

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MIAMI UNIVERSITY]

The Hydrolytic Decomposition of Diazonium Salts. I. The Determination of Very Precise Rates in Very Dilute Solutions

BY JAY E. TAYLOR AND THORA J. FELTIS

A very accurate apparatus has been developed for the determination of the rate of formation of nitrogen from diazonium compounds. The outstanding features are a high speed "aeration" stirrer which will effect instantaneous desupersaturation of nitrogen, a constant pressure nitrometer, an internal temperature control unit, and a device for starting the reaction at the desired temperature. Very pure *p*-tolylidiazonium hydrogen sulfate has been prepared and its rate of hydrolytic decomposition measured at 30.00, 39.96 and 49.90°. The rate constants $\times 10^5$ are 0.960 ± 0.001 , 4.11 ± 0.02 and $15.7 \pm 0.2 \text{ sec.}^{-1}$, respectively, in 0.01059 *M* solutions. The tendency of nitrogen to supersaturate is very marked. In an unstirred solution the concentration of the dissolved gas may build up to 5.9 times its normal solubility at 40° and atmospheric pressure.

Aryl diazonium salts react in the presence of water to form the corresponding phenol and nitrogen. Although many investigations of this reaction have been made, there are insufficient data of a high order of accuracy to determine the true nature of the reaction. The authors have begun an extensive mechanism study and have found the experimental accuracy requirements very high.¹ The purpose of this paper is then to describe the precision techniques which have been developed and to present sufficient data to support their reliability. Extensive data and calculations will be presented in a forthcoming paper.

All factors which may influence the accuracy of measurement of the rate of reaction have been taken into consideration. Time was measured to the nearest five seconds or less, and the reaction temperature was held constant within $\pm 0.01^\circ$. Crystalline *p*-tolylidiazonium hydrogen sulfate of a high degree of purity was prepared and used in concentrations² of 0.01 to 0.01059 *M*. Since nitrogen, as it will be shown, may supersaturate to nearly six times its normal solubility at 40°, many developments were necessary in order that the gasometric method of analysis³ might be used. The various desupersaturating devices used by previous workers such as stirring, shaking, or bubbling carbon dioxide through the solution were quite unsatisfactory for a precise rate determination in solutions of concentration of about 0.01 *M*. After much experimentation the "aeration" stirrer^{4,5} (G and H in Fig. 1 and 2) was developed. It has given excellent results.

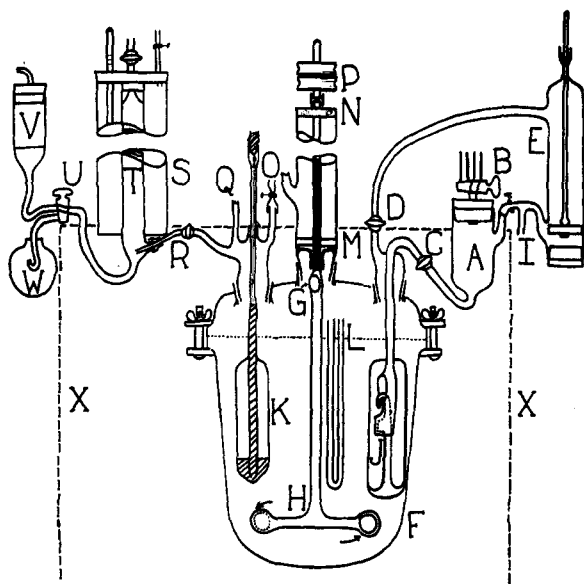


Fig. 1.—A, container (50 ml.) for solid diazonium salt; B, three-way stopcock leading to nitrogen supply and water pump; E, pump with rubber plunger; F, 500-ml. resin reaction flask (total capacity 1100 ml.); G and H, "aeration" stirrer; I, to a mercury manometer; J, removable baffle made by splitting a 30-mm. Pyrex tube in half lengthwise; K, acetone-mercury thermoregulator; L, cooling coil which enters a fourth opening in the cover; M, lucite bearing cemented to a glass inner seal; N, ball bearing; P, clutch; Q, to ethyl phthalate manometer; S, 51-mm. insulated jacket containing water from the constant temperature bath; T, 50-ml. buret filled with saturated (25°) $(\text{NH}_4)_2\text{SO}_4$ solution; V, leveling bulb containing $(\text{NH}_4)_2\text{SO}_4$ solution; W, receiver for $(\text{NH}_4)_2\text{SO}_4$ solution; X, outline of constant temperature bath.

