tion subsided and then for an additional ten minutes. The mixture was cooled and the product distilled.

Procedure B. From Olefin, Phosphorus Pentachloride and Phosphorus Pentasulfide.—The olefin-phosphorus pentachloride reaction products were prepared as described in section I. To the resulting slurry were added a catalytic amount of iodine and the theoretical amount of phosphorus pentasulfide. The reaction temperature was maintained at 25 to 50° until all of the solids had reacted and the solution was clear. The products were separated by distillation.

PREPARATIONS OF STYRYL-, ISOÖCTENYL- AND ISOBUTENYLTHIONOPHOSPHONIC DICHLORIDES

Compound	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
$C_8H_7PSCl_2$	51	130	1	1.6563	13.1	13.0	13.5	..	30.0	30.2
$C_8H_{15}PSCl_2$	65	95–100	2	1.5330	12.7	12.5	13.1	13.0	29.0	29.7
$C_4H_7PSCl_2$	95	115–125	30	1.5560	16.4	14.9	16.9	15.4	37.5	45.2

DI-*p*-NITROPHENYL DERIVATIVES OF ISOÖCTENYL- AND ISOBUTENYLTHIONOPHOSPHONIC DICHLORIDE

Compound	M.p., °C.	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
$C_8H_{15}PS(OC_6H_4NO_2)_2$	81–82	6.9	7.0	7.1	7.1	6.2	6.2	0.0	0.0
$C_4H_7PS(OC_6H_4NO_2)_2$	103–105	7.9	7.9	8.1	8.1	7.1	7.2	0.0	0.0

The reaction was found to be highly exothermic; hydrogen chloride was evolved from the exhaust tube throughout the entire course of the reaction. Yields of over 80% styrylthionophosphonic dichloride have been obtained using procedure B but the resulting product contained from 2 to 3% excess chlorine. Purification by careful fractionation reduced this yield considerably.

Isobutenylthionophosphonic dichloride obtained by procedure A or procedure B is always contaminated with what is presumed from the analytical data to be chlorobutylthionophosphonic dichloride. The contaminant can neither be separated by fractional distillation in a Vigreux column nor can it be dehydrohalogenated without decomposition of the main product.

III. Hydrolysis of Alkenylphosphonous Dichlorides.—Ten grams of alkenylphosphonous dichloride was slurried in 100 ml. of concentrated hydrochloric acid until hydrolysis was complete. Styrylphosphinic acid was recrystallized from water.

The following table shows the results of these experiments.

Compound	M.p., °C.	Molecular wt. (titrn.) Calcd.	Molecular wt. (titrn.) Found	Phosphorus, % Calcd.	Phosphorus, % Found
Styrylphosphinic acid	74–75	168	168	18.4	18.3
Isoöctenylphosphinic acid	Oil	176	176	17.5	17.5

Both acids are monobasic indicating the phosphinic acid structure.

IV. Derivatives of Alkenylthionophosphonic Dichlorides. Di-*p*-nitrophenyl Esters.—A mixture of 28.3 g. (0.2 mole) of *p*-nitrophenol, 21.6 g. (0.204 mole) of sodium carbonate and 0.1 mole of alkenylthionophosphonic dichloride was refluxed for four hours in 150 ml. of acetone. The product was isolated by pouring the mixture into water and extracting the compound with benzene. The product was recrystallized from benzene.

Acknowledgment.—The authors wish to extend their thanks to Messrs. A. R. Wreath and D. Bernhart for carrying out the analytical determinations and to Dr. A. D. F. Toy and Dr. L. F. Audrieth for their interest and constructive suggestions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XVII. The Hydrolysis of 2,4-Dinitrobenzenesulfenyl Chloride

BY NORMAN KHARASCH, WILLIAM KING AND THOMAS C. BRUICE

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The hydrolysis of 2,4-dinitrobenzenesulfenyl chloride yields a variety of products, including 2,4-dinitrobenzenesulfenic anhydride, ArS–O–SAr (Ar = 2,4-dinitrophenyl), bis-(2,4-dinitrophenyl) disulfide (ArSSAr), 2-amino-4-nitrobenzenesulfonic acid, *m*-dinitrobenzene and 2,4-dinitrobenzenesulfonic acid. 2,4-Dinitrobenzene sulfenic acid is the probable precursor of all of these substances, but its isolation was not effected. A convenient synthesis of the 2-amino-4-nitrobenzenesulfonic acid, in 70% yield, also is described.

