

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the *o*-Semidine Rearrangement of *p*-Hydrazotoluene and of the Accompanying Disproportionation and Reduction Reactions¹

BY ROBERT B. CARLIN AND GROSVENOR S. WICH²

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The rate of conversion of *p*-hydrazotoluene in 95% ethanolic hydrochloric acid to 2-amino-4',5-dimethyldiphenylamine (an *o*-semidine), *p*-toluidine and *p*-azotoluene is first order in concentration of hydrazo compound and second order in acid concentration. The product distribution could be measured with an average precision of only about $\pm 5\%$ by means of the spectrophotometric analytical method employed to follow rates, but within this limit it appeared that the distribution did not change during a rate run, nor was it affected by changes in temperature, ionic strength or dielectric constant of the medium. A positive salt effect was observed, and a small rate increase occurred when the solvent was changed from 95 to 75% aqueous ethanol. The facts that all three reactions that occur simultaneously under these conditions follow the same kinetic law and that the product distribution is unaffected, within experimental error, by change in conditions, seem most nearly consistent with the postulate that all three reactions have the same rate-determining sequence, probably the formation in two steps of the second conjugate acid of *p*-hydrazotoluene, and that this sequence is followed by three fast, concurrent reactions from the common intermediate. The formation of most of the *p*-azotoluene and of an equivalent weight amount of *p*-toluidine must be attributed to a disproportionation reaction. A nearly 2:1 weight excess of *p*-toluidine over *p*-azotoluene in the products can be rationalized only by postulating a reduction, presumably by solvent ethanol, of *p*-hydrazotoluene or its conjugate acids.

Although the kinetics of the rearrangements of aromatic hydrazo compounds have been extensively studied, particularly in recent years,³ nearly all of the compounds examined have been those known to yield products of the diaminobiphenyl or benzidine, type. Only Biilman and Blom,^{3b} who measured the rate of transformation of 3,3'-diamino-4,4'-dimethylhydrazobenzene, Dewar,^{3c} who determined rate constants for the reactions of *p*-hydrazotoluene in buffered acid solutions, and Bunton, Ingold and Mhala,^{3j} who also observed the rate of transformation of *p*-hydrazotoluene in acidic aqueous dioxane, have studied compounds that cannot yield benzidines on rearrangement. *p*-Hydrazotoluene in aqueous or alcoholic mineral acids had earlier been shown⁴ to form an *o*-aminodiphenylamine (an *o*-semidine) along with the disproportionation products *p*-azotoluene and *p*-toluidine. The product(s) from 3,3'-diamino-4,4'-dimethylhydrazobenzene were not determined; Biilman and Blom assumed that an *o*-semidine was the chief product. The order of involvement of acid concentration in the rate expression was not investigated during Dewar's study of the rearrangement of *p*-hydrazotoluene; Ingold's group observed that the pseudo first-order rate constant for the transformation of *p*-hydrazotoluene was proportional to the square of the acid concentration; and Biilman and Blom submitted evidence indicating that their pseudo first-order rate constants for the transformation of the diaminodimethylhydrazobenzene were proportional to the square root of acid concentration at constant ionic

strength, but of course the presence of two amino groups in the hydrazo compound complicates the interpretation of this observation. The significance of all three investigations is impaired because the rate measurements were carried out on unknown total reactions; in no case were the products determined under the conditions imposed in the kinetic runs, so that the contribution of disproportionation and of other possible side reactions to the total reactions of the two aromatic hydrazo compounds remains unknown. Thus it is that even the limited kinetic data now in existence pertaining to the reactions of aromatic hydrazo compounds that should rearrange to semidines may not actually represent measurements on the semidine rearrangement.

The work described in this report was undertaken in an effort to obtain unequivocal kinetic data on a semidine rearrangement; this information is necessary to afford a comparison of the semidine with the closely related benzidine rearrangement. A search of the literature revealed that a semidine rearrangement unaccompanied by disproportionation and perhaps other side reactions probably could not be found⁵; indeed, *p*-hydrazotoluene, which was reported to yield an *o*-semidine as the principal product and no by-products other than those of disproportionation, appeared to be the compound likely to give an *o*-semidine rearrangement least complicated by side reactions. The first experiments in the present investigation consisted in thirteen rearrangements, each of five or more grams of *p*-hydrazotoluene, by hydrogen chloride under a variety of conditions, including some that approached those to be imposed in the rate runs. Three products, and no others, were isolated from these reactions: 2-amino-4',5-dimethyldiphenylamine, the *o*-semidine (I); and the disproportionation products *p*-azotoluene and *p*-toluidine. Although an accounting for more than half of the initially charged *p*-hydrazotoluene could not be given after any of the thirteen experiments, most of the losses apparently were caused by the water solubility of the components of the mixture, particularly that of *p*-toluidine. Accordingly, a

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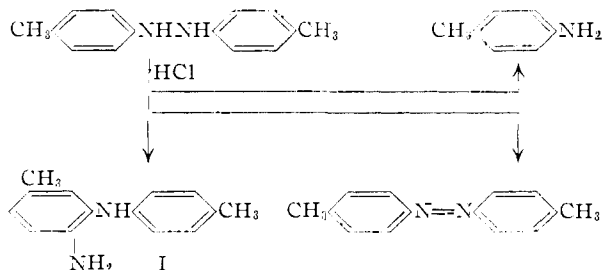
(2) National Science Foundation Fellow, 1952-1953.

(3) (a) J. P. Van Loon, *Rec. trav. chim.*, **23**, 62 (1904); (b) E. Biilman and J. H. Blom, *J. Chem. Soc.*, **125**, 1719 (1924); (c) M. J. S. Dewar, *ibid.*, **777** (1946); (d) G. S. Hammond and H. J. Shine, *This Journal*, **73**, 220 (1950); (e) R. B. Carlin, R. G. Nelb and R. C. Odioso, *ibid.*, **73**, 1002 (1951); (f) M. D. Cohen and G. S. Hammond, *ibid.*, **75**, 880 (1953); (g) L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953); (h) R. B. Carlin and R. C. Odioso, *ibid.*, **76**, 100, 2345 (1954); (i) G. S. Hammond and W. Grundemeier, *ibid.*, **77**, 2444 (1955); (j) C. A. Bunton, C. K. Ingold and M. M. Mhala, *J. Chem. Soc.*, 1906 (1957); (k) D. A. Blackadder and C. N. Hinshelwood, *ibid.*, 2898 (1957).

(4) E. Täuber, *Ber.*, **25**, 1019 (1892); F. Melnas, *ibid.*, **3**, 549 (1870); A. Goldschmidt, *ibid.*, **11**, 1624 (1878).

(5) Cf. P. Jacobson, *Ann.*, **428**, 76 (1922).

spectrophotometric analytical method for following the concentrations of all of the components of the reaction throughout its course was prepared on the assumption that only the three products isolated and unchanged *p*-hydrazotoluene would be present in the solutions during the kinetic runs. Development of this analytical scheme followed somewhat similar, but simpler, procedures employed in previous investigations.^{3e,b} The complex analysis of the four-component mixture encountered in this work is described in the Experimental section. Application of this analytical method, suitably tested on known solutions, to kinetic runs disclosed that all of the hydrazotoluene initially charged could be accounted for throughout the course of each run, within experimental error. Therefore, the assumption that no more than three products were formed under these conditions apparently was justified.



Experimental

Materials. *p*-Hydrazotoluene.—A vigorously stirred, hot suspension of 317 g. of 90% zinc dust in a solution of 118 g. of recrystallized *p*-nitrotoluene in 945 ml. of methanol was treated with a solution of 264 g. of sodium hydroxide in 630 ml. of water at a rate sufficient to maintain gentle boiling. Following the addition of the sodium hydroxide, boiling was continued for two hours; then the gray-white mixture was filtered quickly through a large, preheated Buchner funnel. The collected solid was not permitted to dry but was extracted immediately with hot benzene. Concentration of the benzene solution yielded 79 g. (85%) of yellow-orange flakes, m.p. 121–126°. Reported m.p.'s for *p*-hydrazotoluene have ranged all the way from 124° to 135°; it seems likely that the compound exists in polymorphic modifications.

Reversing the order of addition of the zinc dust and the sodium hydroxide gave a mixture that was substantially more difficult to work with; the yield of product was 73%. An attempt to effect the reduction by means of zinc dust and acetic acid in hot ethanol solution gave but a 26% yield of impure *p*-hydrazotoluene.

For spectroscopic studies, nearly colorless *p*-hydrazotoluene was prepared from purified *p*-azotoluene (see below) by an adaptation of the method of Biehringer and Busch.⁷ A solution of 8 g. of *p*-azotoluene in 250 ml. of hot ethanol and 20 ml. of glacial acetic acid was treated with enough zinc dust to bring the color of the solution to a pale yellow. Partially oxidized (crude) *p*-hydrazotoluene samples were purified by subjecting them to the same procedure, except that only 5 ml. of glacial acetic acid was used. The mixture was filtered under an atmosphere of purified nitrogen through a Celite bed, and the filtrate was diluted with its own volume of water and cooled. The precipitated snow-white plates were collected by filtration, washed repeatedly with water and dried between sheets of filter paper. Pale yellow plates, m.p. 119–122°, obtained by this means were stable when stored at 0°, but ethanol solutions colored rapidly when exposed to air at room temperature.