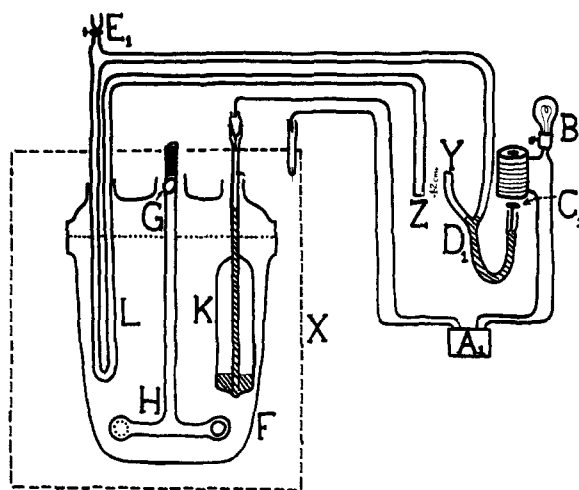


Fig. 2.—F to X, see Fig. 1; Y, cooling water inlet from a source of constant head; Z, cooling water outlet; A₁, electronic relay; B₁, series resistance; C₁, iron nail floating in mercury and electromagnet; D₁, mercury valve; E₁, air bubble trap.

(1) For example, the presence of certain salts may change the observed reaction rate constant by only a few per cent.

(2) At this concentration range the yields of phenol approach 100%. M. L. Crossley, R. H. Kienle and C. H. Benbrook, *THIS JOURNAL*, **62**, 1400 (1940).

(3) The rapidity and greater over-all reliability of the gasometric method made it preferred over precipitation, titration, or colorimetric techniques.

(4) The authors have done appreciable experimentation with ordinary stirrers. In all cases there was a period of induction followed by a flow of nitrogen more or less dependent on the rate of stirring.

(5) The authors are indebted to Dr. Floyd L. James, Miami University, for the suggestion of the principle of the stirrer.

Tiny gaseous nuclei serving as desupersaturation centers are responsible for the effectiveness of this "aeration" stirrer. The stirrer is a modified inverted T-tube which rotates very rapidly. The lowered pressure in the wake of the rotating blades causes a flow of nitrogen from the upper opening to be dispersed into the solution through the open ends of the blades. The relatively large openings increase agitation and thus further promote aeration by increasing the flow of gas and decreasing the bubble size.

A device for rapid mixing of the diazonium salt with water at the desired temperature, an internal temperature control unit, and a device which maintains a constant pressure in the reaction flask at all times and yet allows the change in volume to be accurately measured were incorporated into the apparatus. Using these refinements the starting time and concentration of the reactant could be exactly determined. The temperature and pressure inside the flask were constant from the starting time until the completion of a reaction. No approximation methods such as graphing to determine the starting time or concentration were necessary.