While 1-anthraquinonesulfenic acid is the only example of this class of substances to have been isolated,[1] three selenenic acids, including 2,4-dinitrobenzeneselenenic acid,[2] have been reported. The hydrolysis of 2,4-dinitrobenzenesulfenyl chloride (I) was examined therefore as a possible route to 2,4-dinitrobenzenesulfenic acid (II, Ar = 2,4-dinitrophenyl).

Hydrolysis of I, in aqueous acetic acid at room temperature, occurred readily and with quantitative release of chloride ion; but instead of II, several products were found, including VII and IV (Ar = 2 4-dinitrophenyl, below) in major amounts, and III, IV and VIII in smaller proportions. The formation of all of these substances can be interpreted conveniently on the basis that II is the unstable, first product in the hydrolysis of I.[3] Compounds V and VI are also logical intermediates, but they were not isolated.

2,4-Dinitrobenzenesulfenic anhydride (IV) is a new product. It was characterized by elementary analysis, quantitative titration with iodide ion ($ArS\text{-}O\text{-}SAr + 2H^+ + 2I^- \rightarrow ArS\text{-}SAr + I_2 + H_2O$), conversion to acetonyl 2,4-dinitrophenyl sulfide

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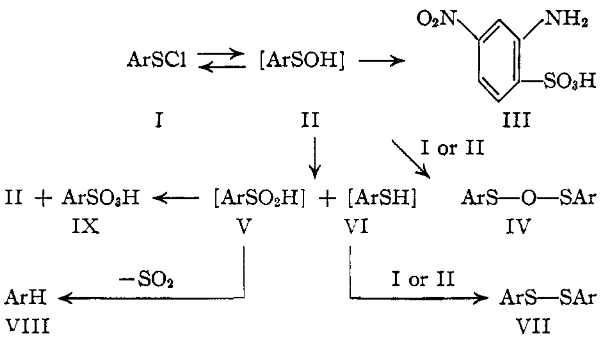
[1] K. Fries, *Ber.*, **45**, 2965 (1912).

[2] O. Behaghel and W. Miller, *ibid.*, **68**, 1540 (1935).

[3] *Cf.* N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946); N. Kharasch and T. C. Bruice, THIS JOURNAL, **73**, 3240 (1951). For paper XVI of this series, *cf.* S. J. Assony and N. Kharasch, *Chem. and Ind.*, **45**, 1388 (1954).



(by reaction with acetone), and formation of 2,4-dinitrobenzenesulfenanilide by reaction with aniline. It is an excellently crystalline, pale yellow solid, which is stable if kept dry at ordinary temperatures, but which decomposes vigorously at 116–118°. Suspension of IV in excess water also effects its decomposition slowly, supposedly *via* II, since considerable VII was found as product. This hydrolysis of IV also explains why the ratios of IV and VII observed varied with the amount of water used in the hydrolysis of I and with the duration of contact of the products with water. Treatment of IV with concentrated sulfuric acid gives the bright red color characteristic of 2,4-dinitrobenzenesulfenium ion.[4]

The presence of a small quantity of III in the hydrolysis mixture was shown by derivative formation. The formation of this acid by a modified procedure, suitable for preparative purposes, as well as the proof of its structure are given below. The other products in the hydrolysate were identified by standard procedures.