(6) F. Helms, *Ber.*, **3**, 553 (1870); J. V. Janovsky, *Monatsh.*, **9**, 829 (1888); B. Rasso and K. Rülke, *J. prakt. Chem.*, [2] **65**, 108 (1902); G. O. Curme, Jr., *THIS JOURNAL*, **35**, 1171 (1913); E. Bamberger, *Ber.*, **69**, 427 (1926); M. Busch and K. Schultze, *ibid.*, **62**, 146; (1929).

(7) J. Biehringer and A. Busch, *ibid.*, **36**, 339 (1903).

Purification of crude *p*-hydrazotoluene could also be effected by saturating its ethanol solution with hydrogen sulfide over a 30-minute period and allowing the solution to stand stoppered under hydrogen sulfide overnight. The filtered solution was diluted with water, and the precipitated hydrazo compound was finally obtained as yellow plates, m.p. 122.5–126.5°, by reprecipitation from its ethanol solution by addition of water.

***p*-Azotoluene.**—Reduction of 13.0 g. of *p*-nitrotoluene in 100 ml. of methanol by 15.2 g. of 90% zinc dust and a solution of 16.6 g. of sodium hydroxide in 40 ml. of water followed the procedure used to prepare the corresponding hydrazo compound, except that the mixture was boiled for 4 hours following addition of the alkali. The filtered solids were extracted with petroleum ether (b.p. 65–110°), and concentration of the extracts afforded 6.38 g. (78%) of an orange-yellow solid, m.p. 108–115°. This crude material was dissolved in benzene-petroleum ether, and the solution was filtered and concentrated until the solid reappeared. The solid was recrystallized from petroleum ether and then from ethanol-water, shaken with hydrochloric acid, washed with water, again recrystallized from ethanol-water, from benzene, and finally five times from ethanol. Samples obtained in this manner formed transparent orange needles, m.p. 141.5–143.8° (cor.). Cook⁸ reported m.p. 105° for *cis*-*p*-azotoluene; the m.p. of the *trans* form has been variously reported from 140–142° to 145°.⁸

That essentially the same *p*-azotoluene is formed by disproportionation of *p*-hydrazotoluene concurrently with the latter's rearrangement was established by treatment of a solution of 6.9 g. of hydrazo compound in 200 ml. of ethanol under nitrogen with 15 ml. of 12 *N* hydrochloric acid. The mixture was stirred for 15 minutes and then chilled in ice. The *p*-azotoluene appeared in the form of fine golden needles (1.36 g., 20%), m.p. 142.5–144.2° (cor.), without further purification.

An attempt to prepare *p*-azotoluene by oxidation of an ethanol solution of *p*-hydrazotoluene with iodine gave an impure product.

2-Amino-4',5'-dimethyldiphenylamine (I).—A stirred solution of 70 g. of *p*-hydrazotoluene in 3 l. of ethanol was treated under purified nitrogen with 600 ml. of 12 *N* hydrochloric acid. The opaque solution, after chilling in ice, deposited 15.9 g. (23%) of *p*-azotoluene, which was removed by filtration. The filtrate was made basic with 600 ml. of 15 *N* aqueous ammonia, diluted with 4 l. of water and cooled. The precipitated violet-brown solid (42.8 g.) was collected by filtration, dried, and extracted in a Soxhlet apparatus with two 200-ml. portions of acetone. Concentration of the extracts afforded 11.9 g. of yellow-violet chunks, together with some tar and a chalky white inorganic powder. The yellow-violet solid was stirred vigorously with hydrochloric acid. The insoluble residue was purified by sublimation at 103–105° (1 μ), which yielded 3.33 g. of orange material, m.p. 127–130°. The acid solution deposited 2.74 g. of a dark brown solid after it was made basic with 15 *N* aqueous ammonia. Vacuum sublimation yielded two fractions: a small amount of a violet solid, which sublimed at 80–85° (0.1 mm.); and 1.60 g. (2.3%) of an orange-white solid, m.p. 102–105° (cor.), which sublimed at 103° (1 μ). Recrystallization of this material from ethanol-water yielded snow-white leaves, m.p. 106.5–107.7°. The highest reported m.p. apparently is 107°.⁴

Anal. Calcd. for C₁₄H₁₆N₂: C, 79.24; H, 7.55; N, 13.21. Found: C, 79.02; H, 7.55; N, 13.41.

The base was only sparingly soluble in hydrochloric acid, and the hydrochloride was precipitated as a pale violet powder from *n*-hexane, but not from benzene, by treating a solution of the base with dry hydrogen chloride.

***p*-Toluidine.**—Commercial *p*-toluidine was recrystallized three times from petroleum ether. Solution of this material in aqueous ethanol and subsequent cooling caused the separation of oils, from which the mother liquors were decanted, warmed again and then permitted to cool slowly. Snow white needles were formed, which, after two more recrystallizations from petroleum ether, gave white plates, m.p. 41.3–43.3° (cor.). Treatment with acetic anhydride yielded a white acetyl derivative, m.p. 148.0–149.0°. The litera-

(8) A. H. Cook, *J. Chem. Soc.*, 876 (1938).

(9) E. R. Atkinson, C. R. Morgan, H. H. Warren and T. J. Manning, *THIS JOURNAL*, **67**, 1514 (1945).

ture reports m.p.'s for aceto-*p*-toluidide ranging from 145°¹⁰ to 153°.¹¹

The presence of *p*-toluidine in mixtures resulting from the acid treatment of *p*-hydrazotoluene was demonstrated by experiments such as the following: A solution of 70 g. of *p*-hydrazotoluene in 3 l. of ethanol was treated under purified nitrogen at room temperature with 600 ml. of concentrated hydrochloric acid. At the conclusion of the reaction, the mixture was filtered free of *p*-azotoluene, and the filtrate was made basic with 12 *N* aqueous ammonia. The precipitated solids, comprising *p*-azotoluene and semidine I, were removed by filtration, and the filtrate was extracted with benzene. The dried benzene solution was treated with dry hydrogen chloride, and the precipitated pinkish powder was heated with acetic anhydride. The brown powder remaining after hydrolysis of excess acetic anhydride with water was recrystallized three times from aqueous ethanol and once from petroleum ether. The product formed tan leaves, m.p. 147.2–148.3° (cor.), which did not depress the m.p. of authentic aceto-*p*-toluidide (above) on admixture.

Ethanol.—Stock 95% ethanol was used throughout this work. This solvent showed no detectable absorption in the ultraviolet region utilized in this work; furthermore, ethanol from the same bottle was always used both to prepare sample solutions whose absorbancies were to be read and to fill the corresponding blank spectrophotometer cell.

Ethanolic Lithium Chloride.—Baker and Adamson lithium chloride was dried over phosphorus pentoxide *in vacuo* and weighed out by difference from a glass stoppered bottle, quickly transferred to a volumetric flask, and diluted with stock 95% ethanol to the mark. Required amounts were measured from this solution with a buret.

Isolation of Products from the Acid Treatment of *p*-Hydrazotoluene.—The isolation of *p*-azotoluene, *p*-toluidine and the semidine I from mixtures obtained by treating *p*-hydrazotoluene with hydrochloric acid in ethanol solutions has already been described in foregoing paragraphs. Thirteen experiments were carried out in which 5 g. or more of *p*-hydrazotoluene was treated with varying amounts of hydrogen chloride at temperatures near that of the room. In general, a solution of the hydrazo compound in ethanol was stirred and treated with concentrated hydrochloric acid. The precipitated *p*-azotoluene and the semidine I were separated from each other (with some difficulty) by hydrochloric acid extraction of the latter. The filtrate from the azotoluene and the semidine was made alkaline and was then extracted with benzene or ether to collect the remainder of the semidine I and the *p*-toluidine.

These experiments were carried out under conditions that differed in two important respects from those prevailing during the rate runs. First, the concentration of hydrazo compound had to be greater in the larger scale runs if inordinate volumes were to be avoided. Second, and for the same reason, the molar excess of hydrogen chloride over hydrazo compound was much smaller in the large scale runs than the 20:1 ratio maintained in the rate runs. Less important differences were the slightly higher (and uncontrolled) temperatures that prevailed in the large scale runs, the presence in these runs of more water in the reaction mixtures, and the smaller degree of protection afforded these mixtures against air oxidation.

In one run of 8.8 g. of *p*-hydrazotoluene, 5 g. of hydroquinone was added to the mixture. At the conclusion of the reaction, *p*-azotoluene was recovered as usual from the mixture. The disproportionation reaction, therefore, was apparently unaffected in any qualitative way by the presence of hydroquinone.

