STRUCTURE AND SPECTRA OF DIAZOTIZED 0-AMINONAPHTHOLS AND THEIR ISOMERIC MONOSULFONIC DERIVATIVES

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The structure and behavior of o-naphthoquinonediazides and their monosulfonic acids in media of different acidity were studied by means of UV and IR spectra. In neutral, weakly acid and weakly alkaline solutions the diazo compounds of 1, 2- and 2, 1- aminonaphthols and their sulfonic acids exist in equilibrium as the diazonium and quinonediazide forms. The sulfonic acids, and also their metal salts, possess an ionic structure; the sulfonyl chlorides of the quinonediazides are not ionized.

It was shown that of the two extreme equilibrium forms of the diazo compounds the quinone diazide was the more photosensitive. The nature of the phototransformation products of 2, 1-naphthoquinonediazide depends to a considerable degree on the medium which causes a shift into one or the other of the diazo forms.

The diazo compounds of o-aminonaphthols and their sulfonic acid derivatives are widely used in the production of permanent azo dyes and as photosensitive compounds. For the latter the condensation products of the sulfonyl chlorides of such diazo compounds with various polyhydroxy and polyamino compounds are of great importance. The specificity of such diazo compounds consists of, in contrast to other aromatic diazo compounds, the conditions of their formation, their significant stability, and their ability to transform into the so-called naphthoquinonediazides.

Only recently has attention been paid to the origination of the properties of such diazo compounds in the quinonediazide and diazonium forms [1-6]. For the p- and oaminophenols, for example, it was shown that transformation of the diazonium cation into the quinonediazide can can be considered as ionic dissociation of a weak acid [1].

In the IR spectrum of 1-diazo-2-hydroxy-4-sulfonic acid, isolated from acidic or neutral aqueous solution, an absorption band at 2220 [3] or at 2229 cm⁻¹ [7] was detected, characteristic for the diazonium group (a). In the spectrum of the potassium salt of the diazo compound isolated from alkaline solution two intense absorption bands at 2089 and 2109 cm⁻¹ [7] or one band at 2110 cm⁻¹ characteristic for the quinonediazide form (b) were detected:



We studied the IR and UV spectra of diazotized 1,2and 2,1-aminonaphthol and their isomeric monosulfonic acid derivatives, and the conditions of transformation from the diazonium form to the quinonediazide form in solutions of differing pH. It was of interest to examine the state of the diazotized 1-amino-2-naphthol in relation to the position in the latter of the sulfur containing group, and to its nature (free acid, salt or sulfonyl chloride).

The Isomeric o-Aminonaphtols. The IR spectra of the isomeric naphthoquinonediazides obtained by alkaline potassium ferricyanide oxidation of the diazotized α - and β -naphthylamines[8], determined as a suspension in hexachlorobutadiene, in paraffin oil and in KBr tablets were identical. They possessed a strong band at 2104 cm^{-1} and a medium intense band at 2136 cm^{-1} . These frequencies almost coincide with the assigned vibrations for the =N=N bond given in the literature [1,3,9]. In addition the spectrum of 2,1naphthoquinone-1-diazide, prepared by diazotization of the hydrochloride of 1-amino-2-naphthol, repeatedly recrystallized and reprecipitated from alcoholic alkali with a melting point corresponding to the pure substance, possessed a weak band at 2215 cm⁻¹, which can be assigned to the -N-N bond vibration (Fig. 1a). The spectra of these naphthoquinonediazides in methanol and chloroform do not possess this band. The spectra of all the compounds possessed a sharp band at 1622 cm^{-1} , assigned to a carbonyl vibration.

The solid chloride of l-diazo-2-naphthol prepared by diazotization of the amine with isoamylnitrite in methanol saturated with hydrogen chloride, even after repeated crystallization from methanol saturated with hydrogen chloride, still did not correspond to the pure diazonium form. Its IR spectrum possessed a broad band at 2210-2200 cm⁻¹ and a band at 2109 cm⁻¹ (Fig. 1b). A complete shift toward the diazonium form occurred only in a strongly acid medium (HC1 > 14%). In this case only one band at 2220 cm⁻¹ was detected in the spectrum, corresponding to the $-N \equiv N$ bond vibration. The solid sulfate of 1-diazo-2-naphthol, prepared by diazotization of the amine in methanol with sulfuric acid, possessed only a solitary band at 2215 cm^{-1} in its IR spectrum corresponding to the -N=N bond vibration (Fig. 1b). In the IR spectrum of methanol or ethanol solutions of this compound a weak band at 2212 cm^{-1} and a strong but somewhat split band at 2109 cm⁻¹ were observed which indicates the presence of equilibrium forms of the diazo compound. In the IR spectra of aqueous solutions of the diazonium sulfate and the corresponding quinone diazide, prepared by different methods, a band at 2092 cm⁻¹ was observed (Fig. 1g).

