[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY OF GENERAL ANILINE & FILM CORPORATION]

Reaction of Diazo Compounds with Sulfamic Acid

BY H. W. GRIMMEL AND JACK F. MORGAN

Sulfamic acid has long been used both in industry and in the laboratory to remove excess nitrous acid following diazotization of amines. Obviously, it has been generally assumed that the diazo compounds were unaffected by sulfamic acid under the conditions employed. It has been demonstrated in this Laboratory that a number of diazo compounds do react with sulfamic acid even in strongly acid solution. In fact, in certain cases this reaction is a rapid and quantitative one yielding the products shown in the net equation

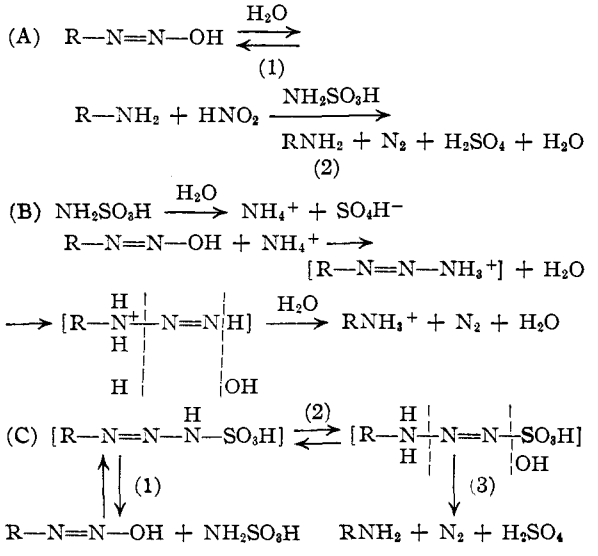
$$R{-}N{=}N{-}OH + NH_2SO_3H \longrightarrow RNH_2 + H_2SO_4 + N_2$$

Scope of the Reaction

Only the most reactive diazo compounds are capable of reacting with sulfamic acid in mineral acid solution. For example, diazo compounds derived from *p*-chloroaniline, aniline or *p*-toluidine do not react with sulfamic acid in strong acid solution. 2,5-Dichloroaniline and *p*-nitroaniline yield diazo compounds which react very slowly with sulfamic acid while the diazo compounds from 2,4-dinitroaniline and 2,6-dichloro-4-nitroaniline react quite rapidly. Most reactive of all are the diazo compounds derived from 5-aminotetrazole and 5-amino-1,2,4-triazole-3-carboxylic acid.

Mechanism

Three explanations of the reaction are listed. Evidence will be presented to show that the first two, A and B, are untenable and that C is probably a true picture of what takes place.



Explanation A is incorrect. If equilibrium (1) existed and the sulfamic acid were merely reacting with nitrous acid, it is obvious that the role of sulfamic acid in (2) could be played by urea. However, it was shown by experiment that urea did not react at all to reverse the diazotization reaction.

Explanation B breaks down on at least two counts. First of all the hydrolysis of sulfamic acid in cold strongly acid solution is at least ten thousand fold too slow to account for the reaction. The reaction of excess sulfamic acid with the diazo compound derived from 5-amino-1,2,4-triazole-3-carboxylic acid at 0–5° is complete within five minutes. However, no barium sulfate precipitate results when an aqueous solution of sulfamic acid, hydrochloric acid, and barium chloride is kept at 5° for a week. Secondly, the 5-diazo-1,2,4-triazole-3-carboxylic acid did not react at all with ammonium chloride in dilute hydrochloric acid.

Explanation C is proposed as the correct mechanism for the reaction. Since the first stage of the reaction does not involve hydrolysis of either of the two reactants (mechanisms A or B) it follows that the first step in the reaction directly involves the diazo compound and the sulfamic acid *per se*. Step (1) of mechanism C appears to be the only logical way for the reaction to start if the final products are to include nitrogen and the original amine.

Experimental

5-Diazo-1,2,4-triazole-3-carboxylic Acid.[1]—5-Amino-1,2,4-triazole-3-carboxylic acid (50 g.) was dissolved by warming in water (400 ml.) and concentrated hydrochloric acid (200 ml.). Diazotization was effected at −5° by addition of a slight excess of sodium nitrite solution. The white solid diazo compound was separated by filtration, washed thoroughly with ice water and pressed on the funnel. One gram of this stable presscake was titrated in cold acid solution with 0.05 *N* 2-naphthylamine hydrochloride solution to determine its strength. The yield of isolated diazo compound usually amounted to 75% of the theoretical.

(a) Reaction with Sulfamic Acid.—The filter cake of the diazo compound (0.05 mole) was slurried in 1 *N* hydrochloric acid solution (200 ml.) and treated with a solution (100 ml.) of sulfamic acid (0.15 mole). Nitrogen was evolved rapidly and the diazo compound was entirely destroyed within five minutes as shown by failure to couple with β-naphthylamine. When acidic solutions of ammonium chloride or urea replaced the sulfamic acid solution, no reaction took place even in several days.

In a second experiment a suspension of the diazo compound was "reversed" to the amine with a slight excess of sulfamic acid, rediazotized, and the newly formed precipitate removed by filtration. This precipitate proved to be identical with the original diazo compound by identical X-ray diffraction patterns.

In a third experiment aliquots of a dilute solution of diazotized 5-amino-1,2,4-triazole-3-carboxylic acid were (a) titrated with 0.05 *N* 2-naphthylamine hydrochloride and (b) "reversed" to the amine with sulfamic acid, rediazotized, and titrated with 2-naphthylamine. The results of these titrations gave a minimum of 94% yield for the "reversal" and rediazotization.