Hydrolysis of 2,4-dinitrobenzenesulfenyl chloride is accompanied by evolution of sulfur dioxide. Since the sulfinic acid V was not found in the hydrolysate (even though the sulfonic acid IX was) and in view of the formation of *m*-dinitrobenzene (VIII), the sulfur dioxide most likely arises through desulfination of the intermediate sulfinic acid V. This observation suggests the reason for the failure of Bradbury and Smith[5] to prepare V, and is in accord with the report of Davies, Storrie and Tucker[6] that heating 2,4-dinitrobenzenesulfonhydrazide (a reaction known to lead to sulfinic acids with other arylsulfonhydrazides) gave a quantitative yield of *m*-dinitrobenzene. The desulfination of sulfinic acids is a known reaction,[7] and V should be particularly susceptible to it—reasoning by analogy with the easy decarboxylation of 2,4-dinitrobenzoic acid and, for example, the fact that 6-chloro-3-nitro-2-methylbenzenesulfinic acid is so unstable[7] that attempts to prepare it always give high yields of 2-nitro-5-chlorotoluene. Further work on the reported[6] and attempted[5] syntheses of V would probably reveal that the unresolved difficulties[5] lie in the facile loss of sulfur dioxide from this sulfinic acid. The absence of sulfate ions in the hydrolysate shows that VIII does not arise by hydrolysis of IX. Formation of IX *via* V is reasonable, for the disproportionation of sulfinic acids, or their oxidation, is a recognized route to the corresponding sulfonic acids.

An alternate, rapid way to hydrolyze I is to shake an ether solution of the sulfenyl chloride with aqueous bicarbonate, which produces an intensely dark solution and a yellow precipitate (consisting mainly of IV and VII). On standing, the solution lost its intense color and became wine red (similar to the color of an alkaline solution of 2,4-dinitrothiophenol). The dark color of the solution could be discharged by adding mineral acid, and restored with alkali—a process which could be repeated at will. Since pure IV showed the same behavior on dissolving in aqueous sodium bicarbonate, the deep color of the aqueous solutions probably is associated with the presence of the sodium salts of II and VI. Hydrolysis of I also may be effected in pure water. The process is slow because of low solubility, but use of a surface active agent hastens it.

In view of the easy formation of sulfenate esters by pyridine catalysis of the reaction of I with alcohols (ArSCl + R′OH → ArSOR + HCl),[8] the similar reaction with water was attempted, but the only product isolated (72% yield) was the disulfide VII. The reaction was very rapid—a result which confirms the earlier comment[8] that water seriously competes with the alcohols in the formation of the 2,4-dinitrobenzenesulfenates.

In attempts to prepare the sodium salt of II, the alkaline hydrolysis of I and of methyl 2,4-dinitrobenzenesulfenate[8] with sodium hydroxide solutions was studied. This was not, however, promising for this conversion—since dark mixtures resulted, from which the isolation of products was difficult. In contrast, under conditions which permitted the smooth acid hydrolysis of the 2,4-dinitrobenzenesulfenyl derivatives (the chloride, the sulfenamide or the methyl sulfenate) a nearly colorless, excellently crystalline, strongly acid substance was isolated, the best yield (70%) resulting from the methyl ester. Although the analyses for carbon and hydrogen, as well as the neutralization equivalent (213), were near those calculated for 2,4-dinitrobenzenesulfenic acid (II) (neut. equiv. 216), it was established soon that the product was not II, but 2-amino-4-nitrobenzenesulfonic acid (III). Thus: (1) the high thermal stability of the product (dec. 305–310°), its strong acid character, its high solubility in water, and particularly its failure to act as a reducing agent were not in agreement with the postulate that it was a sulfenic acid. (2) Diazotization and coupling with dimethylaniline proved the presence of an amino group. (3) The presence of but one nitro group was clearly shown by a comparison of the polarogram of the product with that of 2,4-dinitrophenol. (4) The preparation of the previously recorded 2-nitro-4-aminobenzenesulfonic acid by the Piria reduction of *m*-dinitrobenzene[9] was carried out. The S-benzylthiuronium salt of this acid was distinctly different from the corresponding

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[4] N. Kharasch, C. M. Buess and W. King, THIS JOURNAL, **75**, 6035 (1953).

