experiment no significant exchange took place. The slightly low initial value immediately after mixing may be attributed to slight contamination or to insufficient time for complete flushing due to rapidity of determinations.

To increase the sensitivity of the method, it is advantageous to determine the enrichment of the oxygen in the nitrate groups in addition to the drop of enrichment in the water used for the exchange reaction. A second set of experiments was performed, using the same weight ratio of cellulose nitrate to solution. After eight hours of contact with the solution at 100°, the cellulose nitrate samples were washed with ethyl alcohol, dried, and treated with sodium iodide in acetone at 115° for twelve hours to form cellulose iodo nitrate and sodium nitrate.[6] The $NaNO_3$ was washed with acetone, recrystallized and heated to incipient fusion. It was then heated with $PbCl_2$ in an evacuated bulb provided with a break seal. An O^{18} analysis of the resulting NO_2 and O_2 from the nitrate groups replaced by iodine in the cellulose nitrate sample showed that within the experimental limits of the measurement less than four oxygen atoms per hundred had exchanged with the O^{18} enriched water. It is reasonable to assume that the unreplaced nitrate groups were also unenriched.

The exchange between nitric acid and water at 30° was investigated by mixing 4.6 g. of unenriched 100% HNO_3 with 6.9 g. of O^{18} enriched water. The exchange was followed in separate experiments, both by reaction of the samples of the solution with mercury to form NO for O^{18} analysis and by the vacuum distillation of the solution to collect small samples of water for O^{18} analysis on the mass spectrometer. These experiments were not designed for obtaining precise data, but clearly showed an oxygen exchange in a 40% nitric acid solution with a half life of the order of thirty minutes.

Discussion

The apparent *p*H dependence of the oxygen exchange between nitrates and water is to be inferred by comparison of the results of Winter, Carlton and Briscoe, and Hall and Alexander, and the oxygen exchange between nitric acid and water in a 40% solution. This dependence and lack of exchange between the non-ionizable cellulose nitrate and water suggest that the mechanism of oxygen exchange between nitrates and water possibly involves interaction of the ion pair NO_3^- and hydrated hydrogen ion, H_3O^+. A more detailed elaboration of the theory would require an investigation of comparative rates of exchange in solutions of several concentrations and *p*H values.

(6) G. E. Murray and C. B. Purves, THIS JOURNAL, **62**, 3194-3197 (1940).

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Measurement of the Raman Effect with a Small Quantity of Liquid

BY SAN-ICHIRO MIZUSHIMA, TAKEHIKO SHIMANOUCHI AND TADAO SUGITA

In an ordinary measurement of the Raman effect in the liquid state, a Rayleigh tube is used with which the writers have hitherto succeeded in photographing clearly the Raman spectrum of a liquid with a volume as small as 2 cc. For a smaller volume, however, this tube is not practical and we recently constructed a simple apparatus which enables us to photograph the spectrum of less than 1 cc. of liquid.

If we place an electric lamp on the focal plane of the camera lens of as pectrograph (*i. e.*, in the plane of the photographic plate), then the light passing through the spectrograph is emitted from the slit S as monochromatic light. A lens L is placed in front of the slit at such a distance from S that its image formed at I of Fig. 1 is about twice as large as its original size. In the same figure the broken lines indicate the thin beam of light emitted from the slit. A glass plate cut off in part in the form of this beam and held between two other plates is used as the Raman vessel which is placed in the position shown in Fig. 1 in which the shaded part is blacked (or covered with black paper) in order to avoid the entry of unnecessary light into the vessel. The Raman spectrum is photographed in the usual manner with this vessel, with a mercury lamp on one side and a plane mirror on the other.

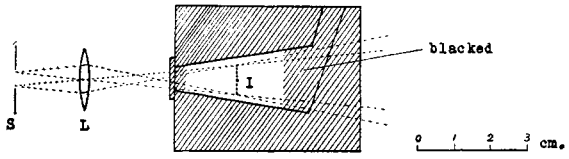

Fig. 1.—The Raman vessel: the vessel is bent upward in the rear to avoid the direct reflection of the incident light.

By dividing this vessel into two parts as shown in Fig. 2, we can photograph on the same plate the spectra of two different substances at the same time and thus the comparison of the two spectra can be made easily and accurately. We can also make polarization measurements with this vessel by covering one part with a polaroid transmitting the light vibrating parallel to the spectrographic axis and the other with a polaroid which transmits light vibrating perpendicular to the axis.

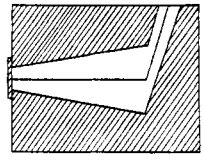

Fig. 2.—The vessel divided into two parts.

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The Synthesis of Some 1-Nitroso and 1-Amino-2-Hydroxy-3-naphthoic Acid Aryl Amides

BY ROBERT F. MILLIGAN AND LOUIS KOCH

A series of 1-amino-2-hydroxy-3-naphthoic acid aryl amides were synthesized by nitrosating[1] some

(1) Battegay, Langjahr and Rettig, *Chimie et Industrie*, **11**, 453 (1924). The present procedure is a modification of their method for the preparation of 1-amino-2-hydroxy-3-naphthoic acid anilide.