Analytical Procedures. Selection of Wave Lengths.—Spectrophotometric analysis of samples withdrawn from rate runs required that the absorbance ($A = \log I_0/I$) of each sample be measured at each of four wave lengths, that the absorptivities ($a = A/bc$, where b = spectrophotometer cell thickness and c = concentration in g./l.) of each of the four solute components of each sample be known at each of the four wave lengths, and that the Beer-Lambert law be obeyed by each component and by mixtures of all components at each wave length employed. If these conditions are met, then a set of four equations

$$A_\alpha = b(a_{1\alpha}c_1 + a_{2\alpha}c_2 + a_{3\alpha}c_3 + a_{4\alpha}c_4) \quad (1)$$

$$A_\delta = b(a_{1\delta}c_1 + a_{2\delta}c_2 + a_{3\delta}c_3 + a_{4\delta}c_4) \quad (4)$$

(10) A. Riche and P. Berard, *Ann.*, **129**, 80 (1864).

(11) S. Feitler, *Z. physik. Chem.*, **4**, 76 (1889).

(numbered subscripts refer to solute component, Greek-lettered subscripts to radiation wave length) permit of solutions for the four concentration terms. The solutions may be represented in the most convenient form (assuming $b = 1$ cm.)

$$c_1 = r_{11}A_\alpha + r_{21}A_\beta + r_{31}A_\gamma + r_{41}A_\delta \quad (5)$$

$$c_4 = r_{14}A_\alpha + r_{24}A_\beta + r_{34}A_\gamma + r_{44}A_\delta \quad (8)$$

where $r_{ij} = (-1)^{(i+j)} D_{ij}/D$, in which D is the fourth-order determinant formed from the sixteen absorptivities (a) of equations 1–4 and D_{ij} are third-order determinants formed by striking out the i th row and the j th column from D . The terms r_{ij} of equations 5 to 8, depending as they do only on the absorptivities (a) of the four components of the mixtures at the four wave lengths chosen, remain constant throughout all runs and therefore constitute "analytical parameters" for the system. Equations 5–8 actually give correct values for the concentrations only if the spectrophotometer cell thickness (b) remains constant throughout the measurements; otherwise, correction factors must be used.

The first experimental step toward establishing a satisfactory spectrophotometric analytical procedure to be used in measuring the rate of transformation of *p*-hydrazotoluene into its three products involved the measurement of the ultraviolet absorption spectra of *p*-hydrazotoluene and of its three transformation products, in the hope that inspection of the extinction curves would reveal four suitable wave lengths for analytical use (Fig. 1). An ideal set of wave

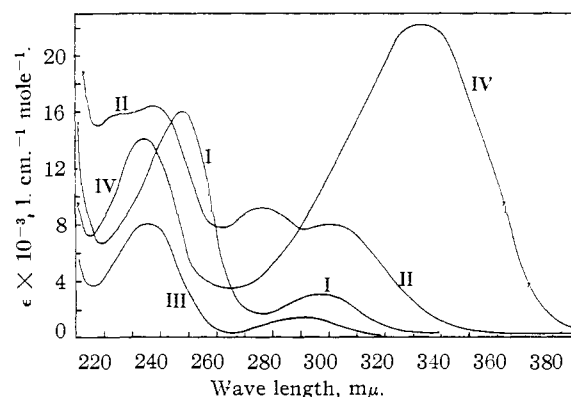


Fig. 1.—The ultraviolet absorption spectra in 95% ethanol solution of: I, *p*-hydrazotoluene; II, 6-amino-3,4'-dimethyldiphenylamine (the *o*-semidine); III, *p*-toluidine; IV, *p*-azotoluene.

lengths should satisfy the following two conditions: (1) They should be located at or near maxima or minima of all four extinction curves, so that small changes in the wave-length setting of the instrument do not correspond to relatively large changes in absorptivity of any of the components; (2) The absorptivities (a) at the selected wave lengths must be so related that no two rows and no two columns of the determinant D have proportional elements. Inspection of the curves of Fig. 1 shows that the wave lengths 235, 250, 275 and 295 $m\mu$ satisfy the second (necessary) condition, whereas the first condition, which is only desirable but not necessary, is as nearly satisfied by these wave lengths as by any other set.

Determination of Absorptivities.—Solutions of each of the four components were prepared by dissolving weighed quantities of the component in ethanol and diluting the master solution to the required concentrations. All volumetric apparatus was calibrated at 20°. Temperature corrections were not applied to operations carried out at other temperatures, because the errors introduced by ignoring these corrections were much smaller than those from other sources. Absorbances (A) were read on each solution for each component at each of the four selected wave lengths; then, for each component at each wave length, absorbance was plotted against concentration. To minimize the effects of errors in weighing and in dilution, three different master solutions of each component were prepared and diluted, and absorbance vs. concentration data from all three solutions were plotted together. In general, absorbances in the range 0.1–0.8,

where the instrument usually yields its most accurate data, were selected for the plot. The linearity of these plots and their extrapolation to or very near to zero showed that the Beer-Lambert law was indeed being obeyed. The slopes of the linear plots, obtained by a least-squares treatment that assumed insignificant errors in the concentrations and an intercept not necessarily equal to zero, were equal to absorptivity times cell thickness (ab). Since b in all cases was 0.996 cm., the slopes were essentially equal to absorptivity alone.

The data for the absorptivity plots for *p*-hydrazotoluene could not be as readily and directly determined as were those for the other three components, owing to the fact that unavoidable air oxidation of the hydrazo compound occurred while solutions were being prepared for measurement. To correct for this oxidation, the concentration of *p*-azotoluene in each solution was determined from the absorbance at 335 $m\mu$, where only the azo compound has an appreciable absorptivity. The contribution of this quantity of azo compound to the total absorbance at each of the four selected wave lengths could then be computed from the concentration and the four known absorptivities, and then both the true concentration of unoxidized hydrazo compound and its contribution to the total absorbance at each wave length could be obtained by difference. The validity of this treatment was supported by the fact that the absorbance *vs.* concentration plots were linear despite the fact that the extent of oxidative conversion of hydrazo to azo compound varied considerably among the several solutions, amounting to as much as 15% in some.

Figure 2 shows a typical plot of absorbance *vs.* concentration, and the absorptivity values determined from the sixteen plots are reported in Table I.

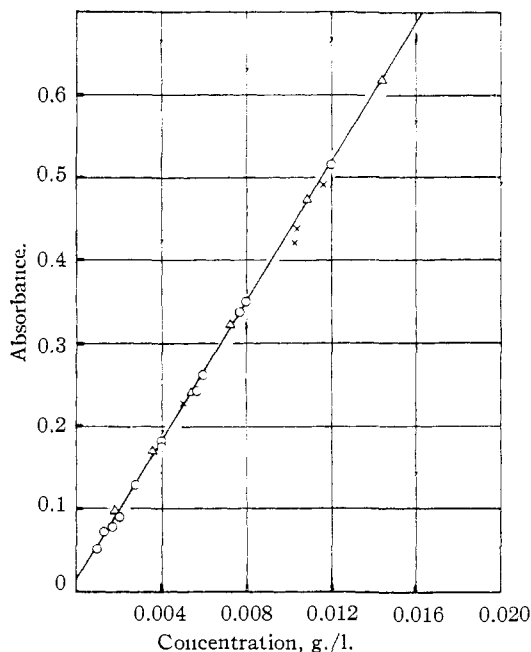


Fig. 2.—Relationship between absorbance at 295 $m\mu$ and concentration of *p*-azotoluene in 95% ethanol solution derived from three different master solutions.

The numbers from Table I were used to compute the analytical parameters (r_{ij} , equations 5-8) for the system. Table II records these values.

The values of Table II, when substituted with the four absorbance readings into equations 5-8, gave concentrations of the four components in units of mg./l.

Analysis of Known Mixtures.—Solutions were prepared by dissolving in ethanol weighed amounts of each of the four pure components, *p*-hydrazotoluene, *p*-azotoluene, *p*-toluidine and the semidine, in relative amounts obtained during several states of the rate runs. Samples were withdrawn and treated as were samples from the rate runs, absorbances were read at the four selected wave lengths, and concentrations of the four components (in mg./l.) were computed by means of equations 5-8 and the parameters of Table II.

TABLE I

ABSORPTIVITY VALUES^a FOR *p*-HYDRAZOTOLUENE, *p*-TOLUIDINE, *p*-AZOTOLUENE AND 2-AMINO-4,5'-DIMETHYLDIPHENYLAMINE IN 95% ETHANOL

Wave length, $m\mu$	<i>p</i> -Hydrazotoluene	<i>p</i> -Azotoluene	<i>p</i> -Toluidine	Dimethyl- <i>o</i> -semidine
235	67.19	62.53	81.13	74.48
250	97.14	26.59	32.18	52.36
275	9.78	18.80	7.59	41.51
295	17.06	42.06	13.63	35.05

^a Actually equal to absorptivity times cell thickness (0.996 cm. in all cases).