[5] H. Bradbury and F. J. Smith, *J. Chem. Soc.*, 2943 (1952).

[6] W. Davies, F. R. Storrie and S. H. Tucker, *ibid.*, 624 (1931).

[7] A. T. Dann and W. Davies, *ibid.*, 1050 (1929).

[8] N. Kharasch, D. P. McQuarrie and C. M. Buess, THIS JOURNAL, **75**, 2658 (1953).

[9] R. Nietzki and G. Helbach, *Ber.*, **29**, 2448 (1896).

thiuronium salt prepared from the aminonitrobenzenesulfonic acid derived from I. However, by reaction with bromine, the sulfonic acid group was eliminated from both of the aminonitrobenzenesulfonic acids, forming—in each case—the same tribromoaminonitrobenzene, as is formed by bromination of *m*-nitroaniline—namely, 2,4,6-tribromo-3-nitroaniline. These observations show that the nitro and amino groups in the hydrolysis product are in positions *meta* to each other; and that the amino and sulfonic acid groups are not *para* to each other. Thus, the only logical structure for the acid is III; and this accords with the expected structure, by analogy with the finding of Zincke and Farr[10] that 2-nitrobenzenesulfenyl chloride forms orthanilic acid as one of the products of hydrolysis. The proof of structure of III was, however, required in the present study, for—although III has been mentioned in the literature several times as the product of sulfonation of *m*-nitroaniline—none of the previous workers[11] characterized this compound suitably.

The synthesis of III from I *via* the readily available methyl 2,4-dinitrobenzenesulfenate provides a convenient route to this acid, for the alternate procedures call for tedious separations of III from excess sulfuric acid and the use of solid fuming sulfuric acid or pressure-tube technique in the sulfonation of *m*-nitroaniline.

Experimental[12]

Hydrolysis of 2,4-Dinitrobenzenesulfenyl Chloride (I) in Aqueous Glacial Acetic Acid.—The sulfenyl chloride,[13] 10.2 g., was dissolved in 150 ml. of warm glacial acetic acid. Water (100 ml.) was added slowly, with stirring. Formation of a yellow precipitate was noted, and 150 ml. more of water was added to complete its precipitation. This orange-yellow solid was collected, washed with cold water, sucked dry and desiccated (wt. 7.0 g.). It was then suspended in 200 ml. of dry benzene and refluxed 3 hours. The benzene-insoluble material (later shown, see below, to be VII) was collected (3.5 g.), and the filtrate—after removing a trace of suspended solid—aspirated to half-volume. On standing, the latter yielded 3.5 g. of excellent, pale-yellow needles (later shown to be IV). After recrystallization from benzene, IV decomposed violently at 116–118°. Treating the hydrolysate filtrate of I with nitric acid and silver nitrate gave 6.1 g. of silver chloride. For full hydrolysis of 10.2 g. of I, 6.25 g. of silver chloride is required.

The identity of VII[14] was proved by its characteristic decomposition (darkening 240–280°, and melting and vigorous decomposition at 290–300°), correct analysis for carbon, hydrogen and sulfur, and its catalytic chlorinolysis[13] to I. The I so obtained was particularly pure and of higher melting point (97–98°) than I which results from disulfide, prepared *via* 2,4-dinitrochlorobenzene and sodium disulfide. The product melting at 97–98° did not depress the m.p. of I melting at 93–94°, and the former (1.0 g.) also gave 0.98 g. acetonyl 2,4-dinitrophenyl sulfide,[14] by reaction with acetone.

Identification of IV.—The product, dec. 116–118°, was analyzed.

Anal. Calcd. for $C_{12}H_6O_9N_4S_2$: C, 34.78; H, 1.46. Found (on different samples): C, 34.66, 34.43; H, 1.40, 1.44.

