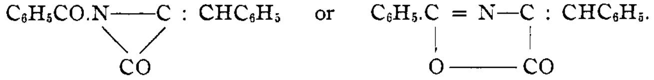

—This lactimide was prepared according to Erlenmeyer's directions by condensing benzaldehyde with hippuric acid. It melted at 164–165°.

Experiment 1.—The lactimide was heated with ammonium thiocyanate in acetic anhydride solution as described in the previous experiments. The lactimide dissolved completely on warming, but there was no evidence of any reaction. On cooling, the lactimide separated and was purified by crystallization from benzene. It deposited in yellow crystals and melted at 165°.

Experiment 2.—The lactimide was converted into β-phenyl-α-benzoylaminoacrylic acid, XIII, by hydrolysis with

$$C_6H_5CH : C(NHCOC_6H_5)COOH$$

XIII.

alkali and the latter, XIII, then warmed with acetic anhydride and ammonium thiocyanate. After heating for 30 minutes the solution was then cooled when the lactimide immediately deposited and melted at 165°. There was no evidence of the formation of a thiohydantoin compound.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THERMAL DECOMPOSITION OF SYMMETRICAL DIARYLHYDRAZINES—A REACTION OF THE FIRST ORDER.[1]

BY GEO. O. CURME, JR.

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Many hydrazines, as is well known, show a tendency to undergo, with great facility, a variety of molecular changes, involving a redistribution of the atoms composing their molecules. The two chief types of such reactions are the following:

(1) Many hydrazines, when heated, decompose into compounds of a lower and a higher state of oxidation. Thus hydrazobenzene decomposes into aniline and azobenzene:

$$2C_6H_5NH.NHC_6H_5 \longrightarrow C_6H_5N : NC_6H_5 + 2C_6H_5NH_2. \qquad (1)$$

(2) Symmetrical arylhydrazines and their derivatives undergo the benzidine and related rearrangements, under the influence of acids. Thus hydrazobenzene changes into benzidine and diphenyline:[2]

$$C_6H_5NH.NHC_6H_5 + 2HCl \longrightarrow ClH_3N.C_6H_4.C_6H_4.NH_3Cl. \qquad (2)$$

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[1] The work presented in this article formed the basis of a dissertation submitted to the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Other products are theoretically possible, but have never been described as occurring as a result of this rearrangement.

A study of the reactions of class (1) constitutes the work to be taken up in this paper. The hydrazines used in the experimental work were hydrazobenzene, *p*-methylhydrazobenzene, and *p*-hydrazotoluene. The investigation was suggested by Professor Stieglitz, and was carried out by the author under his supervision.[1]

A series of quantitative determinations of the velocities of certain reactions of class (2) have also been carried out by us, with the object of making a more critical analysis of the mechanism of the reaction, than that reached by van Loon in a similar investigation.[2] A different method of measurement from that used by van Loon has been followed, and it is hoped that within a short time the conclusions reached can be reported.

The oldest observation on the simultaneous formation of azo- and amino-compounds from hydrazo compounds, under the influence of heat, is due to A. W. Hofmann,[3] who noticed that hydrazobenzene, when heated considerably above its melting point, changes into a mixture of azobenzene and aniline. Biehringer and Busch[4] found that roughly equivalent quantities of azobenzene and of aniline are formed when an alcoholic solution of hydrazobenzene is heated above 130° in a sealed tube. This establishes the equation for the reaction, which the above-mentioned investigators found to proceed irreversibly.[5]

$$2\mathrm{Ph.NH.NH.Ph} \longrightarrow \mathrm{PhN:NPh} + 2\mathrm{PhNH_2}. \qquad (3)$$

While their work establishes the relative quantities involved in the reaction, by which at least the greater part of the hydrazine is decomposed, it gives no clue to the mechanism by which the reaction is effected.

There are, *a priori*, several possible, plausible explanations of the decomposition, each of great interest from the point of view of the theory of organic chemistry. For this reason, the decision between the possibilities by the results of critical experimental work is of unusual interest and importance. We will discuss the three most important of these schemes, distinguishing them, for the sake of convenience, as A, B and C. In the following discussion, the consideration will be limited to that of the decomposition of hydrazobenzene into aniline and azobenzene. However, the theoretical conclusions reached apply equally well to *p*-methylhydrazobenzene and *p*-hydrazotoluene, and probably to a large number of chemically related substances.

A. In the first place, the formation of azobenzene and aniline might be the result of an *intermolecular* oxidation and reduction, one molecule of

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[1] See a preliminary report by Stieglitz and Curme, on the decomposition of hydrazobenzene, *Ber.*, **46**, 911 (1913).

[2] *Rec. trav. chim. Pays.-Bas.*, **13**, 63 (1904).

[3] *Jahresb.*, **1863**, p. 425.

[4] *Ber.*, **36**, 339 (1902).

[5] The symbol Ph represents the phenyl group.

hydrazobenzene being oxidized to azobenzene by a second molecular which itself would be reduced to aniline. The high reducing tension in the hydrogen attached to the nitrogen in the hydrazobenzene could be the cause of such an intermolecular oxidation and reduction. This is the conception of the reaction which has been advocated in particular by Wieland.[1] At a constant temperature, such a reaction would be one of the second order, and its velocity would be expressed by the dimolecular law

$$\frac{dx}{dt} = K_{\text{dimol.}} (A-x)^2, \qquad (4)$$

where A is the original concentration of the reacting substance, x the concentration transformed at any time t, and $K_{\text{dimol.}}$ the characteristic constant of the reaction at the given temperature.

B. In the second place the formation of azobenzene and aniline from the hydrazobenzene may be the result of a primary, measurably slow decomposition of the hydrazine into aniline and phenyl imide, PhN:, a derivative of univalent nitrogen, followed by the condensation of two molecules of phenyl imide to azobenzene, as expressed in the following equations:

$$\text{PhNH.NHPh} \longrightarrow \text{PhNH}_2 + \text{PhN:} \qquad (5)$$

$$2\text{PhN} : \longrightarrow \text{PhN} : \text{NPh} \qquad (6)$$

The consideration of this possibility grew out of Stieglitz's theories[2] on the formation of univalent nitrogen derivatives as intermediate products in the Hofmann-Curtius-Lossen-Beckmann rearrangements, in the benzidine[3] rearrangement, and in other reactions. The decomposition of symmetrical diaryl hydrazines into aromatic amines and azo compounds held out the hope of a very simple experimental test, by velocity measurements, of the applicability of such views to the reaction in question.

At a constant temperature such a decomposition would be one of the first order, and its velocity would be subject to the monomolecular law:

$$\frac{dx}{dt} = K_{\text{mono.}} (A - x), \qquad (7)$$

where the symbols have the same significance as in equation (4).