TABLE II

ANALYTICAL PARAMETERS

Compound	r_{235}	r_{250}	r_{275}	r_{295}
<i>p</i> -Hydrazotoluene	-5.30	14.46	-12.32	4.24
<i>p</i> -Azotoluene	-3.83	-2.186	-26.40	42.7
<i>p</i> -Toluidine	20.35	-9.70	-6.28	-21.36
Dimethyl- <i>o</i> -semidine	-0.738	-0.643	40.1	-16.42

Fourteen known solutions of all four components and thirty-five known solutions of the three products of the reaction (or of two of these) were subjected to the analytical scheme. The results showed that over the range of concentrations (0.0-9.0 mg./l.) found in the rate runs, the analytical method yielded values that were often no more than 0.1 mg./l. different from the "true values," and the difference was rarely more than 0.2 mg./l. Exceptions to this rule were encountered in analyses for *p*-hydrazotoluene, which were consistently low, and for *p*-azotoluene, which were consistently high. That these deviations from the true value could be attributed to air oxidation of the hydrazo compound during the weighing and preparation of the solutions was indicated by (a) the fact that the sum of the analyzed values for these two components agreed with the sum of the true values, and (b) the fact that analysis of binary and ternary mixtures containing the azo but no hydrazo compound gave good values for the azo compound. Thus, it appeared that the analytical values for these two components were correct within the cited limits.

The analytical method gave values for the *o*-semidine that were consistently high by about 0.4 mg./l.; therefore, the computed values for this compound from the rate runs were arbitrarily reduced by this amount.

Stability of Products under Conditions of Rate Runs.—To ascertain whether the products of the reaction were affected by the conditions imposed during the rate runs, individual purified products and pairs of these at about 10^{-4} *M* ethanolic solution were treated with hydrogen chloride in 95% ethanolic solution. The ultraviolet absorption spectra of single-solute solutions were compared before and after treatment, and two-solute solutions were analyzed by the spectrophotometric method. *p*-Azotoluene was unaffected by a 20-min. treatment with 0.290 *M* ethanolic hydrogen chloride at 0° and by exposure to 0.0310 *M* ethanolic hydrogen chloride for 39 hours at room temperature. *o*-Semidine was stable to 0.0238 *M* ethanolic hydrogen chloride at room temperature for 100 minutes. *p*-Toluidine and *o*-semidine were stirred together in 0.0235 *M* ethanolic hydrogen chloride for 16 hours at room temperature without any measurable effect. No interaction between *p*-azotoluene and *o*-semidine occurred under similar conditions.

Independent Estimation of *p*-Toluidine.—Because the relative amounts of *p*-toluidine and of *p*-azotoluene observed by spectrophotometric analysis of mixtures formed in the rate runs was inconsistent with the hypothesis that a simple disproportionation reaction of *p*-hydrazotoluene accounts for both products (see "Results" section), an independent analytical method for *p*-toluidine, the "disproportionation" product formed in larger amount, was worked out on a semi-micro scale. A 1.0-ml. aliquot for spectrophotometric analysis was withdrawn from a solution of 63.3 mg. of *p*-hydrazotoluene in 250 ml. of 95% ethanol, and the remainder of the solution was stirred for 4.5 hours at 0° with hydrogen chloride (0.0692 *M*) in the solution. The rearrangement having been completed, another 1.0-ml. aliquot was with-

drawn, diluted to 25 ml., and the dilute solution read on the spectrophotometer in the usual way. The remaining solution was permitted to evaporate to dryness under a gentle air stream. The orange-white, powdery residue was dissolved in a minimum volume of hot distilled water, and the solution was transferred to a semi-micro steam distillation apparatus similar to that described by Fieser,¹² except that a Kjeldahl trap was interposed between the distilling flask and the condenser. The solution was treated with 2 ml. of 0.491 *M* sodium hydroxide and was subjected to steam distillation for 30 minutes. The distillate was collected in an ice-cooled receiver containing 25 ml. of 0.00940 *M* hydrochloric acid. The resulting solution was transferred to a 250-ml. volumetric flask that contained another 25 ml. of 0.00940 *M* hydrochloric acid, and the acid solution was diluted to the mark. The *pH* of the final solution was determined to be 3.00 by means of a MacBeth model T *pH* meter that had been calibrated against buffer solutions of *pH* 7.00 and 3.80. The amount of standardized acid consumed by the steam distillate was equated to the number of milliequivalents of *p*-toluidine contained therein, and the *p*-toluidine content of the reaction mixture was thereby calculated to be 23.6 mg. Another run afforded 22.3 mg. of *p*-toluidine, determined similarly. Spectrophotometric analyses of the two mixtures for *p*-toluidine recorded 26.9 and 22.2 mg., respectively. It appears, therefore, that the spectrophotometric analyses for *p*-toluidine from the rate runs were not artifacts.

Rate Runs. Apparatus.—The thermostat for the runs at 0° was an insulated glass jar filled with a slush of clean crushed ice and distilled water. The runs carried out between 0° and room temperature were conducted in a kerosene-filled thermostat equipped with cooling coils and an immersion heater controlled by a mercury-toluene regulator. Water at about 5° below the thermostat temperature was circulated through the coils, and the cooling action was balanced by the action of the immersion heater. Temperatures were read on a 0–60° mercury thermometer, marked in tenths of a degree, that had been calibrated against a thermometer certified by the National Bureau of Standards. This thermometer registered no temperature fluctuation in the 0° thermostat, and variations were estimated to be ±0.1° at 10° and ±0.05° at 15° and at 20°.

The reaction vessel for the runs that provided the data collected in Table III was a 500-ml. three-neck flask provided with a mercury seal stirrer, a capillary inlet for nitrogen and a capillary vent to the atmosphere that was removed whenever samples were withdrawn from the flask. Nitrogen was purified by passage through a heated copper pile and then through freshly prepared Fieser solution.¹³ This gas was then bubbled through a saturating device; when it was to be used to provide an inert atmosphere over the solution of hydrazotoluene before acid was added to start the reaction, the oxygen-free nitrogen was first bubbled through 95% ethanol contained in the thermostat; after acid was added to start the reaction, the gas was first bubbled through thermostated ethanolic hydrogen chloride at the same concentration employed in the reaction vessel.

Determination of Rate Constants.—For a typical run an accurately weighed sample of about 35 mg. was dissolved in ethanol and diluted to the mark of a 250-ml. volumetric flask at the reaction temperature. The solution was transferred to the reaction vessel, where it was stirred and provided with a nitrogen atmosphere. The acid catalyst was prepared by measuring the required amount of a standardized solution of about 0.4 *M* hydrogen chloride in 95% ethanol and the required amount (if any) of a stock solution of lithium chloride in 95% ethanol into a 25-ml. volumetric flask and diluting to the mark. Before addition of the catalyst solution, a 2-ml. aliquot was pipetted from the contents of the reaction vessel for measurement of "zero time" concentrations. The thermostated catalyst solution was added over a period of 4–5 sec. to the thermostated solutions of *p*-hydrazotoluene, and zero time was taken as the instant of half-addition. Aliquots were removed by means of calibrated 2-ml. pipets that had been rinsed with the reaction solution at the thermostat temperature. Removal and delivery of these aliquots required 6–8 sec., and the time was taken at the instant of half-delivery. The quenching solutions into which the aliquots were delivered were stored in a series of 25-ml. volu-

metric flasks which were immersed in ice-water. Each flask contained 1.0 ml. of 0.2791 *M* aqueous sodium hydroxide, 2.0 ml. of water (which prevented the precipitation of inorganic salts when the aliquot was delivered) and enough 95% ethanol to fill about two-thirds of the volume. After addition of the aliquot, the solution was diluted to the mark with 95% ethanol, and the absorbances of this solution were measured at the four selected wave lengths within a two-hour period. Measurable air oxidation of unchanged *p*-hydrazotoluene occurred in these solutions, even when they were stored in ice-water, if they were permitted to stand more than two hours.

The validity of the analytical method was checked in each run by (a) comparing the analyzed concentrations of all components with the known initial concentration of *p*-hydrazotoluene (and of any contaminating *p*-azotoluene) and by (b) comparing the analyzed concentrations of products formed with the analyzed decrease in concentration of *p*-hydrazotoluene. For purposes of the comparison (b) concentrations of any of the products (e.g. *p*-azotoluene) found in the "zero time" solution were subtracted from the concentrations of the same products observed in aliquots withdrawn after the reaction started. Agreement in both comparisons (a) and (b) was kept within a 10% limit; otherwise the results of the run were discarded. Agreement often lay within 5%.

The pseudo first-order rate constants were computed from the slopes of the linear plots of the logarithm of *p*-hydrazotoluene concentration *vs.* time. For the determination of the constants employed in the computation of the activation energy, the least-squares slopes were calculated; indeed, the method of least squares was used to determine the slope whenever it was not obvious to the eye. More commonly, however, the slope was determined from the line drawn by eye through the points. A typical plot, in which the data from two independent runs are combined, is shown in Fig. 3.