The foregoing indicates the great lability of the diazo group in diazotized 1-amino-2-naphthol which readily forms, in different solvents and in weakly acid solutions, an equilibrium mixture of the two extreme forms — the quinonediazide and the diazonium salt. The equilibrium state of the solid diazonium chloride of 1-amino-2-naphthol which we noted con-

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270.0 (3.62) 356.0 (4.01) λ. mμ (lge) 34.2% HCI 1 ١ Diazo cation 356.0 (4.01) 270.0 (3.62) mµ (1ge) 14.2% HCI 1 1 ź Region of transition of quinonediazide into the diazo cation 347.5 (3.89) 270.0 (3.57) 11.05% HCI λ. mμ (lgs) ł 1 275.0 (3.65) 342.5 (3.71) mµ (1ge) 3.8% HCI 1 1 ź 247.5 (4.10) 285.0 (3.70) 340.0 (3.65) 385.0 (3.68) λ. mµ (lgε) 0.4 % HCI 247.5 (4.07) 285.0 (3.75) 335.0 (3.59) 385.0 (3.68) mμ (lge) 0.4 Hq ż Quinonediazide 285.0 (3.75) 335.0 (3.57) 385.0 (3.67) 247.5 (4.03) mµ (1ge) pH 7.0 ż 335.0 (3.57) 385.0 (3.67) 247.5 (4.03) 285.0 (3.75) λ, mµ (lge) 79.9 Hq

Table 2

| | | | lsomer | | |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Substituent | 1, 2, 4 | 1, 2, 5 | 1, 2, 6 | 1, 2, 7 | 1, 2, 8 |
| SQ ₃ H | 2228 | 2220 | 2215 | 2220 | 2230 |
| SO ₃ Na | 2107 sh 2090 | 2103 sb 2080 | 2100 sb 2076 | 2105 sb 2080 | 2112 sb 2095 |
| SO ₃ Ba/2 | 2137 2120 | 2140 2115 | 2136 2108 | 2140 2120 | 2150 2129 |
| SO2CI | 1 | 2130 2112 | 2124 2107 | 2120 sb 2104 | 2132 2115 |

Table 3

The $\nu(SO_2)$ cm⁻¹ Frequencies of the Isomeric Monosulfonic Acids of 1-Diazo-2-naphthol and Their Derivatives (in paraffin oil; the sulfonyl chlorides in hexachlorobutadiene)

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|----------------------|------------------|-------------------|------------------|-------|------------------|-------------------|------------------|-------------------|-------------------|--------------------|
| Cult at it and ' | 1, | 2, 4 | ١, | 2, 5 | 1, | 2,6 | 1, | 2, 7 | 1, 5 | 2, 8 |
| Substituent | v _{sym} | ^v asym | ^v sym | vasym | ^v sym | v _{asym} | v _{sym} | ^v asym | v _{sym.} | ^v asym• |
| SO ₃ H | 1052 | 1206 | 1032 | 1243 | 1040 | 1227 | 1049 | 1216 | 1037 | 1208 |
| SO ₃ Na | 1070 | 1226 | 1059 | 1231 | 1052 | 1230 | 1056 | 1230 | 1049 | 1231 |
| SO ₃ Ba/2 | 1030 | 1210 | 1032 | 1227 | 1041 | 1206 | 1023 | 1218 | 1037 | 1212 |
| SO₂Cl | | - | 1177 | 1387 | 1180 | 1380 | 1178 | 1376 | 1170 | 1396 |

firms the literature data [10]. Such diazo compounds can be secured in the extreme diazonium forms either



Fig. 1. IR spectra of diazotized 1-amino-2-naphthol: a) in hexachlorobutadiene; b) diazonium chloride in paraffin oil; c) diazonium sulfate in paraffin oil; d) chlorohydrate in water.