Titration of IV with potassium iodide, in glacial acetic acid solution released one mole of iodine per mole of VII, with less than 1% error in three determinations, using the method described for analysis of I by Orr and Kharasch.[15]

Treatment of IV, 0.10 g., with excess acetone gave 0.06 g. of acetonyl 2,4-dinitrophenyl sulfide, m.p. 141–142° (and not depressing the m.p. of the authentic sulfide[14]). The yield of sulfide is lowered because of formation of an alcohol-insoluble residue (0.05 g.), presumably consisting of the decomposition products of II, since II is expected to be formed in reaction of IV with acetone. Similarly, reaction of IV with aniline, in benzene solution, gave the known[3] 2,4-dinitrobenzenesulfenanilide, but the yield was again low (about 20%) and, once more, an insoluble residue was found as a major product.

Formation of the typical color of 2,4-dinitrobenzenesulfenium ion was observed by dissolving a small crystal of IV in concd. sulfuric acid and noting its identity, by visual inspection with a similar solution of I in sulfuric acid.

Another 10-g. sample of I was hydrolyzed, as above, the precipitate collected and the clear filtrate concentrated to half-volume by heating and simultaneous aspiration. A pale yellow precipitate (0.1 g.) was collected (and identified as VII), and evaporation continued until white crystals (0.2 g.) separated. These were identified, by physical properties and the S-benzylthiuronium salt derivative (see below), as III. Continued evaporation of the filtrate, and cooling, gave dinitrobenzene, identified by analysis, m.p. and mixed m.p. with authentic product. Further evaporation, and treatment with a saturated solution of sodium chloride, gave 0.6 g. of a yellow salt, which was converted by reaction with phosphorus pentachloride to the known 2,4-dinitrobenzenesulfonyl chloride. Treatment of the concentrated filtrate with hot aqueous sodium hydroxide gave small amounts of 2,4-dinitrophenol, which probably arises by reaction of alkali with IX. The phenol was not observed if the alkali treatment was omitted.

The evolution of sulfur dioxide from the hydrolysis of I was detected by sweeping the hydrolysis mixture (3 g. of I, 100 ml. of glacial acetic acid and 5 ml. of water) with nitrogen gas, and allowing the effluent gas to pass through a trap filled with aqueous potassium permanganate. The latter was decolorized and formation of sulfate ions detected by adding barium nitrate. A control without I added gave no precipitate on adding barium nitrate. A test for sulfate ions in the hydrolysis mixture of I, itself, was also negative.

The ratios of IV and VII obtained varied considerably if the hydrolysis of I was carried out with a lesser excess of water, and therefore more slowly. Thus a solution of I (10 g.) in dry acetic acid (150 ml.) and 2.5 ml. of water was set aside. There was no immediate reaction apparent. However, five days later, 5.7 g. of a pale yellow precipitate was collected. (About 1.5 g. less than generally was obtained by the above, rapid hydrolysis procedures.) When dried, and extracted with benzene (compare above), 5.3 g. of VII remained, and only 0.3 g. of IV was obtained from the benzene extract. Suspending 6.0 g. of IV in water for 15 hours, led to formation of 2.0 g. of VII. Adding hydrochloric acid to the hydrolysis mixture of I in glacial acetic acid retarded the formation of the insoluble precipitate, presumably because of the mass action effect on the reaction for conversion of I to II ($ArSCl + HOH \rightleftarrows ArSOH + HCl$).

Hydrolyses with Pyridine and Sodium Bicarbonate Present.—The hydrolyses of I with pyridine present were very rapid, and were carried out by the general procedure of ref. 8, using water as reactant in place of an alcohol. A heavy precipitate of VII was formed rapidly in these hydrolyses. Hydrolyses of I in presence of sodium bicarbonate were carried out by dissolving I in ether, and shaking with aqueous bicarbonate solution, in a flask having a vent for escape of carbon dioxide. The dark-colored solutions obtained were not extensively studied (*cf.*, however, text for effects of acidification of these reaction mixtures).

2-Amino-4-nitrobenzenesulfonic Acid (III).—Into 300 ml. of a 50% aqueous solution of methanol, in a one-liter flask, was placed 3 g. of methyl 2,4-dinitrobenzenesulfenate (prepared by addition of the sulfenyl chloride to absolute methanol).[8] Concentrated hydrochloric acid (5 ml.) was added and the solution refluxed 3 hours. The resulting

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(10) T. Zincke and F. Farr, *Ann.*, **391**, 55 (1912).