The high precision of the apparatus, particularly at the lowest temperature, may be clearly seen from the data in Table I. Further the close obedience of the stirred reactions to the first order rate equation is demonstrated in Fig. 3 by the straight lines beginning at the origin. There is obviously no period of induction or other variation. The excellent efficiency of the stirrer was shown by stopping it for periods of several minutes during a run. There was no discernible effect upon the observed rate constants. The stirrer has been further shown to effect release of the bulk of the excess nitrogen from a supersaturated solution within a few seconds time. At 30° the deviation averages about $\pm 0.1\%$, and this value is undoubtedly a reasonable approximation of the

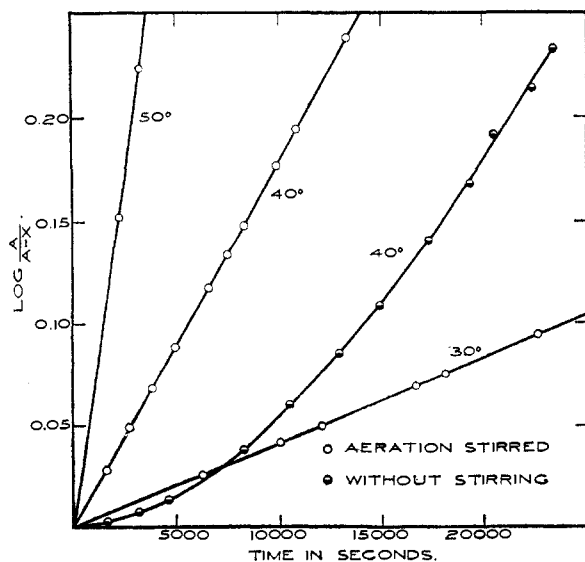


Fig. 3.—The first order nature of the decomposition of *p*-tolyldiazonium hydrogen sulfate: without stirring, $A = 0.01 M$; with stirring, $A = 0.01059 M$.

absolute accuracy of the apparatus at this temperature. In view of the accuracies usually attained in kinetic studies this value is excellent.

TABLE I
REACTION RATE CONSTANTS AND DEVIATIONS, 0.01059 *M*
p-TOLYLDIAZONIUM HYDROGEN SULFATE

<i>t</i> , °C. ± 0.02	$k \times 10^3$ sec. ⁻¹	No. of points averaged ^a	Average deviation	Maximum deviation
30.00	0.960	10	0.001	0.003
39.96	4.11	11	.02	.05
49.90	15.7	7	.2 ^b	.3

^a At 30° the reaction rate constants were measured between 6 and 32% completion, at 40° between 6 and 45% completion, and at 50° between 30 and 72% completion. ^b Since the construction materials used limited the temperature to about 50°, the reliability of the data at this temperature may not be as high as is inferred by the average deviation.

In the majority of studies dealing with gases the supersaturation factor has been either ignored or very lightly treated. The tendency of nitrogen to supersaturate is very marked as evidenced by Fig. 4. At any given point on the time axis the numerical difference between the ordinates of the two curves is the value in moles per 900 ml. of the amount of supersaturated nitrogen contained in the unstirred solution. The maximum was at 15,000 seconds when the concentration of dissolved nitrogen in excess of its normal solubility was 2.12×10^{-3} mole per 900 ml. at 737 mm. (atmospheric pressure) and 40°. At this same temperature and total pressure the solubility of nitrogen is 4.82×10^{-4} mole per liter.⁶ The concentration of the dissolved nitrogen was then 5.9 times that of a saturated solution.

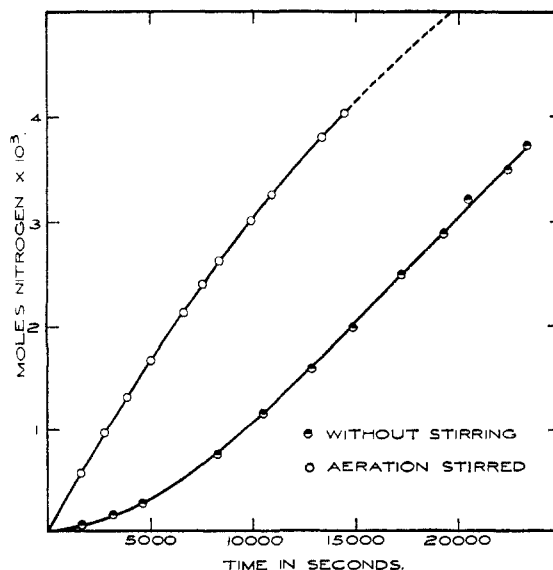


Fig. 4.—Decomposition of *p*-tolyldiazonium hydrogen sulfate: effect of stirring upon the rate of evolution of nitrogen at 40°; unstirred solution, 0.009 mole in 900 ml.; stirred solution, 0.009 mole in 850 ml.