C. Very closely related to this view and growing out of it[4] is the third

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[1] *Ann. Chem.*, **392**, 133 (1912).

[2] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); Stieglitz and Earle, *Ibid.*, **30**, 399 and 412 (1903); Slosson, *Ibid.*, **29**, 289 (1903); Hilpert, *Ibid.*, **40**, 155 (1908); Stieglitz and Peterson, *Ber.*, **43**, 782 (1910); G. Schroeter, *Ibid.*, **42**, 2336 and 3356 (1909), etc.; Wieland, *Ibid.*, **42**, 4207 (1909). Stieglitz and Curme, *Ibid.*, **46**, 911 (1913).

[3] The application of this theory to the benzidine rearrangement, *Am. Chem. J.*, **29**, 62, footnote, has now been abandoned as a result of Wieland's work, *Ber.*, **39**, 150 (1906), on the rearrangement of fully substituted hydrazines, and also of our measurements of the velocity of the benzidine rearrangement (see Stieglitz and Curme, *loc. cit.*).

[4] Preliminary report, *Ber.*, **46**, 911 (1913).

possibility, namely, that the formation of the azobenzene and aniline from hydrazobenzene is preceded by a primary, measurably slow decomposition of hydrazobenzene into phenyl amide, PhNH, a derivative of bivalent nitrogen. Such a decomposition would be entirely analogous to that assumed by Wieland for fully substituted hydrazines[1] in a series of reactions investigated preparatively:

$$\text{Ph}_2\text{N.NPh}_2 \rightleftarrows 2\text{Ph}_2\text{N}. \qquad (8)$$

Wieland, however, explicitly[2] stated that he considers the thermal decomposition of hydrazobenzene *not* to be of this type, but rather, as explained above, an *intermolecular* oxidation and reduction reaction. We can express this third view, a variation of the second one, in the following equations:

$$\text{PhNH.NHPh} \longrightarrow 2\text{PhNH}, \qquad (9)^3$$

followed either by the action:

$$4\text{PhNH} \longrightarrow 2\text{PhNH}_2 + \text{PhN:NPh}, \qquad (10)$$

or by the actions:

$$2\text{PhNH} \longrightarrow \text{PhN:} + \text{PhNH}_2 \qquad (11)$$

and

$$2\text{PhN:} \longrightarrow \text{PhN : NPh}. \qquad (12)$$

At a constant temperature the primary reaction expressed in equation (9) would also be one of the first order and its velocity would obey the law for a monomolecular reaction.

The experimental results obtained showed that at a given temperature the velocity of the reaction is independent of the concentration of the reacting substance and consequently the decomposition cannot be a dimolecular reaction. When the proper substitutions are made in the equation for the velocity of a monomolecular reaction, concordant "constants" are obtained, both when the analyses are made for unchanged hydrazobenzene at the end of measured time intervals, and when the amount of

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[1] *Ann. Chem.*, 381, 202 (1911).

[2] *Loc. cit.*

[3] We may consider the nitrogen atoms in hydrazobenzene to be united by a positive charge on the one and a negative charge on the other (cf. W. A. Noyes, THIS JOURNAL, 23, 460 (1901); 35, 767 (1913); Stieglitz, *Ibid.*, 30, 1798 (1908) and Stieglitz and Curme, *loc. cit.*). In the dissociation the fragments might retain their charges (*loc. cit.*) but it is better to assume that the electron passes from the negative to the positive nitrogen atom and *thus disrupts the molecule* and that the dissociation product contains radicals with only two valences of the nitrogen atom satisfied, *i. e.*, that the latter has gained only *two* electrons forming $\overset{+}{\text{Ph}}.\overset{-\;-}{\text{N}}.\overset{+}{\text{H}}$. This is the view expressed in equation (9). The alternative hypothesis that the nitrogen atoms retain their charges represents a simple ionization, which the character of the compound renders much less likely than the decomposition expressed in equation (9). J. S. and G. C.

aniline[1] formed in the same time intervals is determined. On the other hand, widely discordant values for the "constants" are obtained when the equation for a dimolecular reaction is used, both in the values of a single experiment and in the values obtained for $K_{\text{dimol.}}$ for solutions of varied concentration (see Tables I and III, p. 1158). The assumption that an *intermolecular* oxidation and reduction represents the course of the action is therefore disposed of.

Close inspection of the velocity determinations (see Tables I, II, III, p. 1158, and IV, V and VI, p. 1160) shows that there is a slowing down of the action, amounting to a falling off in the constant for a monomolecular reaction of about 10%[2] during the decomposition of about 75% of the substance. A falling off in the value of the constant calculated for a pure monomolecular reaction would result if the action really consisted of two parallel reactions, one monomolecular (equation 5 or 9) and the other dimolecular[3] (equation 3[4]), as expressed in the equation:

$$\frac{dx}{dt} = K'_{\text{mono.}} \times (A - x) + K'_{\text{dimol.}} \times (A - x)^2. \qquad (13)$$

Inspection of Tables I, II, III, p. 1158, and IV, p. 1160, shows, however, that three solutions, varying in concentration as 4 : 2 : 1 all *start out with the same velocity*, when referred to a monomolecular reaction, and show exactly the same characteristic droop in the same time. If a parallel dimolecular reaction were the cause of the droop, then the constant found for a monomolecular reaction should start out with smaller values in the more dilute solutions, in which the parallel dimolecular re-

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[1] The separate analysis for both substances was performed only for the decomposition of hydrazobenzene.

[2] As calculated for the decomposition for long time intervals. The sag in the constant would be still greater if calculated for small time intervals.

[3] Such a parallel dimolecular reaction is suggested by the behavior of hydrogen peroxide, which is closely related in structure and behavior to the hydrazines. Hydrogen peroxide, according to Nernst [*Z. Elektroch.*, 11, 710 (1905)], decomposes as a gas at 270° in a *dimolecular* reaction ($2H_2O_2 \longrightarrow 2H_2O + O_2$), but exposed to ultraviolet light at low temperatures [Tian, *Compt. rend.*, **151**, 1040 (1910)] or to a series of catalytic agents (see references to the literature by Tian, *loc. cit.*), it decomposes in a monomolecular reaction, $H_2O_2 \longrightarrow H_2O + O$ and $2O \longrightarrow O_2$. The latter monomolecular reaction is strictly comparable with that proved by us for the thermal decomposition of hydrazobenzene. Tian considers that Wolffenstein's study of the decomposition of hydrogen peroxide at 80° [*Ber.*, **27**, 3310 (1894)] shows that the thermal decomposition of the peroxide in solution must also be dimolecular. But Wolffenstein's data, obtained for preparative purposes simply, are neither rigorous nor consistent and according to the choice of experiments, one can consider a dimolecular, a monomolecular, or parallel dimolecular and monomolecular reactions to be indicated. Mr. Denton J. Brown has taken up this problem for rigorous study, as well as the problem of the thermal decomposition of peroxide derivatives. J. S.