(11) J. Post and E. Hardtung, *Ber.*, **13**, 40 (1880); M. Boyle, *J. Chem. Soc.*, **95**, 1708 (1909); F. Bayer and Co., German Patent 295,547 [*cf. Chem. Zentr.*, **88**, II, 780 (1916)].

(12) We are indebted to Dr. Adalbert Elek and Mr. W. J. Schenck for the microanalyses. The melting points recorded are not corrected.

(13) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).

(14) N. Kharasch, H. L. Wehrmeister and H. Tigerman, *ibid.*, **69**, 1612 (1947).

(15) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

suspension was filtered while hot to remove insoluble VII, and the filtrate concentrated to small volume by aspirating the solvent. After refrigerating for several hours, the crop of nearly white needles of 2-amino-4-nitrobenzenesulfonic acid (III) was collected and dried. Additional quantities of the acid were obtained by further concentrating and refrigerating the mother liquor. The total yield of the sulfonic acid (practically pure, as obtained), was 2.2 g. (70%). A similar hydrolysis of 2,4-dinitrobenzenesulfenyl chloride yielded the same product, but only in 40% yield; and from 2,4-dinitrobenzenesulfenamide only a 20% yield of III resulted. The analytical sample was prepared by repeated crystallization from water. The product decomposed at 305–310°.

Anal. Calcd. for $C_6H_6O_5N_2S$: neut. equiv. 218; C, 33.03; H, 2.77; N, 12.84. Found: neut. equiv. 213; C, 33.18; H, 2.77; N, 13.04.

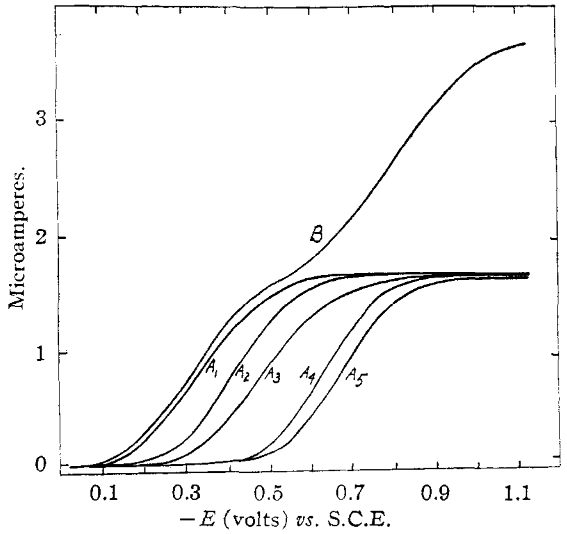

Fig. 1.—Polarographic reduction of 2-amino-4-nitrobenzenesulfonic acid, 10^{-3} *M* (curves A_1 to A_5, at *p*H values 1.0, 2.8, 5.0, 8.1 and 9.0, respectively); and of 2,4-dinitrophenol (curve B), 10^{-3} *M*, at *p*H 3.3.

The S-benzylthiuronium salt of the above acid crystallized from alcohol as orange-yellow needles, m.p. 136–137°.

Anal. Calcd. for $C_{14}H_{15}N_4O_6S_2$: C, 43.85; H, 3.94; N, 14.61. Found: C, 44.03; H, 4.24; N, 14.91.

2-Nitro-4-aminobenzenesulfonic acid was prepared from *m*-nitroaniline by the method of Nietzki and Helbach.[9] The S-benzylthiuronium salt of this acid, rhombic olive crystals, melted at 177–180°.

Anal. Calcd. for $C_{14}H_{15}N_4O_5S_2$: C, 43.85; H, 3.94; N, 14.61. Found: C, 43.69; H, 3.77; N, 14.82.

