seems probable that an electron transfer occurs like that postulated for the reaction of benzoyl peroxide with dimethylaniline.[1]

Recently[4] it has been reported that phenol reacts with benzoyl peroxide in chloroform to give a high yield of benzoic acid and only a minor amount of catechol monobenzoate. The high yield of benzoic acid means that the radical chain reaction cannot be important in this case either. But since the decomposition in chloroform is not appreciably accelerated by phenol, Cosgrove and Waters' explanation in terms of unimolecular decomposition into radicals need not be abandoned.

Experimental

To 13 g. of freshly distilled dimethylaniline, b. p. 192°, was added 1.13 g. of *p*-methoxy-*p'*-nitrobenzoyl peroxide.[3] The addition of the peroxide was carried out very cautiously, since if a mass of several mg. of the peroxide is added all at once it usually explodes instead of dissolving quietly. Before the addition of the peroxide was complete a mixture of anisic and *p*-nitrobenzoic acids began to precipitate. The total yield of acids was 0.98 g.

The melting point of the mixed acids was 225° (end of melting), raised by addition of *p*-nitrobenzoic acid. The melting point of an equimolar mixture of anisic and *p*-nitrobenzoic acids is 224.5°.[3]

Two flasks, one containing 7.75 g. of benzoyl peroxide in 50 cc. of chloroform, the other containing *in addition* 3.0 g. of phenol, were heated together on the same hotplate under reflux for one hour. Aliquots removed at the end of the reflux period and analyzed by the method of Nozaki[5] showed that there remained in the control run 6.7 g. of benzoyl peroxide compared with 6.6 g. for the run containing phenol.

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[4] Cosgrove and Waters, *J. Chem. Soc.*, 3193 (1949).

[5] Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

METCALF CHEMISTRY LABORATORY
BROWN UNIVERSITY
PROVIDENCE 12, RHODE ISLAND

RECEIVED MARCH 4, 1950

Oxygen Exchange between Nitrates and Water[1]

BY RALPH KLEIN AND ROBERT A. FRIEDEL

In connection with research on the mechanism of burning of propellants, studies have been made of the mechanism of thermal decomposition of nitrocellulose containing O^{18}. In the course of the preparation of O^{18}-enriched nitrocellulose it became necessary to study a number of oxygen-exchange reactions, among them oxygen exchange between nitrates and water.

Investigation has shown no oxygen exchange between nitrate ions and water in neutral solution,[2] and Hall and Alexander have determined that no exchange occurs in basic solutions. Winter, Carlton and Briscoe reported complete exchange at 100° in twenty-four hours in approximately 1 *N* sulfuric acid. On the other hand, Hall and Alexander found no exchange for potassium nitrate in 0.2 *N* nitric acid within the precision limits of their experiments. If their results are correct (the experimental method consisted in careful measurements of the density of the water before and after the reaction and appears to be rather precise), it would seem that the reaction is *p*H-dependent. We have found, using mass-spectrometer analysis, that nitric acid in a 40% solution undergoes an oxygen exchange with water at 30°. The question may be raised whether the nitrate groups need be present in an ionizable form for exchange. This may be tested with cellulose nitrate, which is known to be only slightly hydrolyzed by dilute sulfuric acid.[3] No exchange was observed experimentally between cellulose nitrate (12.9% nitrogen) in a 1 *N* sulfuric acid solution at 23° or 100°.

Experimental

The O^{18} enrichment of the water was determined by means of a mass spectrometer (Consolidated Model 21-102). The use of this instrument for quantitative analysis[4] of water and for isotopic analysis is complicated by adsorption of ordinary water on the walls of the high-vacuum system, which is gradually desorbed and thus interferes considerably with the determination of isotopes in enriched water. The difficulty is overcome by repeated flushing and pumping out of the system, using the enriched water to be analyzed. After three such cycles, consisting of three minutes flushing and three minutes pumping, the ratio $H_2O^{18}:H_2O^{16}$ approaches a constant value, indicating that the ordinary water on the walls has been substantially removed or diluted to a negligibly low value.

Cellulose nitrate and 1 *N* sulfuric acid were agitated at 23° in a 1:3.5 weight ratio in a cell similar to that of Frilette, Hanle and Mark.[5] The water had an O^{18} content of 1.31 ± 0.01%. The natural abundance being 0.2%, this corresponds to an enrichment factor of 6.55 ± 0.05. If oxygen exchange occurred, the enrichment factor should have been decreased. Assuming that two oxygen atoms per nitrate group are exchangeable, the enrichment factor should have dropped from 6.5 to 6.0, calculated on the basis of the weight ratio of cellulose nitrate to water. Table I shows that under the conditions of this

TABLE I

O^{18} ENRICHMENT OF WATER MIXED WITH NITROCELLULOSE

Time after mixing	O^{18} enrichment factor
0	[a]6.55 ± 0.05
12 minutes	[b]6.3
19 minutes	[b]6.4
28 minutes	6.5
35 minutes	6.7
47 minutes	6.6
56 minutes	6.7
66 minutes	6.6
24 hours	6.5
25 hours	6.6
2 days	[a]6.65 ± 0.08
7 days	[a]6.51 ± 0.06

[a] Average of 4 runs, each in duplicate. [b] Initial low values due to incomplete flushing or to slight contamination.

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[1] Publication approved by the Public Information Division, National Defense Department. Article not copyrighted.

[2] (a) R. Titani and K. Goto, *Bull. Chem. Soc. Japan*, **14**, 77-85 (1939); (b) E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131-138 (1940); (c) N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455-3462 (1940).

[3] J. Desmaroux, *Compt. rend.*, **206**, 1483-1484 (1948).

[4] R. C. Taylor, R. A. Brown, W. S. Young and C. E. Headington, *Anal. Chem.*, **20**, 396-401 (1948).

[5] V. J. Frilette, J. Hanle and H. Mark, THIS JOURNAL, **70**, 1107-1113 (1948).

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.

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(6) G. E. Murray and C. B. Purves, This Journal, **62**, 3194–3197 (1940).

EXPLOSIVES BRANCH AND RESEARCH AND DEVELOPMENT BRANCH
FUELS AND EXPLOSIVES DIVISION
BUREAU OF MINES
PITTSBURGH, PA.

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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.

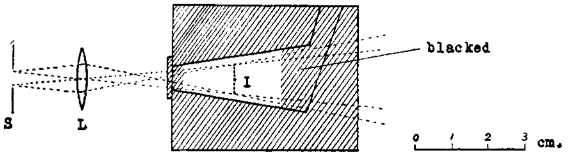

Fig. 1.—The Raman vessel: the vessel is bent upward in the rear to avoid the direct reflection of the incident light.

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.

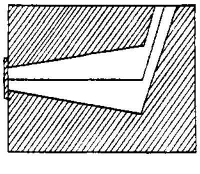

Fig. 2.—The vessel divided into two parts.

CHEMICAL LABORATORY
FACULTY OF SCIENCE
TOKYO UNIVERSITY
BUNKYOKU, TOKYO, JAPAN

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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

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(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.