(1) W. Manchot and R. Noll, *Ann.*, **343**, 1 (1905).

Comparison of Reaction Rates of Various Diazo Compounds with Sulfamic Acid.—Tenth normal solutions of diazo compounds were prepared by known procedures and 50-ml. aliquots (0.005 mole) employed in each experiment. For each diazo compound the 50-ml. aliquots were treated with solutions (50 ml.) containing 0, 1, 10, or 20 equivalent amounts of sulfamic acid and the nitrogen gas evolved measured continuously by means of a rate nitrometer.[2] In all cases the *p*H was <1 and the temperature 25° except in the case of diazotetrazole which was run at 0–5°.

The original amine was isolated and identified as the primary reaction product except in the case of 2-chloro-4-nitroaniline. In this latter case, the diazoamino compound was isolated in good yield with the expected (50%) amount of N_2 liberated. Typical reaction rate curves are shown in Fig. 1.

2,5-Dichloroaniline and *p*-Nitroaniline.—The diazo compounds of these two amines were not sufficiently reactive for study with the rate nitrometer. Consequently, 0.05 *N* solutions of these diazo compounds were treated with 0, 1 and 10 equivalent amounts of sulfamic acid and stored at 5° for ten days. At the end of this time the solutions were filtered and the amounts of solid diazoamino compounds determined. Yields are given in Table I.

TABLE I

YIELD OF DIAZOAMINO COMPOUNDS

Sulfamic acid	% Yield from diazotized *p*-nitroaniline	% Yield from diazotized 2,5-dichloroaniline
None	..	..
1 equiv.	3.6	6.2
10 equiv.	12.0	19.0

Summary

1. Certain diazo compounds were shown to react with sulfamic acid in acid solution to yield the original amine from which the diazo compound was derived together with nitrogen and sulfuric acid.

2. A mechanism has been proposed to explain the reaction.

3. Relative reaction rates of various diazo compounds with sulfamic acid were compared by means of a rate nitrometer.

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(2) M. L. Crossley, R. H. Kienle and C. H. Benbrook, *Ind. Eng. Chem., Anal. Ed.*, **12**, 216 (1940).

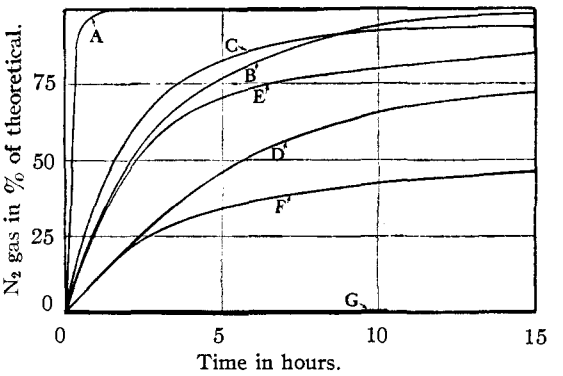

Fig. 1.—Rates of reaction of the diazo compounds of the following amines with sulfamic acid at the indicated concentration: A, 5-aminotetrazole, 20 equivalents of sulfamic acid; B, 2,4-dinitroaniline, 10 equivalents of sulfamic acid; C, 2,6-dichloro-4-nitroaniline, 20 equivalents of sulfamic acid; D, 2,6-dichloro-4-nitroaniline, 1 equivalent of sulfamic acid; E, 2-amino-5-nitro-N-ethylbenzenesulfonanilide, 20 equivalents of sulfamic acid; F, 2-chloro-4-nitroaniline, 20 equivalents of sulfamic acid; G, blank.

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, COLLEGE OF AGRICULTURE, THE DEPARTMENT OF BACTERIOLOGY, UNIVERSITY OF CALIFORNIA, AND THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

α-L-Glucose-1-phosphate

BY A. L. POTTER, JOHN C. SOWDEN, W. Z. HASSID AND M. DOUDOROFF

An enzyme obtained from the bacterium *Pseudomonas saccharophila* has been named sucrose phosphorylase because it catalyzes the reversible reaction between fructose and α-D-glucose-1-phosphate to form sucrose. This enzyme is also capable of catalyzing the reaction between other monosaccharides and the same ester, thus forming a number of disaccharides, namely, D-glucosido-L-sorboside, D-glucosido-D-xyloketoside, D-glucosido-L-araboketoside, and D-glucosido-L-arabinose.[1] The formation of these disaccharides demonstrates the versatility of the enzyme with regard to the non-glucose substrates which act as "glucose acceptors" in the synthetic reactions. However, the enzyme appears to be specific toward the glucose portion of its substrate. It has been found that the sucrose phosphorylase will not form compound sugars when α-maltose-1-phosphate, α-D-galactose-1-phosphate, or α-D-xylose-1-phosphate is substituted for α-D-glucose-1-phosphate. Similarly, potato and muscle phosphorylases will not form polysaccharides when these phosphorylated sugars are substituted for α-D-glucose-1-phosphate.

In this connection, it was of interest to test whether or not α-L-glucose-1-phosphate could be substituted for its optical isomer, α-D-glucose-1-phosphate in the enzymatic reaction with potato phosphorylase for polysaccharide synthesis or with sucrose phosphorylase for disaccharide formation.

In the present work the preparation of α-L-glucose-1-phosphate from L-glucose is described and

(1) M. Doudoroff, W. Z. Hassid and H. A. Barker, *J. Biol. Chem.*, **168**, 733 (1947); W. Z. Hassid, M. Doudoroff, A. L. Potter and H. A. Barker, THIS JOURNAL, **70**, 306 (1948).