in strongly acid solutions, or as the solid form of the comparatively stable sulfates. A mutual shift of the vibrational bands, assigned to the triple ($-N \equiv N$) and the cumulative (=N = N) bonds, the broad band at 3400-3300 cm⁻¹ characteristic of the OH group stretching vibration which is observed in IR spectrum of the solid diazonium sulfate, and finally the band at 1622 cm⁻¹, characteristic of the carbonyl stretching vibration in the quinonediazides, point to the possible existence, depending on the medium, of the equilibrium system



The UV absorption spectral data of the diazonium chloride and quinonediazide of 1-amino-2-naphthol in solutions of differing pH are presented in Table 1. The spectra of the substances in water, in buffered solutions of pH 7-4, and in alkaline solutions were practically identical, and the solutions themselves were colored yellow. Only at pH 4 did the spectrum begin to change owing to the observed transition of the quinonediazide form into the diazonium form. Complete transition into the diazonium form is concluded only at high concentrations of mineral acid (~4 N HCl). Such a gradual transformation of naphthoquinonediazide into the hydroxynaphthyldiazonium salt and the need for a more acidic medium differs from the conditions for transformation of o-benzoquinonediazide [1]. This is explained by the considerable stability of the naphthoquinonediazide, by its lower solubility and by the liability of the o-hydroxynaphthyl diazonium salt.

On passing to more acidic media a shift toward the shortwave region in the UV spectrum of 1-diazo-2-naphthol is observed. The progressive change of the absorption spectra of naphthoquinonediazide with change in acidity of the medium is shown in Fig. 2, from which it is evident that the set of curves which are derived possess isobestic points at 273, 308 and 410 m μ . This confirms the presence of equilibrium forms of the diazo compound in the solutions studied. In Fig. 2 the UV spectra of 2-diazo-i-naphthol in water and in 34% HCl are also given.

Table 4

Absorption Frequencies $\nu_c = 0$, cm⁻¹ of Derivatives of the Isomeric Monsulfonic Acids of 1-Diazo-2-naphthol in the 1700-1600 cm⁻¹ Region (in paraffin oil; the sulfonyl chlorides in hexachlorobutadiene).

| | | | Isomer | | |
|------------------------------------------------------------------|--------------|----------------------|----------------------|----------------------|----------------------|
| Substituent | 1, 2, 4 | 1, 2, 5 | 1, 2, 6 | 1, 2, 7 | 1, 2, 8 |
| SO ₃ Na SO ₃ Ba/2 SO ₂ Cl | 1615 1606 | 1618 1604 1618 | 1609 1604 1619 | 1618 1603 1618 | 1615 1606 1616 |

The light sensitivity of diazo compounds existing in the quinonediazide form, in weakly buffered acidic solution (pH 5) is somewhat higher than of those in the diazonium form (Fig. 3). The quantum yields in

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Absorption Bands in the UV spectra of the Isomeric Monosulfonic Acids of 1-Amino-2-naphthol and Their Derivatives

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|----------------------------------------------------------|---------------------------------------------------------|------------------------------------------------------|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------------|
| Substituent | 2,1-naphthoquinone- 1-diazide | 1, 2, 4 | 1, 2, 5 | 1, 2, 6 | 1, 2, 7 | 1, 2, 8 |
| | λ, mμ (lgε) | λ, mμ (lge) | λ, mμ (lge) | λ, mμ (lge) | λ, mμ (lge) | λ, mμ (lgε) |
| SO ₃ Na (buffered aqueous solution pH7) | 247.5 (4.08) 285. (3.75) 335 (3.57) 385 (3.67) | 245 (4.27) 285 (4.07) 335 (3.78) 398 (3.91) | $\begin{array}{cccc} 227 & (4.50) \\ \hline 290 & (4.05) \\ 328 & (3.78) \\ 380 & (3.93) \end{array}$ | 228 (4.51) 257 (4.23) 285 (4.01) 329 (3.63) 378 (3.95) | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 227 (4.41) 250 (4.22) 282 (4.00) 330 (3.64) 375 (3.87) |
| SO ₃ H (80% H ₂ SO4) | 268 (3.62) 360 (4.01) | 248 (4.26) 371 (3.97) | 262 (4.28) 339 (3.95) | 256 (4.20) 340 (3.97) | 257 (4.20) 336 (3.99) | 245 (4.26) 337 (3.91) |
| SO ₂ CI (dioxan) | 250 (4.16) 285 (4.14) 333 (3.39) 387 (3.78) | | 291 (4.46) 320 (3.97) 345 (3.93) 387 (4.02) | $\begin{array}{c} 285 \\ 322.5 \\ 337.5 \\ (4.05) \\ 337.5 \\ (3.90) \\ 380 \\ (4.00) \end{array}$ | 290 (4.56) 327 (4.04) 341 (3.86) 386 (4.02) | $\begin{array}{ccc} 287 & (4.49) \\$ |