Experimental

Preparation of the Crystalline *p*-Tolyldiazonium Hydrogen Sulfate.—A solution containing 5.35 g. of *p*-toluidine (re-

(6) "Handbook of Chemistry and Physics," 30th Ed., Chemical Rubber Publishing Co., Cleveland, O., 1948, p. 1396.

crystallized four or more times from petroleum ether) and 4.5 ml. of 95% sulfuric acid in 14 ml. of water was cooled to 0° with the formation of a thick paste of the precipitated sulfate. Ethyl nitrite was bubbled with stirring into this paste until the precipitate almost completely dissolved. The temperature was maintained between 0 and 5°. This solution was filtered through a sintered glass funnel, and then was mixed with 150 ml. of cold acetone. The white crystalline solid which precipitated was filtered into a sintered glass funnel, washed five or six times with acetone, and then was dried by drawing air, desiccated with sulfuric acid, through the crystalline salt. The diazonium salt was very white and of high purity. It may be preserved for long periods of time in the dark at a freezing temperature.

Anal. HSO₄, 44.7; calcd. 44.9; C₇H₇N₂ (by precipitation with β -naphthol and purifying and weighing the product), 55.2, calcd. 55.1.

Description of the Apparatus. (a) **The Mixing of the Diazonium Salt with Water.**—After the apparatus had been set up, 850 ml. of doubly distilled water was placed in the reaction flask (F, Fig. 1). While the water came to temperature in the bath (constant within $\pm 0.01^\circ$) the entire system was flushed out with nitrogen. Next 1.9460 g. (0.009 M) of the crystalline diazonium salt was placed in tube A. Tubes A and E were then filled with nitrogen. To start the run stopcocks C and D were opened and plunger E was raised. The water drawn into Tube A dissolved the diazonium salt, and this solution was immediately forced back into the reaction flask. After several rinsings stopcocks C and D were closed. The pressure inside the reaction flask was equalized to atmospheric pressure by opening the outlet at O. The time at which the diazonium salt first dissolved was taken as the starting time.

(b) **The Stirrer.**—The efficiency of the apparatus de-

(7) Ordinary stopcock greases were generally unsatisfactory at 40 or 50°, and silicone grease was unsatisfactory at any temperature. A very satisfactory stopcock preparation was made by emulsifying finely powdered graphite with a rubber base stopcock grease.

pended upon the efficiency of the "aeration" stirrer. The speed of rotation was 1750 r.p.m. In order to avoid vibration the stirrer was kept carefully balanced and centered. Paraffin sealed the lucite bearings at M against mercury leakage, and the mercury seal made the bearing gas tight.

Since an overly rapid rotation of the solution reduced the efficiency of the aeration process by reducing the speed of flow of the liquid past the stirrer outlets, the baffle at J was introduced to slow the rate of flow of the liquid.

The heat resulting from stirring has caused a temperature rise as much as 0.2°. Therefore, it was necessary to install a temperature control unit inside the reaction flask. The diagram of the system is shown in Fig. 2. The flow of cooling water through tube L was controlled by the magnetic mercury valve at D₁. In operation this unit allowed a temperature variation of less than $\pm 0.01^\circ$.