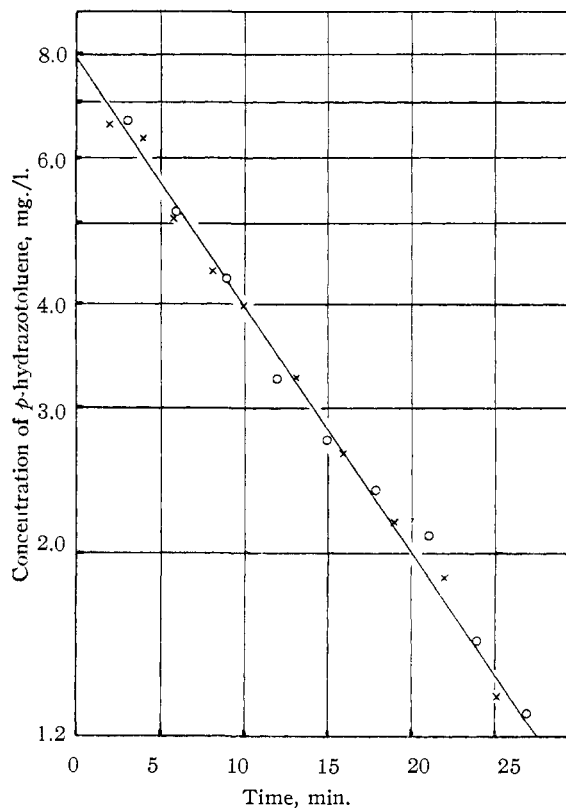


Fig. 3.—Rate data from two independent runs (32 and 33), both in 0.0150 *M* HCl in 95% ethanol at 15.1°.

Results

Simultaneous Reactions.—The three products formed from *p*-hydrazotoluene under the conditions

(12) L. F. Fieser, "Experiments in Organic Chemistry," second ed., D. C. Heath and Co., New York, N. Y., 1941, p. 161.

(13) L. F. Fieser, *THIS JOURNAL*, **46**, 2639 (1924).

of the rate runs were that of rearrangement (the *o*-semidine I) and those of disproportionation (*p*-azotoluene and *p*-toluidine); the weight ratios of these three products was consistently of the order 2:1:2 (respectively). Since the rearrangement reaction accounted for only about 40% of the total product under these conditions, it was clear that any assumption that the total reaction kinetics must be identical with the kinetics of the rearrangement reaction is unjustified. Furthermore, disproportionation of *p*-hydrazotoluene to *p*-azotoluene and *p*-toluidine could not have been the sole side reaction, for the stoichiometry of this reaction requires that the azo compound and the amine be formed in nearly equal weight amounts. Since almost twice as much *p*-toluidine as *p*-azotoluene (by weight) was consistently obtained, a third reaction, effectively a reduction of *p*-hydrazotoluene to *p*-toluidine, must also have been occurring. The nature of this third reaction never was elucidated. Attempts to minimize or eliminate this reduction reaction by ridding the reaction mixtures and apparatus of metals and other trace impurities were completely ineffective. The fact that the ratio of the amount of *p*-toluidine formed to those of the other products remained sensibly constant during each run also appeared to be inconsistent with the hypothesis that the reduction reaction was caused by trace impurities. The possibility that the "excess" of *p*-toluidine (over the azo compound) was formed from one or both of the other products was eliminated by the observation that the products, alone or in combinations of two, were stable under the imposed conditions (see Experimental section). By a process of elimination, therefore, it appeared that the "excess" *p*-toluidine must have been the result of a reduction reaction in which solvent ethanol served as the reducing agent, but no effort has been made to verify this conclusion.

The evidence cited in the preceding paragraph indicates that *p*-hydrazotoluene, in the rate runs, underwent three independent, simultaneous reactions: rearrangement, disproportionation and reduction.

Total Kinetics—The rate of disappearance of *p*-hydrazotoluene was measured in 95% ethanol solutions about $6.5 \times 10^{-4} M$ in initial concentration of hydrazo compound. Owing to the speed of the reaction, the rates could not be measured when concentrations of hydrochloric acid were as great (*ca.* 0.1 *M*) as those employed in preceding studies on the rates of the rearrangements of hydrazobenzene^{3e} and of *o*- and *m*-hydrazotoluenes^{3h}; the acid concentrations employed were in the range 0.00716–0.02866 *M*, and the molar ratio of acid to *p*-hydrazotoluene was never less than 20:1. Plots of $\log [Hy]$ *vs.* time indicated that pseudo first-order kinetics was being observed. In general, extrapolation of these plots to zero time gave an initial value of *p*-hydrazotoluene concentration slightly less than that determined spectrophotometrically from the starting solution. Most of the rate runs were carried out at 0°; however, enough runs were made at 10, 15 and 20° to permit the activation energy and related quantities to be determined. In some runs lithium chloride was

present in the solutions to maintain the total ionic strength above that provided by the presence of hydrogen chloride alone. Two runs were carried out in 75% ethanol so that some qualitative estimate of the solvent effect on the rate could be derived. In six runs, the initial concentration of *p*-hydrazotoluene was reduced about tenfold, to the limit that could be followed spectrophotometrically. The results of 33 rate runs are collected in Table III.

TABLE III
PSEUDO FIRST-ORDER RATE CONSTANTS FOR THE TOTAL REACTION OF $6.5 \times 10^{-4} M$ *p*-HYDRAZOTOLUENE IN 95% ETHANOL

Run	Temp., °C.	[HCl], <i>M</i>	Total ionic strength ^a	$k_1 \times 10^3$, min. ⁻¹
1	0.00	0.01428	0.01428	1.07
2	.00	.01428	.01428	1.00
3	.00	.01428	.01428	1.04
4	.00	.01428	.02856	1.52
5	.00	.01428	.02856	1.52
6	.00	.01428	.04284	1.86
7	20.13	.01500	.01500	11.9
8	20.15	.01500	.01500	11.8
9	20.13	.01500	.01500	11.2
10	20.16	.01500	.01500	13.6 ^d
11	20.16	.01500	.01500	14.1 ^b
12	0.00	.02866	.02866	6.08
13	.00	.02866	.02866	6.19
14	.00	.02866	.02866	6.15
15	.00	.02866	.02866	6.02 ^c
16	.00	.02866	.02866	5.79 ^c
17	.00	.02866	.02866	5.48 ^c
18	.00	.00716	.00716	0.172 ^d
19	.00	.00716	.00716	0.170 ^d
20	.00	.00716	.00716	0.163 ^d
21	.00	.01433	.02866	1.46
22	.00	.01433	.02866	1.49
23	.00	.01821	.02866	2.40
24	.00	.01821	.02866	2.39
25	.00	.02242	.02866	3.43
26	.00	.02242	.02866	3.41
27	.00	.02512	.02866	4.69
28	.00	.02512	.02866	4.74
29	.00	.01500	.01500	1.09 ^e
30	10.13	.01500	.01500	3.87
31	10.07	.01500	.01500	3.79
32	15.12	.01500	.01500	6.56
33	15.12	.01500	.01500	6.59

^a Where the value in this column exceeds [HCl], the difference is caused by the presence of lithium chloride. ^b The solvent was 75% (by weight) ethanol. ^c Initial *p*-hydrazotoluene concentration *ca.* $6.7 \times 10^{-5} M$; points on rate plot scattered about straight line. ^d Same as *c*, except that initial concentration was *ca.* $5.6 \times 10^{-5} M$. ^e This compares with the value 1.12 computed from the average of runs 13 and 14 (6.17) in the following way: multiplication of 6.17 by $(0.01500/0.02866)^2$ corrects for the difference in acid concentrations, assuming the rate to be dependent upon the square of the acid concentration; now, division by 1.47 (from k_1 's from runs 1–5) corrects for the salt effect and gives the final value 1.12 for the calculated k_1 .

Rate Dependence on Acid Concentration.—Runs 13, 14 and 21–28 all were carried out at 0° in 95% ethanol at constant ionic strength. Only the acid concentration was varied (from 0.01433 to 0.02866 *M*) throughout these runs; the ionic strength was maintained constant at 0.02866 by

adding lithium chloride to the solutions having acid concentrations less than 0.02866 *M*. Figure 4 is a plot of $\log [\text{HCl}]$ vs. $\log k_1$, in which each of the five rate constants shown in the plot is an average of two values measured under identical conditions. The least-squares slope of the straight line is 2.08; therefore k_1 is proportional to $[\text{HCl}]^2$, and the total reaction of *p*-hydrazotoluene, like that of hydrazobenzene and of *m*-hydrazotoluene,^{3e,h} follows the rate expression

$$-d[\text{Hy}]_{\text{obs}}/dt = k_3[\text{Hy}]_{\text{obs}}[\text{HCl}]^2 \quad (1a)$$

where $[\text{Hy}]_{\text{obs}}$ is the observed concentration of *p*-hydrazotoluene and k_3 may be termed a "third-order rate constant" which is independent of acid concentration.