[4] Such a dimolecular reaction could be due to the reduction of phenyl imide to aniline by hydrazobenzene.

action would consume the substance at a slower rate than in the more concentrated solution. It is apparent, therefore, that a parallel dimolecular reaction cannot be considered to account for the sag in the constant for a monomolecular reaction. Mathematical analysis of the data fully confirms this conclusion (see. p. 1160).

The experimental data therefore do not agree with the assumption that the decomposition of hydrazobenzene is either wholly or in measurable part the result of a *dimolecular* reaction of oxidation and reduction.

The data agree, on the other hand, with the conclusion that we are dealing primarily with a monomolecular reaction, with some secondary action causing a small droop in the constant *during the course of the decomposition, but not in the initial rates of decomposition*, when solutions of concentrations in the ratio 4 : 2 : 1 are used. This result raises the question whether a *product* of the action is not a retarding factor by virtue of a reversal of the action. Aniline and azobenzene are the products and it was thought, in particular, that aniline might retard the decomposition by combining reversibly with phenylimide to form hydrazobenzene (theory B, equation 5). Such a reactive compound as phenyl imide must in fact tend to combine with aniline, just as isocyanides RN : C combine with amines. Velocity measurements were therefore made with mixtures of hydrazobenzene and aniline; it was found that the action followed exactly the same course as in the absence of aniline, starting at the same initial rate and showing the same slight droop (see Table VIII, p. 1164). While the decomposition of hydrazobenzene into phenylimide and aniline *may be* reversible, it is evidently not *measurably so*[1] and thus the droop in the constant cannot be due to a reversed action of this nature.[2] Exactly the same result was obtained when an initial addition of azobenzene was made to the hydrazobenzene (see Table IX, p. 1164). Neither of the recognized products of the action can therefore be held to account for the falling off of the velocity constant.

The possibility that the *solvent*, alcohol, is the cause of the secondary action indicated, producing some reducible substance[3] other than hydrazobenzene, was excluded by the fact that the same characteristic result was obtained when the velocity was measured by analysis for aniline formed and still more conclusively by the fact that the velocity of decomposition in benzene solution, although much slower than in alcohol, at a given temperature, shows exactly the same character.

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[1] The concentration of phenyl imide at any moment might be too minute and the change too slow to bring the reverse action into the range of our measurements.

[2] The question of reversibility was tested only in the case of hydrazobenzene. While the result is apparently conclusive, the importance of the conclusion is such that in the continuance of these studies, special attention will be paid to this question. J. S.

[3] The reducing power of hydrazobenzene toward iodine is used in measuring the velocity of the action.

While we have thus been able to exclude a parallel dimolecular reaction, a reversed reaction of aniline or azobenzene, and an action of the solvent[1] as the sources of the falling off in the constant for a monomolecular reaction, we have not succeeded in finding the actual nature of the conflicting secondary reaction. It is probable that some derivative is formed, with reducing power, that is tolerably stable and that has not been recognized as yet as a product either by Biehringer and Busch,[2] the first investigators of the decomposition, or by ourselves. In view of the great reactivity of the substances involved and the many transformations hydrazobenzene is known to undergo, such a secondary reaction would not be unnatural. An observation, made during the course of the analysis, that some substance accumulates that forms with iodine a dark-colored product, interfering with the delicacy of the titrations, is the only direct clue we have as to the presence of such a product.

While the nature of the secondary reaction has not been discovered, we consider that the perfect agreement in the *initial rates* of change of hydrazobenzene in solutions of concentrations in the ratio 4 : 2 : 1 as well as in solutions containing an excess of aniline or of azobenzene *proves conclusively the monomolecular character* of the thermal decomposition of hydrazobenzene. This result demonstrates that a primary, measurably slow decomposition of hydrazobenzene into *free unsaturated radicals, phenyl imide*, C_6H_5N, or *phenyl amide*, C_6H_5NH, *must occur and that these radicals must have at least a temporary existence*, however brief it may be. This quantitative proof of the formation and existence of such free radicals, as intermediate products of reaction, we consider the most important conclusion arrived at through this investigation.

A monomolecular reaction, in itself, would agree with the assumptions made either in the secondary theory presented (*B*, p. 1145) or in the third, *C* (p. 1145). The fact that the reaction velocity is not retarded by the presence of an excess of aniline might, at a first glance, be considered to favor theory *C* as against *B*, inasmuch as phenyl imide, a necessary product according to *B* (equation 5), would be expected to act reversibly with aniline. However, as stated above, the reversibility need not be *measurably great*. But theory *C* would not demand any reversible action of aniline at all, if aniline and azobenzene are formed directly (equations 9 and 10) from phenyl amide. A very careful test of the reduction of azobenzene to hydrazobenzene (by a quantitative test for the formation of a reducing agent active towards iodine, when a mixture of an iline and azo-

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[1] Tests for benzidine showed that no discoverable quantities of benzidine are formed and therefore excluded also the benzidine rearrangement as the secondary reaction (a benzidine rearrangement would proceed faster at first than later in the more strongly alkaline solutions).

[2] *Loc. cit.*

benzene was heated) showed in fact that no hydrazobenzene is formed from these compounds under the conditions of the experiment. The observation that the thermal decomposition of hydrazobenzene is not retarded by aniline would therefore agree directly with theory *C*, postulating the primary formation of phenyl amide, *provided the further course of the action were that indicated in equation 10.* But this course would involve a *tetramolecular* reaction for the formation of aniline and azobenzene (see equation 10). Reactions of such high order are exceedingly rare and they should not be assumed without strong confirmatory evidence. For this reason it is much more probable that if phenyl amide is the primary dissociation product, it forms aniline and azobenzene by way of phenyl imide[1] (see equations 11 and 12), which, as in theory *B*, would be expected to act reversibly with aniline (although not necessarily *measurably so*).

It is clear then that the basis for a choice between theories *B* and *C*, postulating, respectively, a primary decomposition into phenyl imide and into phenyl amide, is too slight for any conclusive decision at present. The vital fact remains established, however, that there is a measurably slow, monomolecular decomposition *into free radicals*, which may be either phenyl imide *or* phenyl amide.