Both 2-amino-4-nitrobenzenesulfonic acid (our product) as well as 4-amino-2-nitrobenzenesulfonic acid yielded 2,4,6-tribromo-3-nitroaniline, which was identical with the authentic product prepared by bromination of *m*-nitroaniline. The tribromo compound obtained from 2-amino-4-nitrobenzenesulfonic acid melted at 102°, and was analyzed.

Anal. Calcd. for $C_6H_3O_2N_2Br_3$: C, 19.22; H, 0.81. Found: C, 19.54; H, 0.83.

There was no depression in m.p. of a mixture of the above products with a sample of 2,4,6-tribromo-3-nitroaniline, prepared from *m*-nitroaniline.[16] A typical indicator dye (similar to methyl orange) resulted when diazotized III was coupled with dimethylaniline.

Polarographic comparison of III with dinitrophenol (Fig. 1) showed only one nitro group in III. The reductions of 2-amino-4-nitrobenzenesulfonic acid were carried out at several *p*H values. Plotting the half-wave potentials for A_1 to A_5 (respectively, 0.32, 0.34, 0.42, 0.49 and 0.67 v.) against the corresponding *p*H gives a linear relation. The determinations were carried out with a manually operated Fisher Elecdropode. The concentration of nitro compound in each case was 10^{-3} *M*, and drop time was one drop per three seconds at 21 ± 1°. Degassing was carried out for 15 minutes with nitrogen flowing at 1.5 ml. per sec. Potassium chloride (1 *N*) was used as the supporting electrolyte, and 0.01% of gelatin was used as maxima suppressor. Buffering between *p*H 1.2–3.2 was done with 0.2 *M* sodium hydroxide, regulated to the desired *p*H with hydrochloric acid; for *p*H 3.9–5.8, 0.2 *M* sodium acetate, regulated with acetic acid, was used; and *p*H 8.6–10.5 was obtained with 0.2 *M* sodium hydroxide, adjusted to the desired *p*H with ammonium chloride.

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[16] E. Nolting and A. Collin, *Ber.*, **17**, 266 (1884).

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[Contribution from the Department of Chemistry and Laboratory for Nuclear Science and Engineering, Massachusetts Institute of Technology]

Hydrolysis of Alkyl Halides and Sulfonium Salts by Light and Heavy Water[1]

By C. Gardner Swain, Robert Cardinaud and Arthur D. Ketley

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t-Butyl chloride hydrolyzes 40% faster in light water than in heavy water, whereas *t*-butyldimethylsulfonium ion and methyl halides hydrolyze at the same rate in the two media. The reaction of methyl halides with pyridine also is unaffected by this solvent change. The significance of these results is discussed.

One of the most powerful and subtle methods for studying reaction mechanisms involves measuring the difference in chemical reactivity between two isotopes of the same element, *i.e.*, the so-called "isotope effect." We have measured rates of some especially simple reactions in both light and heavy water (protium and deuterium oxides) to learn more about the role of the medium. The results are shown in Table I.

Methyl halides react at the same rate in the two solvents within experimental error, with either water or pyridine. On the other hand, *t*-butyl chloride hydrolyzes 40% faster in light than in heavy water. This compound is much more dependent on electrophilic solvation in the rate-determining step and more discriminating between different electrophilic reagents than the methyl halides.[2] Although light and heavy water have

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[1] Supported in part by the programs of research of the Atomic Energy Commission and the National Institutes of Health.

[2] Relative rates of solvolysis in 100% ethanol, 50% acetone–50% water and water are 1:10:27 for methyl bromide at 50° but 1:1900:340,000 for *t*-butyl chloride at 25°. The entropy of activation of hydrolysis of methyl chloride in water at 38° is −8 e.u. (E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949)) whereas our data give + 9 e.u. for *t*-butyl chloride (and + 20 e.u. for *t*-butyldimethylsulfonium ion) in 90% water–10% dioxane at 25°. The transition state for *t*-butyl chloride is thus much looser, *i.e.*, there is considerably more disruption of the carbon–halogen bond and of water–water hydrogen bonds at the transition state with *t*-butyl chloride than with methyl chloride.