TABLE I

1-NITROSO- AND 1-AMINO-2-HYDROXY-3-NAPHTHOIC ACID ARYL AMIDES

	Condensation product of 2-hydroxy-3-naphthoic acid with	Commercial name, naphthol	1-Nitroso derivative, m. p., °C. (uncor.)	Nitrogen content, % Calcd.	Found	1-Amino derivative, m. p., °C. (uncor.)	Nitrogen content, % Calcd.	Found
1	Aniline	AS	221–222	9.58	9.55	190–192[a]	...	...
2	*o*-Toluidine	ASD	207–208	9.78	9.60	162–164	9.58	9.38
3	2,4-Dimethylaniline	ASMX	212–213	8.75	8.74	166–168	9.15	9.08
4	*o*-Anisidine	ASOL	216–217	8.69	8.52	161–163	9.09	8.96
5	*p*-Anisidine	ASRL	217–218	8.69	8.61	160–162	9.09	8.93
6	*o*-Phenetidine	ASOP	234–235	8.36	8.35	151–153	8.70	8.44
7	Alpha-naphthylamine	ASBO	236–237	8.19	8.01	201–203	8.54	8.40
8	Beta-naphthylamine	ASSW	222–223	8.19	7.99	184–186	8.54	8.51
9	*m*-Nitroaniline	ASBS	255–256	12.46	12.25	183–185[b]	14.33	14.24
10	*p*-Chloroaniline	ASE	241–242	8.57	8.46	160–162	8.96	9.00
11	5-Chloro-*o*-toluidine	ASTR	221–222	8.22	8.16	182–184	8.58	8.51
12	5-Chloro-2,4-dimethoxyaniline	ASITR	233–234	7.24	7.19	215–217	7.52	7.36

[a] M. p. literature, 188–190°. [b] Diamine formed by reduction of nitro group on condensing amine.

Naphthol AS intermediates, and reducing the resulting nitroso compounds with zinc dust and glacial acetic acid, in a dioxane solvent. Comparison with the amino derivatives of the coupling components from the corresponding Naphthol AS type pigments, disclosed that both were identical.

Experimental

Materials.—The compounds reported in this paper were prepared from commercially available Naphthol AS dyestuff intermediates, which were found to be true to type and sufficiently pure for immediate use.

Preparation of 1-Nitroso-2-hydroxy-3-naphthoic Acid Aryl Amides.—Nitrosation of the aryl amides was achieved in 85–90% yields by the general method described below: One-twentieth gram mole of the amide was suspended in 200 ml. of dioxane, which had been previously cooled to 20° and the mixture was mechanically agitated while 20 ml. of a 25% sodium nitrite solution was added, followed at once by 10 ml. of concd. hydrochloric acid. During the first five minutes, the mixture progressively changed color, sometimes accompanied by solution of the amide. After one hour, the precipitated nitroso derivative was collected on a Buchner funnel, washed with 25 ml. of cold alcohol, and dried. Portions of the yellow to brick-red precipitates were crystallized from dioxane, for purposes of establishing melting point and analytical data, Table I.

Preparation of 1-Amino-2-hydroxy-3-naphthoic Acid Aryl Amides.—Three-gram portions of the crude nitroso were reduced, by refluxing for one hour, with a mixture of 10 g. of zinc dust, 50 ml. of dioxane and 10 ml. of glacial acetic acid. The hot reaction mixture was filtered, to remove insoluble matter, which was then washed with 25 ml. of dioxane, and the filtrate was acidified at once with 50 ml. of hydrochloric acid, to precipitate the amino hydrochloride. After cooling overnight to achieve maximum yield, the solid was collected on a Buchner funnel, washed with a small volume of dioxane and transferred to a 500-ml. extraction funnel with about 50 ml. of alcohol.

The suspended amino hydrochloride was buffered with 10 ml. of a 10% sodium acetate solution, to liberate the free base, and the mixture was diluted with 250 ml. of ether. Any remaining solid was solubilized by the addition of 200 ml. of a 2.5% sodium acetate solution, and the ether layer was then washed several times with water, dried with anhydrous sodium sulfate, filtered and evaporated to near dryness. Resolution of the residue was effected with 50 ml. of hot benzene, and incipient crystallization of the amino-arylamide was attained by dilution with petroleum ether. Yellow to greenish crystals were precipitated, after standing overnight in the refrigerator, and the product was purified from benzene–petroleum ether.

Occasionally, solution of the amino-Naphthol AS compound could not be accomplished with ether. When this occurred, 100 ml. of benzene and 50 ml. of xylene were added to the ether layer, and the mixture was evaporated until only xylene remained. This caused solution of the amino-arylamide, which was then precipitated with petroleum ether, and purified as previously described. Amine yields of 60–85% were obtained.

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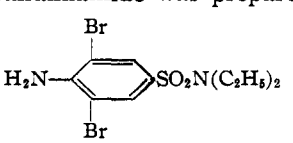
The Desulfonamidation of N^1,N^1-Diethyl-3,5-dibromosulfanilamide

BY CARL M. MOSER AND G. S. MELVILLE, JR.

An N^1-bromo sulfonamide may be a necessary intermediate in the formation of 2,4,6-tribromoaniline from the desulfonamidation of 3,5-dibromosulfanilamide in the usual manner.[1] Displacement of Br+ by a proton from the primarily formed 2,6-dibromoaniline, reaction of this fragment with the dibromo sulfanilamide to form the N^1-halo compound, and bromination of the dibromo aniline with the latter compound would complete the sequence of the steps in the mechanism.

In order to test this hypothesis N^1,N^1-diethyl-3,5-dibromosulfanilamide was prepared and subjected to desulfonamidation by refluxing a solution of the sulfanilamide in 70% sulfuric acid. The formation of an N^1-bromosulfonamide is not possible here, and, if such a compound is a necessary intermediate in the formation of 2,4,6-tri-



(1) The report of Fuchs, *Monatsh.*, **36**, 124 (1915), that only 2,6-dibromoaniline is formed in this reaction could not be confirmed; *cf.* Seikel, *Organic Syntheses*, **24**, 47 (1944).