The determination of the velocity of decomposition of hydrazobenzene[2] at different temperatures shows that the rate of decomposition varies very rapidly with small changes of temperature. Van't Hoff's[3] equation for the change of velocity with change of temperature is

$$\frac{d \ln \mathrm{K}}{d\mathrm{T}} = \frac{\mathrm{A}}{\mathrm{T}^2}, \qquad (15)$$

where K is the velocity constant of the reaction, T the absolute temperature, and A a characteristic constant where only small ranges of temperature are being considered. By integration of equation 15 and solving for A, an expression is obtained,

$$A = \frac{\mathrm{T}_0\mathrm{T}_1}{\mathrm{T}_1 - \mathrm{T}_0} \times \ln \frac{\mathrm{K}_1}{\mathrm{K}_0}, \qquad (16)$$

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[1] The assumed intermolecular formation of phenyl imide and aniline from phenyl amide corresponds, step by step, with what presumably occurs when alkalin liquids are electrolyzed and hydroxide ions discharged: $2HO \longrightarrow H_2O + O$ and $2O \longrightarrow O_2$ (14). Bivalent radicals are much more stable and perhaps more likely to be formed in the free state than univalent ones. Ammonia and amines, oxygen and sulfur compounds and isocyanides are instances of well-known compounds whose molecules contain atoms with two free valences and which are known in the free condition, although extremely reactive. Triphenylmethyl, through Gomberg's classical researches, has become known as one of the best studied of the free *univalent* radicals but, in a characteristic fashion, it polymerizes and exists primarily as a polymer $[(C_6H_5)_3C]_2$.

[2] The influence of temperature on the velocity of decomposition was investigated only with the one substance, hydrazobenzene.

[3] *Etudes de Dynamique Chemique,* 1884, p. 114.

which should give a constant value for A at different temperatures, when the corresponding values of T and K are substituted. Using the three velocity constants[1] obtained experimentally with hydrazobenzene (see Tables IV, V and VI, p. 1160) at the temperatures 140° (= 413° Abs.), 145° (=418° Abs.), and 150° (=423° Abs.), respectively, we can calculate three values for A.

(1) $T_0 = 413°$; $T_1 = 418°$; $K_0 = 0.00145$; $K_1 = 0.00253$.
$\therefore A = 19{,}210$.
(2) $T'_0 = 413°$; $T'_1 = 423°$; $K'_0 = 0.00145$; $K'_1 = 0.00436$.
$\therefore A = 19{,}230$.
(3) $T''_0 = 418°$; $T''_1 = 423°$; $K''_0 = 0.00253$; $K''_1 = 0.00436$.
$\therefore A = 19{,}240$.

A here is a function of the heat of reaction, but as it is safe to assume that this is very close to constant over such a short range of temperature, the excellent agreement of the different values of A shows that the rate of decomposition changes regularly with the temperature in accord with the thermodynamic principles on which van't Hoff's deduction is based.

It was not convenient experimentally to examin the behavior of the three hydrazines, *i. e.*, hydrazobenzene, *p*-methyl hydrazobenzene, and *p*-hydrazotoluene, at the same temperature, and so to get a direct comparison of their velocities of decomposition. However, a comparison of the temperatures at which they show approximately the same rate of change shows clearly that the introduction of methyl groups has a marked weakening effect upon the force which holds the two nitrogen atoms together. If the temperature coefficient of the velocity change were determined for all of the substances, this would afford a quantitative measure of the change of this force as well. In the tetra-arylhydrazine series Wieland[2] showed qualitatively this same tendency, but here for the first time we have an accurate method of detecting the change in stability of the substance with the change in substituent groups. It is further noticed that, contrary to the experience of Wieland,[3] those hydrazines most sensitive to the influence of heat are also most sensitive to rearrangement by acids. The fuller study of this detail will be published later, but the qualitative fact is very well shown by the behavior of the different hydrazines on oxidation in neutral (initially) solution, as was observed incidental to the analysis of the pure substances. Here an alcoholic solution of the hydrazine was added to an alcoholic solution, containing a known amount of iodine, which was more than sufficient to oxidize the hydrazine to the corresponding azo body. In the case of all hydrazines studied, under these conditions

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[1] The average value of K at each temperature is used for the purpose of this calculation.

[2] *Ann. Chem.*, **392**, 128 (1912).

[3] *Loc. cit.*, p. 132.

the amount of iodine consumed did not correspond rigorously to the amount of hydrazine added. The acid formed in the earlier part of the oxidation,

$$^{1}\text{ArNH.NHAr} + \text{I}_2 \longrightarrow \text{ArN : NAr} + 2\text{HI}, \qquad (17)$$

caused a rearrangement of a part of the hydrazine, and so prevented its reaction with iodine, according to this equation. In the case of hydrazobenzene, with certain conditions fixed, about 1% is rearranged by the acid formed in the earlier part of the reaction, before the oxidation is complete; in the case of *p*-methylhydrazobenzene this amount rearranged is about 3% under the same conditions; and with *p*-hydrazotoluene it is about 10%. The three hydrazines are sensitive to thermal decomposition in this same order. This shows qualitatively then that they are probably[2] sensitive to rearrangement by acid in the same order that they are sensitive to decomposition by heat.

In the case of *p*-methylhydrazobenzene there exist three ways in which the thermal decomposition may take place. Aniline and *p*-azotoluene may be formed:

$$2\text{CH}_3\text{C}_6\text{H}_4\text{NH.NHC}_6\text{H}_5 \longrightarrow \text{CH}_3\text{C}_6\text{H}_4\text{N : NC}_6\text{H}_4\text{CH}_3 + 2\text{C}_6\text{H}_5\text{NH}_2, \qquad (18)$$

p-toluidine and azobenzene may be formed:

$$2\text{CH}_3\text{C}_6\text{H}_4\text{NH.NHC}_6\text{H}_5 \longrightarrow \text{C}_6\text{H}_5\text{N : NC}_6\text{H}_5 + 2\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2, \qquad (19)$$

or *p*-toluidine, aniline, and *p*-methylazobenzene may be the products:

$$2\text{CH}_3\text{C}_6\text{H}_4\text{NH.NHC}_6\text{H}_5 \longrightarrow \text{CH}_3\text{C}_6\text{H}_4\text{N : NC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{C}_6\text{H}_4\text{NH}_2. \qquad (20)$$

Qualitatively both aromatic amines were identified[3] in the reaction mixture, and by an indirect method of analysis it was found possible to estimate with rough accuracy the relative amounts of each formed. The results showed that of the total amount of amine formed 33% was aniline and 67% was *p*-toluidine. This seems qualitatively in accord with the observed fact that *p*-hydrazotoluene has the greater tendency to decompose, the diminution in attraction of the two halves of the hydrazine molecule for each other, caused by the introduction of methyl, expresses itself here in the increased tendency of the tolyl group to exist in the simpler molecule toluidine, rather than as a part of an azomolecule.

In the case of *p*-methylhydrazobenzene, an opportunity offered itself to attempt to prepare two *electromeric* substances.[4] *p*-Methylazobenzene

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[1] The symbol Ar here represents a simple or substituted phenyl radical.

[2] The relative speeds of oxidation were not determined.

[3] An effort will be made as soon as time allows to identify the three possible azo compounds.