Table 6

Degree of Ionization (pK_a) of Diazotized 1-Amino-2-naphthol and Its Isomeric Monosulfonic Acids

| Diazo com- pound | λanalyt. m μ | E.quinone- diazide | . Diazo- nium salt | pKa |
|---------------------|-----------------|-----------------------|-----------------------|-----------------|
| 1,2 | 360 | 0669 | 9640 | 0.66+0.05 |
| 1, 2, 4 | 371 | 8450 | 9870 | 0.21 ± 0.03 |
| 1, 2, 5 | 339 | 8130 | 9780 | 6.40 ± 0.04 |
| 1, 2, 6 | 340 | 8280 | 9870 | 0.54 ± 0.05 |
| 1, 2, 7 | 336 | 7920 | 0266 | 0.37 ± 0.05 |
| 1,2,8 | 337 | 7920 | 9580 | 0.25 ± 0.03 |



Fig. 2. UV spectra of diazotized 1-amino-2naphthol: 1) in buffer solution, pH 7; 2) in 0.42% HCl; 3) in 3.8% KCl; in 11.05% HCl; 5) in 34% HCl.

The substance melted at 160° and no marked depression was displayed on melting of a mixed probe with indene carboxylic acid [11]: Photolysis of the same naphthoquinonediazide, dissolved in concentrated sulfuric acid, leads mainly to the formation of 1,2-dihydroxynaphthalene, identified by its melting point and IR spectrum.

Thus, the contradictory statements recorded by many investigators regarding the nature of the photochemical transformation products of quinonediazides [11, 12, 13] are possibly due to disregard of the medium's effect on the equilibrium shift of the extreme forms of the diazo compound. Under conditions favoring the existence of the diazo compound in the quinonediazide form, the phototransformation is accompanied by ring contraction and formation of a compound of another cyclic system. Under conditions favoring the predominant existence of the diazonium form of the diazo compound, photolysis leads predominantly to formation of a product in which the diazo group is replaced by a hydroxyl.

Sulfonic Acid Derivatives of 1-Diazo-2-Naphthol. From the data of Table 2, it is evident that for all solid isomeric monosulfonic acids of diazotized 1amino-2-naphthol the vibrational frequency $\nu(N_2)$ lies within the limits 2215-2230 cm⁻¹. The diazonium group is characterized by a single absorption band which is located not far above the absorption band of the solid diazonium sulfate of unsubstituted 1-amino-2-naphthol (2215 cm⁻¹). In addition, although the difference is not large, there is a tendency for the vibrational value to increase in the presence of an SO₃H group in the para and peri positions with respect to the diazo group. In these positions, closest to the diazo group, the SO_2O groups form the most stable and most difficultly soluble intramolecular diazonium salts. Such sulfonic acids are stronger than the other isomeric diazonium sulfonic acids (see Table 6).

In the spectra of all the isomeric diazonium monosulfonic acids of 1-amino-2-naphthol, and also the diazonium sulfate of this amine, there is a broad band at 3400-3300 cm⁻¹ (in hexachlorobutadiene), characteristic for OH group stretching vibrations, and the absorption band of the carbonyl frequency was not detected. Examination of the IR spectra of the sodium salts of the isomeric monosulfonic acids of diazotized 1-amino-2-naphthol showed that the frequencies of the ν (N₂) vibrations lay 135-138 cm⁻¹ below the frequency of the main band of the corresponding free sulfonic acid of these diazo compounds. Furthermore these bands, assigned to the =N=N bond vibration, are split (see Table 2).

By comparing these vibrations for the separate isomers, the same tendency for the vibration to increase in value for compounds with sulfonic acid groups situated in the para and peri positions with respect to the diazo group can be noted. By assigning these vibrations to the unsubstituted 2, 1-naphthoquinone-1-diazide (in the solid state 2104, 2136 cm⁻¹) the conclusion can be drawn that the presence of the SO₃Me group markedly lowers the frequency of the second split band (by 9 to 28 cm⁻¹). In the IR spectra of the barium salts of the same sulfonic acids of the diazo compounds, the main band undergoes a significant change; the frequencies rise on average by 30-35 cm⁻¹ with respect to the unsubstituted naphthoquinonediazide, and to the sodium or potassium salts.



