphthol and 9.46 for 2-naphthol at 25° C.

Table 3. Properties of the nitrosonaphthols.

Property	1-nitroso-2-naphthol	2-nitroso-1-naphthol
Dissociation constant pk_a in 0.1 M NaClO$_4$	7.63 ± 0.02	7.24 ± 0.02
Partition coefficient log k_d between chloroform and water ($I = 0.1\ M$)	2.97	2.11
Partition coefficient log k_d between hexone and water ($I = 0.1\ M$)	2.55	2.23
Solubility in chloroform (aq) in moles per liter	1.35$_2$	0.096$_4$
Solubility in hexone (aq) in moles per liter	0.416	0.133
Solubility in water (pH $= 4.6$, $I = 0.1\ M$)	1.06×10^{-3}	0.84×10^{-3}
Melting point °C.	112	160

Schenkel [19] has given an explanation of Lauer's results based on earlier conceptions of the electron distribution in naphthalene. However, the electron distribution is now known to be somewhat different.

Besides the spectra and dissociation constants the solubilities show a striking difference, 1-nitroso-2-naphthol being much more soluble in chloroform. In hexone, which contains an oxygen atom, the difference is not so large and in water the difference is still less. From these facts it might be concluded that the chelate ring is not so well stabilized in 2-nitroso-1-naphthol, and since this ring stabilisation lowers the acidity, 1-nitroso-2-naphthol should be a weaker acid. It therefore seems as if the inductive effect mentioned above has an effect on the resonance in the chelate ring. Infrared measurements [10] on 2-nitroso-1-naphthol were difficult because of its low solubility in CCl$_4$. A somewhat weaker hydrogen bond and a weaker carbonyl band were however discernable. The melting points and partition coefficients also support the conclusion that the chelate ring is more stable in 1-nitroso-2-naphthol.

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