(c) **The Measurement of Gas Volume.**—While the stirrer was in operation stopcock R was kept open, and the three-way stopcock U was turned so that the ammonium sulfate solution, which was replaced by the nitrogen bubbling into buret T, dripped into flask W. Since the outlets at W and R were stationary and approximately equal in height, a pressure equal to atmospheric was maintained within the reaction flask. When it was desired to read the volume of gas in the buret, the stirrer was stopped, the pressure in the reaction flask was exactly equalized to atmospheric pressure by tapping the tube at R and observing the manometer at Q. Stopcock R was then closed and stopcock U reversed. The nitrogen within the buret was adjusted to atmospheric with the aid of the leveling bulb V. After the reading had been taken this procedure was reversed, and the collection of nitrogen continued again. The observed volumes were corrected to standard conditions with the aid of the readings of the temperature of the buret jacket, the reading of atmospheric pressure, and the value for the vapor pressure of the ammonium sulfate solution. If there was a change of atmospheric pressure during a run, a small correction was made for the change in volume of the gas within the reaction flask.

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[CONTRIBUTION NO. 1614 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Coördination of Silver Ion with Unsaturated Compounds. IV. The Butenes¹

BY F. R. HEPNER, K. N. TRUEBLOOD AND H. J. LUCAS

The coördination of aqueous silver ion with the four isomeric butenes has been studied by a distribution method. The constants K_f for the formation of 1:1 complexes are: 1-butene, 119.4; *cis*-2-butene, 62.3; *trans*-2-butene, 24.6; 2-methylpropene, 71.5. This variation is provisionally interpreted in terms of steric effects involving the hydrated silver ion. Approximate values for the constants for the formation of the comparatively unimportant disilver complexes are estimated.

Within recent years there has been a growing interest in three-membered cyclic positive ions because of their importance as intermediate species in organic reactions. Such ions may be formed in a variety of ways, such as coördination of a metallic ion with an olefinic compound,² coördination of a metallic ion with an acetylenic compound,³ or participation of a neighboring atom or group during various reactions.⁴ The transient formation of

(1) Some preliminary results were presented at the 25th meeting of the Pacific Division, A.A.A.S., Pasadena, California, June 20, 1941.

(2) (a) W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas, *THIS JOURNAL*, **59**, 45 (1937); (b) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (c) H. J. Lucas, F. Hepner and S. Winstein, *ibid.*, **61**, 3102 (1939); (d) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943); (e) H. J. Lucas, F. W. Billmeyer, Jr., and D. Pressman, *ibid.*, **65**, 230 (1943); (f) R. M. Keefer and L. J. Andrews, *ibid.*, **71**, 1723 (1949); R. M. Keefer, L. J. Andrews and R. E. Kepner, *ibid.*, **71**, 2381, 3906 (1949).

(3) See for example R. N. Keller, *Chem. Rev.*, **28**, 239 (1941); A. Hel'man, S. Bukhovets and E. Meilakh, *Compt. rend. acad. sci. U.R.S.S.* **46**, 105 (1945); W. S. Dorsey, Ph.D. Thesis, California Institute of Technology, 1950.

(4) For a general review see S. Winstein, *Bull. soc. chim.*, [5] **18**, C. 55 (1951).

cyclic ions in the addition of halogens to olefinic compounds explains the well-known phenomenon of *trans* addition.^{4,5}

These three-membered cyclic positive ions may be formulated as resonance hybrids of a number of simple structures^{2b,4}; alternatively, it is sometimes useful to consider them as π -complexes formed by the interaction of the coördinating ion with the π -orbitals of the unsaturated compound.⁶ The latter view is especially attractive in extending the picture to coördination with aromatic compounds.⁷⁻¹⁰

The present study of the complexes formed by

(5) I. Roberts and G. E. Kimball, *THIS JOURNAL*, **59**, 947 (1937).

(6) M. J. S. Dewar, *Nature*, **156**, 784 (1945); *J. Chem. Soc.*, 406, 777 (1946); A. D. Walsh, *Nature*, **159**, 165, 712 (1947); A. E. A. Werner, *ibid.*, **160**, 644 (1947); M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

(7) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

(8) H. C. Brown and J. Brady, *ibid.*, **71**, 3573 (1949).

(9) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(10) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).