Fig. 3. Rate of photolysis of isomeric diazotized o-aminonaphthols: 1) diazo compound from 2-aminonaphthol at pH 5; 2) diazo compound from 1-amino-2-naphthol at pH 5; 3) diazo compound from 1amino-2-naphthol in 60%H₂SO₄.

An analogous picture is noted for the zinc, calcium and cobalt salts of these diazo compounds. Thus the SO₃Me group in salts of differing dissociation, variously affects the frequency of the vibration of the diazo group. Consider the $\nu(N_2)$ vibrational frequencies of the sulfonyl chlorides: first, they also lie below the vibrational frequencies of the N₂-group of the isomeric

Table 7

Quantum Yields of Isomeric Monosulfonic Derivatives of Diazotized 1-Amino-2-naphthol (0.02 g · · mole of substance, 80 ml of solution (1% NaHCO₃), 25° C, 200-500 mμ).

| | | 1, 2 | 2, 5 | 1, 2 | , ΰ | 1,2 | 2, 7 | 1, | 2, 8 |
|--------|------|-------|-------|-------|------|-------|-------|------|-------|
| Isomer | 1,2 | SO2O- | SO2CI | SO20- | SO₂C | SO2O- | SO₂C1 | SO20 | SO₂CI |
| φ | 0.23 | 0.26 | 0.26 | 0.23 | 0,26 | 0.16 | 0,16 | 0.14 | 0.18 |

Table 8

Characteristics of the Isomeric Monosulfonic Acids of 1-Diazo-2-naphthol and Their Derivatives

| | | % Dia | izo N | | | '% Di | azo N |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|---------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------------|
| Substance | mp | Found | Calc. | Substance | rnp | Found | Calc. |
| $4-SO_{3}H$ $4-SO_{3}Na$ $4-SO_{3}Ba/2$ $5-SO_{3}H$ $5-SO_{3}Na$ $5-SO_{3}Ba/2$ $5-SO_{2}Cl$ $6-SO_{3}H$ $6-SO_{3}Na$ $6-SO_{3}Na$ $6-SO_{3}Na$ | 195—196° — 136—137° — 145—146° 149—150° — | 11.3 10.3 8.90 10.7 10.2 8.70 10.3 11.1 10.1 8.63 | 11.2 10.29 8.81 11.2 10.29 8.81 10.43 11.2 10.29 8.9 | $6-SO_2Cl$ $7-SO_3H$ $7-SO_3Na$ $7-SO_2Ba/2$ $7-SO_2Cl$ $8-SO_3H$ $8-SO_3Na$ $8-SO_3Ba/2$ $8-SO_2Cl$ | 148 | 10.6 11.1 10.4 8.54 10.4 11.2 10.0 8.6 10.2 | 10.43 11.2 10.29 8.81 10.43 11.2 10.29 8.81 10.43 |
| 5-SO ₃ Da/2 5-SO ₂ Cl 6-SO ₃ H 6-SO ₃ Na 6-SO ₃ Ba/2 | 145—146° 149—150° | 10.3 11.1 10.1 8.63 | 0.81 10.43 11.2 10.29 8.81 | 8-SO ₃ Na 8-SO ₃ Na 8-SO ₂ Cl | 137—138° — 136—137° | | 1.2 3.0 3.6 0.2 |

sulfonic acids (by 95 cm⁻¹) and are split; and second, the value itself lies between the vibrational values of the sodium and barium salts. Although we did not have the isomer with the SO₂Cl group in the 4 position of the diazo compound available, nevertheless there is, evidently (see Table 2), a tendency toward increase in vibrational frequency for the isomers with the SO₂Cl group in the position nearest to the diazo group. These vibrations of the sulfonyl cloride correspond to the vibrations of the =N=N bond characteristics for the naphthoquinonediazides.



Fig. 4. UV spectra of some derivatives of diazotized 1amino-2-naphthol: 1) diazo compound from 1-amino-2naphthol in water; 2) diazo compound from 1-amino-2naphthol-8-sulfonyl chloride in dioxane; 3) diazo compound from 1-amino-2-naphthol-8sulfonic acid in water.