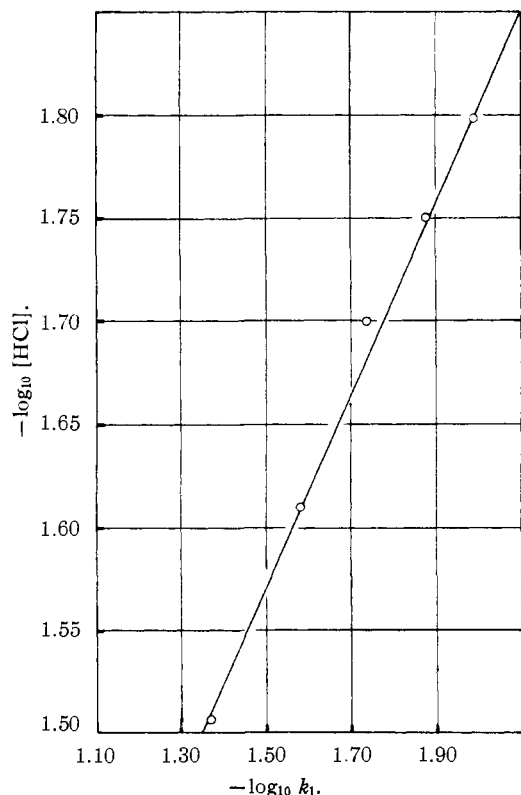


Fig. 4.—Dependency of pseudo first-order rate constant (k_1) on HCl concentration; least-squares slope = 2.08, corresponding to $k_1 = k_3[\text{HCl}]^2$.

Rate Dependence on Ionic Strength and on Dielectric Constant.—The results of runs 1–6 disclose a strong positive salt effect on the rate. At constant acid concentration and temperature, doubling and tripling the ionic strength caused about 50 and 80% increases in the rate constants, respectively. The magnitude of this salt effect is essentially identical with those observed on benzidine rearrangements carried out under similar conditions.^{3e,h}

A comparison of the results of runs 10 and 11 with those from runs 7, 8 and 9 indicates that a small but significant rate increase is observed when the solvent is changed from 95 to 75% aqueous ethanol. The effect is much smaller in magnitude but is the same in direction as that on the rate of rearrangement of *o*-hydrazotoluene^{3h} under similar conditions.

Effect on Product Distribution of Ionic Strength, Dielectric Constant, Concentration and Temperature.—In order that the contribution of each of the three component reactions to the total kinetics could be evaluated, the variations, if any, in product distributions during individual rate runs and over different runs under different conditions had to be measured. Plots of concentration of product formed vs. *p*-hydrazotoluene consumed afford the most revealing portrayal of the data. Figure 5 shows such a plot of concentration of the *o*-semidine

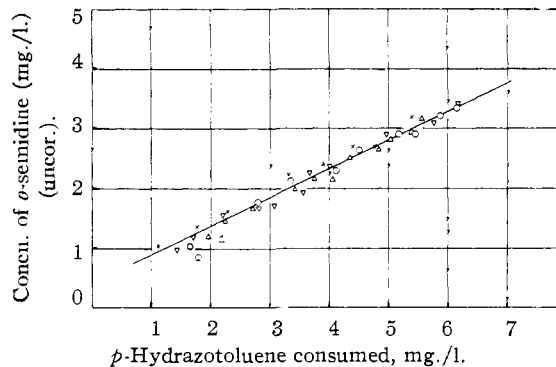


Fig. 5.—Effect of changing $[\text{HCl}]$ at constant ionic strength (0.02866) and temperature (0°) on ratio of *o*-semidine formed to *p*-hydrazotoluene consumed; acid concentrations: O, 0.1432 *M*; x, 0.01821 *M*; Δ, 0.02242 *M*; ∇, 0.02866 *M*.

formed to *p*-hydrazotoluene consumed; the points for this plot were derived from data of runs 21, 23, 25 and 13, in which the temperature and ionic strength remained constant while the acid concentration was increased. Although there is a substantial scattering of points, particularly those from the early stages of each run when precise determination of small quantities of product was impossible, there can be little doubt that the data correspond to a linear relationship that is not affected by variation in acid concentration. The plot does not extrapolate to the origin because uncorrected analytical values for the *o*-semidine concentration were used; however, the slope of the best straight line should correspond to the fraction of *p*-hydrazotoluene being converted to the *o*-semidine. This fraction evidently does not vary sensibly either during any individual run or among the runs plotted. A similar plot of concentration of *p*-toluidine formed vs. *p*-hydrazotoluene consumed, derived from data of the same runs, was also linear and constant among the runs; therefore, a linear relationship must also obtain between concentration of *p*-azotoluene, the only remaining product, and *p*-hydrazotoluene. Another pair of plots of the same concentration variables was constructed from the data of runs 3, 4 and 6, in which the temperature and acid concentration remained constant while the ionic strength varied. Again there was no sensible change in product distribution. Runs 8 and 11 yielded evidence, similarly marshalled, that a change from 95 to 75% aqueous ethanol had no detectable effect on the product distribution.

A comparison of the data from runs 13–20 suggests that the rate constants k_1 and k_3 may not truly be constant with increasing dilution and fur-

ther that the product distribution may also change with initial *p*-hydrazotoluene concentration. However, two factors operate to make these apparent effects suspect: first, the solutions of runs 15–20 were at the lower limits of concentrations that could be analyzed by the spectroscopic method, so that the analytical precision was substantially reduced; second, the long periods of time required, particularly for runs 18–20, increased the probability of accidental oxidation of *p*-hydrazotoluene to the azo compound. The result of the first factor was to scatter the points in the plots of $\log [\text{Hy}]$ vs. t so that precise evaluation of k_1 became difficult and uncertain. This uncertainty was increased as a result of the observation that the point scattering did not appear to be altogether random. Under the circumstances, the apparent difference between the average of k_1 for runs 13 and 14 (0.0615 min.^{-1}) and for runs 15–17 (0.0571 min.^{-1}) could easily be inside the limits of experimental error. With respect to the second factor, accidental air oxidation of part of the *p*-hydrazotoluene would be expected to interfere with the total kinetics and to upset the product distribution in favor of *p*-azotoluene. The scattering of the points in the rate plots of data from runs 15–20 make it difficult to be certain that good pseudo first-order kinetics was no longer being followed and that increased amounts of *p*-azotoluene were being formed, but the data certainly tended in these directions. Thus, the evidence is consistent with the conclusion that the failure of the results from the dilute runs (15–20) to check precisely with those from the normal runs (13, 14) both with respect to k_1 and k_3 and to product distributions probably may be attributed chiefly to experimental difficulties.

A comparison of the product distribution data from runs 3, 8, 30 and 32, in which temperature was the only variable, seemed at first glance to show that more *p*-toluidine and less semidine was formed at 10° than at 0° , but that no further change occurred when the temperature was raised to 20° . However, the apparent change in product ratios over the 0 – 10° interval, though it seemed consistent over several runs, actually covered a range of variation (about 10%) no greater than the normal scattering as represented in Fig. 5 and in similar plots. Thus, although a small shift in product distribution with temperature could not be disproved, any real variations lay within the limits of experimental error.

Apparent Activation Energy and Entropy.—The data from runs 7–9 and 29–33, all carried out at identical ionic strength and acid concentration (both 0.01500) but at four different temperatures, 0.0 , 10.1 , 15.1 and 20.1° , were plotted in the usual manner (Fig. 6), and the apparent activation energy (E_a) was computed from the least-squares slope to be 18.4 kcal./mole . The average of the rate constants observed at each temperature was used in plotting the data. Figure 6 shows the good linearity of the plot of $\log k_1$ vs. $1/T$. For computation of the apparent entropy of activation, the k_1 values obtained at 10.1° were selected (runs 30, 31). Division of the average of the two observed pseudo first-order constants by the square of the

acid concentration gave a " k_3 " that is not a function of acid concentration (see above). This k_3 was substituted into the equation $k_3 = (60ekT/h) \cdot e^{-E_a/RT} e^{\Delta S^*/R}$,¹⁴ where the units of k_3 are $\text{l.}^2 \text{mole}^{-2} \text{min.}^{-1}$ and the other symbols of the equation have their customary meaning and units. The ΔS^* thus computed was $6.6 \text{ cal./mole}^{-1} \text{ deg.}^{-1}$. The apparent E_a for the *p*-hydrazotoluene reactions in 95% ethanolic hydrogen chloride is therefore quite similar to those for the reactions of hydrazobenzene and of *o*- and *m*-hydrazotoluenes in the same medium but at higher acid concentrations (20.6 , 18.7 and 19.6 kcal./mole , respectively)^{3e,h}; but the apparent activation entropy is significantly greater (compare with 2.9 , -0.62 and $3.2 \text{ cal./mole}^{-1} \text{ deg.}^{-1}$, respectively). The substantially greater reaction rate of *p*-hydrazotoluene compared to the rates for its *o*- and *m*-isomers and that of hydrazobenzene under comparable conditions is therefore a reflection of an entropy and not an energy effect.