[4] Falk and Nelson, School of Mines, *Quarterly* 30, p. 179; THIS JOURNAL, **32**, 1637 (1910); W. A. Noyes, *Ibid.*, **35**, 767 (1913).

was formed from nitrosobenzene and *p*-toluidine (see experimental part):

$$C_6H_5.N^{++}O^{--} + CH_3C_6H_4N^{--}H_2^{++} \longrightarrow$$
$$C_6H_5N^{++}:N^{--}.C_6H_4CH_3 + H_2O. \qquad (21)$$

The substance thus prepared should have the indicated distribution of charges on the nitrogen atoms, if no readjustment takes place. On reduction, then, it should give the corresponding hydrazine. In a like manner *p*-nitrosotoluene was treated with aniline:[1]

$$CH_3.C_6H_4.N^{++}O^{--} + C_6H_5.N^{--}H_2^{++} \longrightarrow$$
$$CH_3.C_6H_4.N^{++}:N^{--}.C_6H_5 + H_2O, \qquad (22)$$

and the substance thus prepared should have the indicated distribution of charges on the nitrogen atoms, if no readjustment takes place. On reduction, it too might be expected to give the corresponding hydrazine. However, the two preparations of *p*-methylhydrazobenzene proved identical in melting point, velocity of rearrangement, and percentage of *p*-toluidine and aniline formed. The conclusion must be then, if we cling to the electronic theory, that only one of the two possible electromers is stable under the conditions used.

EXPERIMENTAL PART.

I. Decomposition of Hydrazobenzene.

The hydrazobenzene used in this work was prepared from nitrobenzene by the well-known method of reduction with zinc dust in an aqueous-alcohol medium, strongly alkalin with caustic soda. The crude product was twice recrystallized from 95% alcohol to which a few drops of strong ammonia and several grams of zinc dust had been added.[2] This procedure gave a snow-white product, melting sharply between 126° and 127°, which is oxidized slowly in dry air to the yellow azobenzene. The substance thus prepared was dried for one hour in an oven at 50°, then *in vacuo* over calcium chloride for two hours, and then it was sealed up in glass bulbs under a pressure of 10–20 mm.

The samples were uniformly of the proper melting point, although very slightly tinted with yellow through oxidation during the drying process. Once sealed in the bulbs, no deterioration of the samples was noticed, and they could be kept indefinitely, until used. Assays of the purity of the samples by the iodine method (described below) consistently gave values ranging between 99.7%–100.3%, which deviations represent the experimental inaccuracies of the determination.

Analytical Method. Determination of Hydrazobenzene.

Essentially the same method of analysis as was adopted in determining

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[1] In aniline C_6H_5 probably carries a positive charge; in nitrosobenzene it is also probably positive, but may be negative. Since the distribution of charges between phenyl and nitrogen is not material to the discussion, it will be omitted.

[2] Van Loon, *Rec. Trav. Chim. Pays.-Bas.*, **13**, 63 (1904).

the purity of the hydrazobenzene was used in the velocity measurements, for the determination of the quantity of unchanged hydrazobenzene left at the end of any time interval, *t*. Accuracy demands certain precautions, and so the method will be given in detail.

The method of analysis was based on the fact that iodine in alcoholic solution oxidizes hydrazobenzene to azobenzene, with the formation of two molecules of hydriodic acid per molecule of hydrazobenzene used (equation 17).

Further on (p. 1162), a second method of analysis, used to follow the velocity of decomposition of hydrazobenzene by the determination of the aniline formed, will be described.

The solutions used for the first method were:

(1) 0.1 *N* iodine made from 13.1 g. of resublimed iodine, 18 g. of potassium iodide, 1,000 g. of 50% alcohol. The solution was allowed to stand one week before standardization, and after that time it did not change appreciably.

(2) 0.1 *N* sodium thiosulfate, made from 25.7 g. of $Na_2S_2O_3.5H_2O$, 2 g. ammonium carbonate, 1,000 g. of water. This solution was also allowed to stand for one week before standardization, and after that time it did not change appreciably.

As the iodine solution was very volatil, weight burets, with ground glass stoppers, were used in all titrations with both solutions. With the aid of a weight buret, a weighed quantity of thiosulfate solution was titrated against a measured volume of a standard potassium permanganate solution by means of acidified potassium iodide and starch indicator. The potassium permanganate solution was standardized against iron wire of known composition. In this way the value of one gram of the sodium thiosulfate solution was fixed in terms of cubic centimeters of 0.1 normal solution. For the purposes of this investigation, then, a 0.1 *N* solution of the standard solutions used was considered as one containing 0.1 gram-equivalent per 1,000 grams of solution.

In the assay of hydrazobenzene, first a known quantity of the standard iodine solution, amounting to about 10 grams excess over the theoretically required quantity, was run into a 500 cc. glass-stoppered bottle. To this was added an amount of 0.1 *N* alcoholic aniline solution, slightly more than sufficient to neutralize the hydriodic acid which would be liberated in the subsequent oxidation. The weighed sample of hydrazobenzene was then dissolved in the least necessary amount of absolute alcohol and the solution was added at once, with rinsing, to the alcoholic iodine and aniline solution. After standing for ten minutes the solution was acidified with 10 cc. of 6 *N* sulfuric acid and the standard thiosulfate solution was added from a weight buret until, judged by the color, the excess of iodine was nearly consumed. 400 cc. of water was then added, which precipitated out the yellow azobenzene in fine yellow crystals and formed nearly 500 cc. of a solution entirely opaque, and colored bright yellow by the suspended azobenzene. To this were then added 10 cc. of starch indicator solution, which produced a greenish black coloration. Then more thiosulfate was added until the bright yellow color of the solution was just restored. Duplicate experiments agreed within 0.3% of the mean value.

	Wt. sample. Gram.	Grams 0.1 N I.	Per cent. found.
1...........	0.2004	21.71	99.7
2...........	0.2002	21.82	100.3

It was found that no loss of accuracy was occasioned by the presence of the suspended azobenzene, although some of the iodine was temporarily retained by the suspended solid, which caused an apparent end point to come just before the true end point was reached. If the solution was allowed to stand for one minute after the starch color first cleared, the color darkened again, and one or two drops of thiosulfate solution permanently cleared the color (until it discolored from oxidation from the air). Separate trial experiments showed that the aniline had no reducing effect on the iodine unless allowed to stand with it for some time in rather great concentration, when, owing to the alkalinity, the alcohol present was attacked slowly. Independent experiments showed that the solution must be ultimately diluted so that the alcohol content was under 10%, in order to get a sharp color change with the starch indicator.