A study of the position of the bands of the SO_2 group stretching vibration showed that the sulfonic acids and metal salts of the sulfonic acids of diazotized 1-amino-2-naphthol possess an ionic structure (Table 3). The band of the symmetrical stretching vibration ν_{sym} (SO₂) is a strong symmetrical band at 1028-1056 cm⁻¹; the antisymmetrical stretching vibration v_{asym} (SO₂) is represented by a broad band at 1206-1243 cm⁻¹. The highest vibrational frequency is observed for diazo compounds with the sulfonic group in one ring in the β -position to the strong electron acceptor diazonium group (1,2,4-isomer). The frequencies of the SO₂ group stretching vibrations for the isomeric sulfonyl chlorides lie within the limits: ν_{asym} (SO₂) 1373-1396 cm⁻¹, ν_{sym} (SO₂) 1167-1186 cm⁻¹. Both bands are single, symmetrical, and narrow, which indicates the nonionized state of this group (see Table 3).

If the stretching vibration of the C=O bond at 1622 cm⁻¹ x is a characteristic band for unsubstituted 2, 1-naphthoquinone-1-diazide, then introduction of a sulfonate (SO₃Me) or sulfonyl chloride group into any position of the naphthalene nucleus insignificantly reduces the value of the C=O group vibration (Table 4). The greatest reduction is noted for the barium salts of the sulfonic acids of naphthoquinonediazide (1603-1606 cm⁻¹). In all these compounds corresponding to OH group vibrations were not detected.

In order to clarify the character of the intramolecular interactions in the sulfonic acid derivatives

of the diazo compound of 1-amino-2-naphthol we have studied the electronic spectra of these compounds. In aqueous solution of the sodium sulfonates of the diazo compound, the absorption curve of each one completely preserves all the features characteristic of the absorption of the unsubstituted 2, 1-naphthoquinone-1diazide (see Table 5 and Fig. 4). A small bathochromic shift of the absorption band was observed, primarily of the shortwave group. All this indicates the inductive character of the interaction of the sulfonate group with the diazo group and the whole aromatic system. In the electronic spectra of the isomeric sulfonyl chlorides the total character of the absorption characteristic of the unsubstituted naphthoquinonediazide is preserved. However, both with respect to the unsubstituted naphthoquinonediazide, and to the sodium salts of its sulfonic acids, the absorption curve is somewhat shifted toward the longwave region wherein the value of the shift does not depend on the position of the SO_2O^- group in the molecule. The total bathochromic shift of the absorption curve confirms that an electron acceptor substituent such as the SO₂ Cl group has been introduced.

The UV spectra of the isomeric sulfonic acids of 1-diazonium-2-hydroxynaphthalene in 80% sulfuric acid are similar to the spectrum of the unsubstituted diazonium sulfate of 1-amino-2-naphthol, but with a small shift of the absorption bands toward the shortwave region. This shift of the absorption maxima was noted also for the diazotized 1-amino-2-naphthol-4sulfonic acid on passing from its aqueous solution to a solution in concentrated sulfuric acid [3]. The magnitudes of the shifts did not depend on the position of the SO₂O⁻group on the nucleus of the diazo compound. Any effect of the SO₃H⁻group in the diazonium form compared to the naphthoquinonediazide, apparently, is due to the predominant effect of the strong electron acceptor diazonium group. Solutions of 1-diazonium-2-naphthol-4-sulfonic acid or its sodium salt in water or in weak hydrochloric acid solution show a band at 2227 cm⁻¹ corresponding to the $-N \equiv N$ bond. There are no bands in the 2100-2200 cm⁻¹ region corresponding to the vibration of the =N=N bond. On making the indicated solutions weakly alkaline the first band (2230 cm^{-1}) is preserved but a band at 2093 cm⁻¹ also appears. This indicates that alongside the diazonium form there appears in the solution the quinonediazide form. The greater lability of the sulfonic acids of diazotized 1-amino-2-naphthol in solution is analogous to the transformation of the unsulfonated diazo compound noted above.

To determine the degree of ionization of the studied diazo compounds (pK_a) a spectrophotometer [14] was also employed. In accordance with the data of Table 5, there were selected (for 80% H₂SO₄) analytical wavelengths at which the extinction coefficients (ϵ) were measured of the diazo solutions of 1-amino-2naphthol and its monosulfonic acids, containing the quinonoid and diazonium forms, and their mixtures, in equilibrium (Table 6). On this basis [16] the pK_a values were calculated (Table 6). The greatest change in the pK_a values is observed for the isomers in which

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the sulfonic group is in the nearest position to the diazo group (4- and 8-sulfonic derivatives).