Reliability of Rate Data.—The measure of accuracy of the rate constants was again^{3e,h} taken to be the reproducibility of individual rate constants. Average deviations from the mean of constants measured by two or more runs under identical conditions ranged from 0 to $\pm 2.5\%$; most of them lay within $\pm 1\%$. Even the constants from runs 15–17 and 18–20, measured on solutions so dilute as to be at the limit of the analytical method, showed average deviations of only $\pm 4\%$. A 4% average deviation from the mean introduces a probable error of about 250 cal. into the E_a value and of about 1.4 e.u. into ΔS^* .¹⁵

The determination of k_1 was substantially more accurate than the estimation of product distribution simply because of the relative magnitudes of the concentrations involved. Initial concentrations of *p*-hydrazotoluene were about 10 mg./l. ; therefore the concentration values used to fix the first several points on the $\log [\text{Hy}]$ vs. t plot could be determined within 1 – 2% . By contrast, no reaction product reached a concentration appreciably greater than 4 mg./l. even at 100% reaction, and, even though the analytical method yielded values having an average deviation of only 0.1 mg./liter from the true value, the relative error in determining product concentrations at low conversions was large, and the average analytical value for these products could not be considered accurate to within less than $\pm 5\%$. Thus it is that the reported values for k_1 , E_a and ΔS^* have quite small probable errors, but the pseudo first-order rate constants for the three component reactions cannot be assigned with comparable confidence. Data chosen from seven different runs, in which temperature, acid concentration and ionic strength were varied, yielded the following figures for the product distribution: *p*-toluidine, $40.4 \pm 3.1\%$; *o*-semidine, $36.5 \pm 5.7\%$; *p*-azotoluene, $22.7 \pm 2.8\%$. In arriving at these averages, analytical

(14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 197.

(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 122; F. P. Price, Jr., and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

results from each of the seven runs were recorded at each of several conversions, excluding conversions less than 20%, where the relative analytical errors were especially large. These figures correspond to about 40% rearrangement, 45% disproportionation and 15% reduction.

Discussion

The results of the kinetic study of the action of 95% ethanolic hydrogen chloride on *p*-hydrazotoluene are in accord with the rate equation 1a. That the square of acid concentration ($[\text{HCl}]^2$ or $[\text{H}^+]^2$) and not the ion product $[\text{H}^+][\text{Cl}^-]$ is the correct term in the rate expression is demonstrated by reference to the results of runs 1-6, which disclosed a strong positive salt effect. Throughout these runs, the ionic strength was maintained constant by the use of lithium chloride; therefore, if ionization was complete $[\text{Cl}^-]$ was also constant. Had the rate been proportional to $[\text{H}^+][\text{Cl}^-]$, then, a first-order and not a second-order dependency on $[\text{H}^+]$ (or $[\text{HCl}]$) would have been observed.

The good pseudo first-order kinetics observed throughout this work requires that not only the rate of the semidine rearrangement of *p*-hydrazotoluene but also those of the accompanying disproportionation and reduction reactions be first-order with respect to *p*-hydrazotoluene concentration. The second-order dependency of the rate on acid concentration does not eliminate formally the possibility that higher order terms in acid concentration appear in the true rate expression (*e. g.*, $k_1 = k_a[\text{HCl}]^2 + k_b[\text{HCl}]^3 + \dots$); for at the acid concentrations employed, the higher power terms in $[\text{HCl}]$ would make a negligible contribution unless, for example, $k_b \gg k_a$. However, the physical interpretation of such higher power terms would involve such species as a third conjugate acid derived from *p*-hydrazotoluene, and the existence of even minute quantities of such species in dilute 95% ethanolic hydrochloric acid is scarcely credible. Therefore, there emerges the conclusion that the ratio of all three of the concurrent reactions are not only first order in *p*-hydrazotoluene concentration but also second order in acid concentration; they follow the same kinetic law. Furthermore if the product distribution does not vary with changes in temperature, ionic strength, acid concentration and dielectric constant, then the rates of all three concurrent reactions are identically affected by these variables and are therefore subject to the same salt and medium effects; moreover, the reactions must have the same apparent activation energies and closely similar entropies of activation. The experimental uncertainties in the determinations of product distributions make it impossible to say that no variations in distribution occurred with changes in temperature and medium, but certainly any variations lay within the limits of experimental error and could not have been gross in magnitude.

These kinetic results are consistent with the hypothesis that all three of the concurrent reactions pass through the same rate-determining sequence and that the final common intermediate forms the four products as a result of three fast, competitive, irreversible reactions. An attractive interpretation of this hypothesis involves a sequence in which

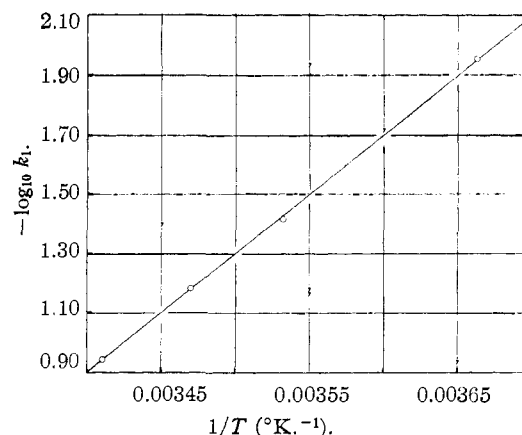
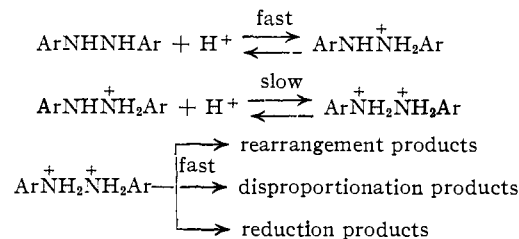
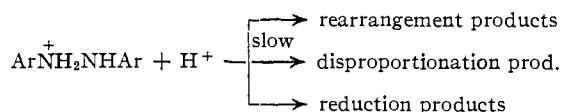


Fig. 6.—Plot of data from which activation energy was computed to be 18.4 kcal./mole.

the second conjugate acid of *p*-hydrazotoluene, formed in a slow step, rapidly undergoes the competitive rearrangement, disproportionation and reduction reactions.



The observed kinetics are also consistent with an alternative reaction sequence in which the first conjugate acid from *p*-hydrazotoluene reacts with the second proton to yield the products in three competitive, slow steps.



Recently, Blackadder and Hinshelwood¹⁶ have called attention to the advantages to be derived in interpreting the benzidine rearrangement by means of this sequence. Some caution must be exercised, however, in postulating the non-existence of the second conjugate acids of aromatic hydrazo compounds, inasmuch as Pongratz, *et al.*, have reported the preparation of stable, crystalline hydrazobenzene dihydrobromide and dihydroiodide.¹⁶

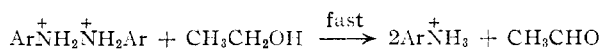
Both of the reaction sequences formulated above require three related but different transition states leading to the products in the three competitive steps; therefore, the three reactions would not be expected in either case to show identical over-all energies and entropies of activation or to be affected in exactly the same way by changes in the medium. However, the differences in these properties of the three competitive reactions could not be great if the reactions are fast and therefore of low activation energy (first sequence), whereas larger differences could develop if the competitive processes are slow and rate controlling (second se-

(16) A. Pongratz and K. Scholtis, *Ber.*, **75**, 138 (1942); A. Pongratz, S. Böhmert-Süss and K. Scholtis, *ibid.*, **77**, 651 (1944).

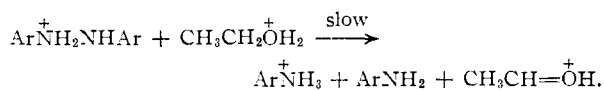
quence). Inasmuch as the experimental results eliminate large but not small variations in product distribution with temperature and medium changes, the first sequence is somewhat the more comfortable one. However, the second sequence is also quite consistent with the results.

The rate behavior observed in this study of the semidine rearrangement of *p*-hydrazotoluene has no features that distinguish this rearrangement from benzidine rearrangements whose rates have been measured under similar conditions.^{3e,h} Compared to these benzidine rearrangements this semidine rearrangement is governed by the same rate law, and the rate is subject to a salt effect of the same size and sign and an effect of changing dielectric constant of the same sign, though of somewhat smaller magnitude. The apparent activation energies are nearly the same, and although the observed entropy of activation for the semidine rearrangement is somewhat greater, the difference is not sufficient to indicate a serious mechanistic change in the rate-governing processes. On the basis of this work, therefore, the semidine rearrangement of *p*-hydrazotoluene is subject to the same interpretation, with the same limitations, as those discussed earlier in connection with analogous studies on benzidine rearrangements.^{3e,h}

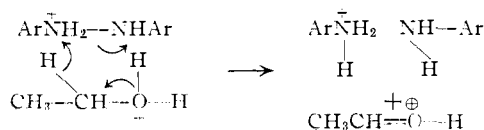
The reduction reaction observed in this investigation does not appear to have been reported previously. Evidence already has been cited that the weight excess of *p*-toluidine over *p*-azotoluene among the products could not be explained by (a) interactions among the reaction products, (b) trace impurities or (c) reduction of part of the *p*-azotoluene formed by disproportionation (by an unknown agent) back to the hydrazotoluene. One remaining way to account for the observed excess of toluidine over azotoluene requires the postulate that the excess of toluidine was formed directly from *p*-hydrazotoluene by reduction. If such a reaction occurs, then the observed kinetics and the other evidence eliminates every possible reducing agent from consideration except the ethanol solvent. The available evidence is in accord either with the postulate that the second conjugate acid from *p*-hydrazotoluene, formed in a slow step, is reduced in a rapid reaction by ethanol



or that the first conjugate acid from *p*-hydrazotoluene is reduced in a slow step by protonated ethanol

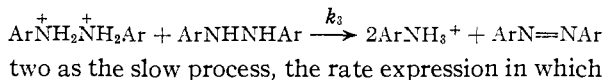
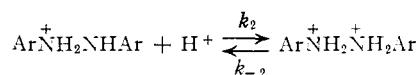


Since a reduction of this nature appears *a priori* more likely to be a slow than a fast process, the latter path seems the more attractive. Either reaction can be rationalized on the basis of a six-ring transition state, *e. g.*



Experiments intended to demonstrate whether acetaldehyde is indeed formed in these reactions in an amount equivalent to that of the excess *p*-toluidine are fraught with severe experimental difficulties, and none have as yet been attempted.