If no aniline was added and the hydriodic acid formed in the oxidation was allowed to remain in the solution, a slight loss of hydrazobenzene was occasioned, since the acid caused a portion of the hydrazobenzene to undergo the benzidine rearrangement before the oxidation was completed. This loss is somewhat variable, depending on (1) the quantity of hydrazobenzene oxidized, (2) the volume of the solution, and (3) the excess of iodine used. However, under the conditions of the analyses, as made, the loss does not exceed 1%. In the calculation of the velocity constant from analytical data, obtained in this way, this loss may be entirely neglected, since the decompositions show itself to be one of the first order. For if it may be assumed in all cases to amount to a constant per cent. of the hydrazobenzene present, the correction factor will cancel out of the expression for the velocity constant (see equation (7)).

Preparations for a Velocity Determination.

The alcohol used as solvent for the substance was prepared by distillation of the commercial "absolute" alcohol from sodium, the middle third only being used. For making the 50% alcohol used as wash-liquid, the commercial "absolute" alcohol was used directly. In all cases it was tested for reducing power toward iodine, and was found to have none.

Since the temperature at which the decomposition was allowed to take place lies above the boiling point of the solvent, sealed tubes were used in all determinations, after the manner described by Rosanoff.[1] To prepare for a velocity determination, a weighed quantity of hydrazobenzene was dissolved in a known volume of absolute alcohol. With the aid of a 5 cc. pipet, equal portions of this solution were transferred to a number of clean tubes. The tubes were then immersed in a freezing mixture and the constrictions sealed off at a pressure of 10–20 mm. The low temperature prevented the loss of any appreciable quantity of the alcohol, as was determined by weighing a large number of the tubes before and after sealing. The portions of the solution thus prepared were always colored with azobenzene, and, on standing, colored still further from the oxygen dissolved in the alcohol. However, since the solution, before taking the samples, was homogeneous, this slight loss of hydrazobenzene was perfectly uniform. Furthermore, since the reaction proved to be monomolecular beyond any doubt, the initial concentration is of no significance, and separate experiments showed that azobenzene in large excess does not affect the velocity of the reaction in any way.

The Thermostat.

The thermostat used in this investigation consisted of a jacketed, seven-gallon iron can filled with a non-volatil oil.[2] It was heated electrically with a primary circuit sufficient to maintain the temperature at a point about ten degrees below the desired temperature. A secondary circuit, controlled by a mercury-in-glass electric thermo-regulator, operated an electric lamp immersed in the oil, and gave the exact temperature regulation. Stirring was furnished by an electrically driven rotary screw stirrer, which kept the liquid of the bath in rapid motion. Under the conditions of the experiment, the maximum variation was within 0.02° of a given temperature. All points of the bath registered a temperature within 0.02° of the mean. In setting the regulator, the accurate measure of the temperature was obtained from the P. T. R. thermometer, No. 39,519, which registers in degrees centigrade, hydrogen scale, accurate to 0.05°. Suitable correction was made for the slight length of exposed mercury column.

Determination of the Velocity of Decomposition.

In the determination of the velocity of decomposition, the tubes prepared as above described, were each wound with copper gauze (as a precaution against explosion) and fastened to a metal deflagrating spoon, which made a very suitable holder. The whole number of tubes was then heated to 70–80° in a small oil bath and immersed simultaneously in the thermo-

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[1] Rosanoff, THIS JOURNAL, 30, 1899 (1908).

[2] Cottonseed oil was used at first, but with continued use it oxidized so badly that it was replaced by a heavy mineral oil for which we are very much indebted to Dr. Humphreys of the Standard Oil Co., Whiting, Indiana.

stat and the exact time recorded as "zero time." After a definit interval (usually one hour) a tube was withdrawn and the time accurately noted as t_1. On removal, each tube was first plunged into oil heated to 70–80°, and then, after thirty seconds, into cold water. At regular intervals, tubes were withdrawn until the reaction was about two-thirds completed. As soon as convenient, after removal, the tubes were opened and the contents analyzed for hydrazobenzene, exactly as described above for the assay of the pure sample, except that no aniline solution was used. As the reaction proceeded, the reaction mixture became more and more alkalin, due to aniline formation. It was found necessary to add an amount of 0.1 *N* hydrochloric acid to the titration mixture to compensate for the aniline formed, for in the alkalin, or very faintly acid solution, a dark coloration appeared which was not noticed either in the analysis of the pure substance or in a faintly acid solution. This coloration must have been caused by the action of iodine on some substance other than the hydrazobenzene or the normal products of the decomposition (see p. 1149).

Proceeding in the manner just described, an examination was made of the rate of decomposition of hydrazobenzene in alcoholic solution of initial concentration roundly 0.2, 0.1 and 0.05 molar, respectively. In the first two concentrations, the amount of solution used was that delivered by a 5 cc. D. R. pipet, on draining fifteen seconds. In the 0.05 molar concentration the sample put into each tube was that delivered by a 10 cc. D. R. pipet on draining fifteen seconds. On the duplicate determination of this concentration, a serious explosion of two of the tubes wrecked the apparatus. It is probable that the cause of this accident was the leaving of insufficient vapor space over the liquid in the tube. However, as the explosion was so violent, in all cases in the subsequent work the sample put into each tube was that delivered by a 5 cc. pipet. In the following tabulated results, apparent discrepancies in corresponding tubes of supposedly the same initial concentration are due to slightly different conditions in making up the solutions, which caused different amounts of oxidation of the hydrazobenzene before the tubes were sealed (see p. 1156), and to irregularities in the heating between the times, t_0 and t_1, occasioned by the plunging of the cold tubes into the hot thermostat. However, *always*, all of the tubes of one series were treated in an identical manner until successively removed from the bath.

From the quantities of hydrazobenzene remaining after the different time intervals a calculation of the velocity constant was made according to the law for a monomolecular reaction:

$$K_{\text{mono.}} = \frac{1}{t_2 - t_1} \log.\ \text{nat.} \frac{A - x_1}{A - x_2}. \qquad (7a)$$

In these and subsequent calculations the grams of iodine solution consumed for a definit volume of the solution (given under I in the tables) were used in the logarithmic term in place of the concentrations $(A—x_1)$ and $(A—x_2)$, since the concentrations are directly proportional to these titration results.

For the purpose of comparison a calculation was also made according to the law for a dimolecular reaction:

$$K_{\text{dimol.}} = \frac{1}{t_2 - t_1} = \frac{x_2 - x_1}{(A - x_2)(A - x_1)}. \qquad (4a)$$

Since the latter formula is so patently inapplicable to this reaction, it was not thought necessary to make the minor correction for the expansion of alcohol between 15° and 140°.