Comparison of the values of the quantum yields of the sulfonyl chlorides with those of the sulfonic acids of 2, 1-naphthoquinone-1-diazide are presented in Table 7.

The representatives of one of the extreme forms of the diazo compound of 1-amino-2-naphthol, as its sulfate, and also the isomeric diazonium sulfonic acids as solids, are gray or weak yellow in color. All representatives of the other extreme form — the isomeric sulfonyl chlorides of diazotized 1-amino-2naphthol — are bright intense yellow. All the sulfonyl chlorides, in contrast to the sulfonic acids of diazotized 1-amino-2-naphthol, do not combine with either resorcinol or with m-toluylenediamine in dioxane or dimethylformamide solutions. Only in dioxane with a weakly alkaline medium does the sulfonyl chloride pass progressively from the stable and unreactive form of the naphthoquinonediazide into an active form able to azo couple.

EXPERIMENTAL

Starting Materials. 2, 1-naphthoquinone-1-diazide synthesized from 1-amino-2-naphthol [17], and also from α -naphthylamine [8], crystallized from hexane as yellow needles, mp 94.5-95°. Found: N, 16.5%. Calc. for $C_{10}H_6N_2O$: N, 16.4% . 1,2-naphthoquinone-2-diazide, synthesized from β -naphthylamine [8], crystallized from hexane, and then chloroform as yellow prisms, mp 74°. Found: N, 16.2%. Calc, for C₁₀H₆N₂O: N, 16.4%. The same substance, synthesized from 2-amino-1-naphthol [17], crystallized from hexane as yellow prisms, mp 74.5-75°. Found: N. 16.3%. Calc. N, 16.4%. 2-naphthol-1-diazonium chloride was prepared by introducing 4 ml of isoamvlnitrite (0.032 g-mole) at $0-5^{\circ}$ into a fine suspension of 6g 1-amino-2-naphthol (0.032 g-mole) in absolute methanol, saturated with HCl, with subsequent precipitation with absolute ether. Found: N, 14.3%. Calc. for C₁₀H₇N₂OC1: N, 13.56%. We prepared 2-naphthol-1-diazonium sulfate analogously in methanol solution with 3 ml of concentrated sulfuric acid, which was a colorless powder mp 136-138°. Found: N, 9.85%. Calc. for $C_{10}H_7N_2SO_5$. N, 10.44%. The monosulfonic acids of 1-diazo-2-naphthol were prepared by diazotization of the isomeric sulfonic acids of 1-amino-2naphthol [18]. The latter were prepared from the corresponding naphtholsulfonic acids, previously purified by chromatography on Al₂O₃ columns and the homogeneity verified on paper chromatograms [19]. The sulfonyl chlorides of the diazo compounds were prepared by treating the sulfonic acids of 2,1naphthoquinone-1-diazide with chlorosulfonic acid[20]. We also established that in the reaction of chlorosulfonic acid on unsubstituted o-naphthoquinonediazides the sulfonyl chlorides were smoothly formed [21]. From 2, 1-naphthoquinone-1-diazide was formed 2. 1-naphthoquinone-1-diazide-6-sulfonyl chloride, from 1,2-naphthoquinone-2-diazide was formed 1,2naphthoquinone-2-diazide-5-sulfonyl chloride (Table 8). Quantum Yields. Determination of the quantum yields was carried out by measuring the quantity of nitrogen liberated during irradiation of a solution of the compound with the unfiltered light from a PRK-4 lamp, in a quartz cell at 21° , and by measuring the quanta of radiation absorbed by uranyl oxalate [22]. The concentration of the compound was $2 \cdot 10^{-2}$ g-mole/*l*, height of column of solution in the cell was 50 mm, irradiated area 4.17 cm [2].

Spectra. Infrared spectra were measured on the IKS-14 spectrophotometer in the range 4000-1800 cm⁻¹ with an LiF prism (spectrum calibrated with indene), in the range 1900-700 cm⁻¹, with a NaCl prism (spectrum calibrated with polystyrene). The spectra in methanol were measured in fluorite cells; in water, methanol saturated with HCl, and in acids they were measured in quartz cells. The UV spectra were measured at room temperature on the SF-4A spectro-photometer.

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