The disproportionation of *p*-hydrazotoluene to *p*-toluidine and *p*-azotoluene is not easy to interpret in terms of the observed first-order dependency of the rate on *p*-hydrazotoluene concentration. Although this relationship appears not to have been reported previously for acid-catalyzed disproportionations, Curme¹⁷ observed first-order dependency of the rate of thermal disproportionations of several aromatic hydrazo compounds, including *p*-hydrazotoluene, on their concentrations; Wieland¹⁸ pointed out that Curme's fragmentation mechanisms were not essential to explain the kinetics; and more recently Holt and Hughes¹⁹ have presented evidence based on isotope experiments indicating that the N-N bond of hydrazobenzene is not cleaved during the formation of azobenzene by disproportionation. Of course there can be no assurance that the observations reported by Holt and Hughes can be extended to the acid-catalyzed disproportionation disclosed in the work reported here; but if such should prove to be the case, then reconciliation of this observation with the observed rate equation again presents a problem. If the reaction sequence includes the forward step



two as the slow process, the rate expression in which

$$\ln \frac{[\text{Hy}]^0_{\text{obs}} - A}{[\text{Hy}]_{\text{obs}} - A} = At/(1 + K[\text{H}^+])$$

$[\text{Hy}]^0_{\text{obs}}$ and $[\text{Hy}]_{\text{obs}}$ are initial observed concentration of hydrazo compound and that observed ($= [\text{Hy}] + [\text{HyH}^+] + [\text{HyH}_2^{++}]$) at time t , respectively, and $A = k_3K[\text{H}^+]^2$, can be derived, but only with the unlikely assumption that the final reaction is fast enough to swamp the reverse of the second reaction. The above expression, however, could readily approximate simple first-order kinetics. Other comparatively apparent reaction sequences involving direct interaction between two hydrazotoluene species yield rate expressions that are second order in concentration of hydrazo compound. The proposal by Wieland¹⁸ that one molecule of hydrazo compound splits off hydrogen in a slow step and that the latter reacts rapidly with a second molecule of hydrazo compound accounts for the kinetics but leaves the question of an intermediate hydrogen acceptor, which is scarcely less difficult.

That the *p*-azotoluene formed in the reactions reported here was truly the result of a disproportionation reaction and not of direct air oxidation of the hydrazo compound is supported by the fol-

(17) G. O. Curme, Jr., *THIS JOURNAL*, **35**, 1143 (1913); J. Stieglitz and G. O. Curme, *Ber.*, **46**, 911 (1913).

(18) H. Wieland, *ibid.*, **45**, 492 (1912).

(19) P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 1666 (1953).

lowing evidence. Some of the azo compound was always present in the sample introduced at the beginning of a rate run, but the amount of this compound initially present was determined and subtracted from the amount detected during the run to obtain the quantity actually formed in the course of the run. Inasmuch as samples introduced into the thermostated reaction vessel and maintained in solution therein before addition of the acid catalyst for at least an hour (to reach temperature equilibrium) failed to show detectable increases in *p*-azotoluene concentration, the protective atmosphere must have been functioning satisfactorily, for samples similarly treated in the absence of the nitrogen stream oxidized very rapidly to *p*-azotoluene. Furthermore, since rapid air oxidation of *p*-hydrazotoluene is known to occur in the absence of acids, any air oxidation taking place during the rate runs should be substantially uncatalyzed, and therefore an appreciable incursion of such a reaction must have changed the kinetics from those observed. Finally one might suspect that the observed azo compound could have been the result of air oxidation occurring between removal of samples from the mixtures and analysis of them, for these samples were not protected from the air. However, experiments showed that samples stored for two hours or less in ice showed no appreciable gain in concentration of azo compound. More-

over, had the azo compound apparently formed during the runs in fact been formed during storage of samples for analysis, then the largest concentrations of azo compound should have been found in the samples withdrawn at the smallest conversions, for these samples contained the greatest amounts of available hydrazotoluene for air oxidation and in general were held in storage for the longest periods before analysis. Actually of course the concentrations of azo compound formed during the reaction was observed to increase continuously as the reaction progressed.

Because the observed rate constants from which E_a and ΔS^* are computed undoubtedly are composites of two or more true rate and equilibrium constants, it follows that the apparent E_a (or ΔH^*) and ΔS^* are also composite energy and entropy functions, respectively. Therefore, these apparent values cannot be used to draw valid conclusions about the mechanisms of the rearrangement, reduction and disproportionation steps of the reaction sequence.²⁰

Acknowledgment.—The authors are grateful to Drs. J. P. Fugassi, D. S. McKinney, R. G. Parr and A. K. Colter of this Department for their interest in this work and for their constructive advice during the preparation of the manuscript.

(20) For further discussion of this point, see ref. 3e. PITTSBURGH 13, PENNSYLVANIA

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

Carbonyl Reactions. IV. The Kinetics of the Acid-catalyzed Reaction of Anisaldehyde with Methyl Ethyl Ketone¹

BY DONALD S. NOYCE AND LLOYD R. SNYDER

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The rate of formation of 3-methyl-4-(*p*-anisyl)-3-buten-2-one in acetic acid from anisaldehyde and methyl ethyl ketone shows simple bimolecular kinetics when both reagents are present in low concentrations. With high concentrations of methyl ethyl ketone, the rate of reaction does not continue to increase as rapidly as is theoretically predicted. Two causes have been shown to be responsible for this behavior. There is formation of a reasonably stable reaction intermediate, which reacts either to regenerate the starting reagents or to lead to formation of the observed product. There is also a decrease in the activity coefficient of methyl ethyl ketone at higher concentrations. The rate sequence and sequence of intermediates is outlined.

Introduction

Of the numerous reactions which lead to the formation of new carbon to carbon bonds, the aldol condensation has been subjected to the most extensive study. Though the base-catalyzed reaction has received considerable attention from a kinetic viewpoint,² the acid-catalyzed counterpart has not been so extensively investigated. It was recently reported that the acid-catalyzed condensation of acetophenone and benzaldehyde could be suitably examined spectrophotometrically³ and the

rate law and general sequence of intermediates were determined.

In the case of the condensation of an aldehyde with an unsymmetrical ketone such as methyl ethyl ketone, there arise the possibilities of two alternative products. Specifically, it has been shown by Harries and Muller⁴ that with basic catalysts, benzaldehyde and methyl ethyl ketone afford 1-phenyl-1-pentene-3-one (I), while with acid catalysts the product is 3-methyl-4-phenyl-3-buten-2-one (II). That this is general with respect to methyl *n*-alkyl ketones is demonstrated by the work of Bogert and Davidson,⁵ and that it is general for aromatic aldehydes is demonstrated by the work of Woodruff and Conger.⁶ In all of these cases the demonstration rests upon the formation of

(1) Supported in part by the Office of Ordnance Research, Contract No. DA-04-200-ORD-171.

(2) R. P. Bell, *J. Chem. Soc.*, 1637 (1937); K. P. Bonhöffer and W. D. Walters, *Z. physik. Chem.*, **181A**, 441 (1938); E. Coombs and D. P. Evans, *J. Chem. Soc.*, 1295 (1940); C. C. French, *THIS JOURNAL*, **51**, 3215 (1929); G. M. Murphy, *ibid.*, **53**, 977 (1931); V. K. LaMer and M. L. Miller, *ibid.*, **57**, 2674 (1935).

(3) (a) D. S. Noyce and W. A. Pryor, *ibid.*, **77**, 1397 (1955); (b) D. S. Noyce, W. A. Pryor and A. H. Bottini, *ibid.*, **77**, 1402 (1955).

(4) G. Harries and G. H. Muller, *Ber.*, **35**, 966 (1902).

(5) M. T. Bogert and D. Davidson, *THIS JOURNAL*, **54**, 334 (1932).

(6) E. H. Woodruff and T. W. Conger, *ibid.*, **60**, 465 (1938).