In the following tables (I–III) is stated, first, the weight of hydrazobenzene used; then under V the total volume of its solution in absolute alcohol at 15°; under *v* the volume of the solution that was put into each tube; and finally the temperature. The time *t* in minutes is given in the first column under T; the amount of iodine, expressed in grams of 0.1 *N* solution,[1] which was consumed by the unchanged hydrazobenzene, is given in the second column under I, and the velocity "constants," $K_{\text{mono.}}$ and $K_{\text{dimol.}}$, respectively, for a monomolecular and a dimolecular reaction, are given in the third and fourth columns. In the fifth and sixth columns (Tables I and II) are given the results of duplicate experiments carried out under the same conditions, with the use of the same time intervals; and in the last column is given an average of the values of $K_{\text{mono.}}$.[2]

The data of a later similar series of experiments (see Table IV, further on), carried out at a slightly lower temperature, are analyzed to determin whether a case of parallel monomolecular and dimolecular reactions is indicated (see p. 1160).

TABLE I.

2 grams hydrazobenzene. V = 50 cc., *v* = 5 cc. Temp. = 140.55° ± 0.05°.

	A.			B.		
T.	I.	10^5 $K_{\text{mono.}}$	10^4 $K_{\text{dimol.}}$	I.	10^5 $K_{\text{mono.}}$	Av. 10^5. $K_{\text{mono.}}$
60	19.67	...	...	19.17	...	...
180	16.35	154	86	15.81	160	157
240	14.83	157	92	14.34	161	159
300	13.35	161	100	13.12	158	159
420	11.24	156	106	10.91	156	156
540	9.42	153	115	9.18	153	153
720	7.34	149	129	7.18	149	149
900	5.93	143	140	5.71	144	144
						154

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[1] See the exact definition given on p. 1154.

[2] In the preliminary report, *loc. cit.*, the temperature at which this series was run was given as 140.2° ± 0.05°. A recalculation of the correction gave this temperature as 140.55° ± 0.05°.

TABLE II.

1 gram hydrazobenzene. V = 50 cc., v = 5 cc. Temp. = 140.55° ± 0.05°.

	A.		B.		
T.	I.	10^5 $K_{mono.}$	I.	10^5 $K_{mono.}$	Av. 10^5 $K_{mono.}$
60	9.45	...	9.51	...	...
180	7.78	162	7.83	162	162
240	7.04	163	6.94	(175)	163
300	6.44	160	6.49	159	159
420	5.31	160	5.37	159	159
540	4.47	156	4.51	155	155
720	3.52	150	3.52	151	150
900	3.14	(131)	2.80	145	145
					Av. 156

TABLE III.

1 gram hydrazobenzene. V = 100 cc., v = 10 cc. Temp. = 140.55° ± 0.05°.

T.	I.	10^5 $K_{mono.}$	10^4 $K_{dimol.}$
60	9.32	...	...
180	7.71	158	370
240	7.01	158	400
300	6.39	157	410
420	5.31	156	450
540	4.51	151	480
720	3.50	148	540
900	2.76	145	610
		Av. 153	

The Effect of Temperature on the Velocity of Decomposition.

Proceeding in a manner similar to that described, series of velocity determinations were run at each of three temperatures, differing by 5.00° ± 0.05°, in order to investigate the temperature coefficient of the action. Each series consisted of determinations made with different initial concentrations, namely approximately 0.2, 0.1 and 0.05 molar. At each temperature the regulator was set by comparison with the P. T. R. thermometer, and a Beckmann thermometer was set so that the slightest variation of temperature could be noticed, and corrected for. In all cases the temperature given is the corrected temperature. In the following tables (IV–VI), each table consists of the results of three separate velocity determinations, each carried out with a hydrazobenzene solution of different concentration. In each case experiment A was carried out with a 0.2 molar solution of hydrazobenzene, experiment B with a 0.1, and C with a 0.5 molar solution [2, 1 and 0.50 grams of hydrazobenzene in 50 cc. solution, respectively (V = 50 cc.)]. In all cases each tube was charged with 5 cc. of solution (v = 5 cc.) The data given and the symbols used have the same significance as in Tables I–III. The calculation of $K_{dimol.}$ has been omitted.

TABLE IV.

Temp. = 140.35° ± 0.05°.

	Experiment A.		Experiment B.		Experiment C.		
T.	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	Av. 10^5 K$_{mono.}$
60	19.15	...	9.47	...	4.68	...	...
	19.17	...	9.47	...	4.66	...	...
180	15.97	151	7.94	147	3.87	156	151
240	14.68	148	7.24	149	3.55	152	150
300	13.51	146	6.65	147	....	...	147
420	11.36	145	5.59	146	2.71	151	147
540	9.69	142	4.76	143	2.33	145	143
720	7.57	141	3.70	142	1.83	142	142
900	6.06	137	2.98	138	1.45	139	138
							Av. 145

TABLE V.

Temp. = 145.35° ± 0.05°.

	Experiment A.		Experiment B.		Experiment C.		
T.	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	Av. 10^5 K$_{mono.}$
30	19.44	...	9.60	...	4.71	...	...
	19.39	...	9.60	...	4.73	...	...
90	16.69	252	8.26	251	4.06	251	251
120	15.37	259	7.61	258	3.74	258	258
150	14.34	253	7.01	262	3.45	261	259
210	12.34	252	6.07	255	2.96	259	255
270	10.73	247	5.20	255	2.52	261	253
360	8.66	245	4.12	256	2.05	252	251
450	7.11	239	3.32	253	1.69	244	245
							Av. 253

TABLE VI.

Temp. = 150.35° ± 0.05°.

	Experiment A.		Experiment B.		Experiment C.		
T.	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	I.	10^5 K$_{mono.}$	Av. 10^5 K$_{mono.}$
45	17.12	...	8.52	...	4.49	...	...
	17.09	...	8.54	...	..	...	...
85	14.30	448	7.11	454	3.75	450	451
105	13.14	440	6.50	453	3.39	468	454
125	12.03	440	6.06	(426)	3.13	451	446
165	10.19	432	5.04	438	2.62	449	440
205	8.66	425	4.27	432	2.21	443	433
265	6.89	413	3.41	417	1.79	418	416
325	5.93	(378)	2.75	404	1.39	419	412
							Av. 436

Analysis of Data for Parallel Monomolecular and Dimolecular Reactions.

For a parallel monomolecular and dimolecular reaction (see p. 1147) we have:

$$\frac{dx}{dt} = K_1 (A - x) + K_2 (A - x)^2. \tag{13}$$

Integrating, we find:

$$K_1 (t_2 - t_1) = \ln \frac{(A - x_1)(K_1/K_2 + A - x_2)}{(A - x_2)(K_1/K_2 + A - x_1)}. \tag{13a}$$

By using the analytical data for two equal time intervals $(t_2 - t_1)$ we obtain simultaneous equations from which the value of K_1/K_2 is found. From the data for the time intervals 60 to 300 minutes and 300 to 450 minutes in experiment A, of Table IV, we find $K_1/K_2 = 0.8$ and $K_1 = 0.00121$, $K_2 = 0.00151$. For the critical consideration of the data of experiments A, B and C, where the concentrations of hydrazobenzene were $^1/_2$ and $^1/_4$ as great, respectively, as in A, we may properly assume that the velocity constant of the monomolecular reaction must remain the same as in A and calculate the value of the dimolecular constant, in order to see whether there is really a parallel dimolecular reaction. Using the value $K_1 = 0.00121$, accordingly, in analyzing the data for the time interval 60 to 300 minutes in experiment B and the interval 60 to 240 minutes in experiment C, we obtain the values for K_2 given in the first line of the following Table, IV*a*. If we use the data of each table for the calculation of the values of K_1 and K_2, the ratio $K_1/K_2 = 0.8$ being assumed to hold in each of the three series, then the values for K_2 as given in the second line of the table are found. The earliest time intervals were selected because a pure case of a parallel monomolecular and dimolecular reaction must show itself at once in the results. The later measurements could have in them a retarding influence of some accumulating product of the main action or of a secondary action (see p. 1149).

TABLE IV*a*.

	A.	B.	C.
10^5 K_2........................	151	331	799
10^5 K_2........................	151	168	181

It is clear that no parallel dimolecular reaction is indicated. The change in the values for K_2 shown in line 1, where the same constant for the monomolecular reaction was used for the three experiments, A, B and C, must be given most weight. In judging the results given in line 2, one must recall that with the increase in the dimolecular constant K_2, the monomolecular constant K_1 also rapidly increases, these calculations assuming that their ratio remains the same. We may safely conclude, therefore, that the thermal decomposition of hydrazobenzene is not a case of a parallel monomolecular and dimolecular reaction, but represents a monomolecular reaction, with some other secondary reaction, causing some retardation of the action (see p. 1149).

Determination of Velocity by Analysis for Aniline Formed.

As a check on the preceding work, an effort was made to analyze the contents of the tubes for aniline in a velocity determination. By a modification of the well-known bromination analysis for aniline, a suitable method was worked out, which gave very consistent results. The reaction in this case runs quantitatively according to the equation:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow Br_3C_6H_2NH_2 + 3HBr.$$

The following aqueous solutions were used:

(1) 10% potassium iodide; (2) 10% potassium bromide; (3) 6 N sulfuric acid; (4) 10 N sodium hydroxide; (5) standard 0.1 N sodium thiosulfate (described before); (6) standard 0.1 N potassium bromate. Also 0.1 N iodine solution in 50% alcohol (described before).

The potassium bromate solution was standardized against the standard sodium thiosulfate solution with acidified potassium iodide and starch indicator.

In performing the analysis in the velocity determinations, the sample was oxidized exactly as before with an excess of iodine solution to remove any reducing substance present (*e. g.*, hydrazobenzene). After 10 minutes, 10 cc. of 6 N sulfuric acid was added, and steam was passed through the solution (in a distilling flask) until all of the azobenzene, excess iodine, alcohol and other possible non-basic volatil substances were removed; 10 cc. of 10 N sodium hydroxide were then added, and the volatile bases distilled with steam, in an ammonia distillation apparatus, into dilute sulfuric acid, until 400 cc. of distillate had passed over. A flame was kept under the distillation flask, and toward the end of the distillation the volume was such that salts began to crystallize out. To the acid distillate were added 10 cc. of potassium bromide solution, and a definite amount of the standard potassium bromate solution. The flask containing this solution was then closed with a stopper, holding a calcium chloride tube of beads, wet with potassium iodide solution. The solution was then warmed to 50° and allowed to stand for fifteen minutes. The white tribromoaniline precipitated out rapidly, and at the end of the time the solution was slightly yellow with free bromine. Potassium iodide solution (10 cc.) was then rinsed through the tube of beads, the solution was cooled, and the end point determined with the standard thiosulfate, with starch indicator. In this case

$$1 \text{ g. of } 0.1\ N\ KBrO_3 = 0.00155 \text{ g. aniline.}$$

In preliminary trials, pure aniline being worked through the entire process, 0.0500 g. could be determined with an accuracy of 0.5%.

In the velocity determination by this method, two tubes at time, t_1, were taken, one of which was analyzed for hydrazobenzene in the usual manner, the other of which was analyzed for the aniline formed during the heating preliminary to the first measurement made at the moment t_1. If we represent by B_1 and B_t the grams of 0.1 *N* solution[1] of bromine consumed to convert aniline into tribromaniline[2] at the first measurement at t_1 and at any subsequent time t, respectively, then we have for N_1 and N_t, the corresponding concentrations of aniline formed, $N_1 = B_1/6$ and $N_t = B_t/6$. We will call A_1 the equivalent concentration[3] of hydrazobenzene at the moment t_1, when the first measurement was made and the hydrazobenzene determined directly, as explained above. Calling A_t the equivalent concentration of hydrazobenzene at any subsequent moment t, we have the relation:[4]

$$A_t = A_1 - 2(N_t - N_1) \text{ or } A_t = A_1 - \frac{B_t - B_1}{3}.$$

By the insertion of the values for A, thus obtained from the experimental data, into the logarithmic term of the equation for a monomolecular reaction, a series of velocity constants was computed similar to those found in the previous work at 140°. Duplicate determinations were made with initial concentrations of hydrazobenzene approximately 0.2 normal (0.1 molar).

In the following table (VII) is stated first the weight of hydrazobenzene

TABLE VII.

1 gram hydrazobenzene. V = 50 cc., v = 5 cc. Temp. = 140.35° ± 0.05°.

	First experiment.			Second experiment.			
T.	B.	A_t.	10^5 K_{mono}.	B.	A_t.	10^5 K_{mono}.	Av. 10^5 K_{mono}.
60	2.13	9.72[5]	...	2.03	9.79[5]	...	...
180	6.94	8.12	149	6.94	8.16	154	151
240	8.98	7.44	149	9.07	7.45	152	150
300	10.95	6.78	150	10.94	6.82	151	150
420	14.33	5.65	151	14.35	5.68	151	151
540	16.84	4.82	146	16.94	4.82	148	147
720	19.98	3.77	144	19.79	3.87	141	142
900	22.52	2.92	143	21.84	3.19	134	138
							Av. 147

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[1] See the definition of normal solution, p. 1154.

[2] An examination of the white crystalline precipitate obtained in these analyses showed it to be practically pure 1,3,5-tribromaniline (m. p. 119° observed; m. p., Beilstein, 121°).

[3] For the calculation of the constant of a monomolecular reaction molar concentrations need not be used and equivalent concentrations were used therefore in this calculation as the analytical data presented these directly. Two equivalents of hydrazobenzene = one mole.

[4] A molecule of aniline is formed from one molecule or *two equivalents* of hydrazobenzene. The aniline formed decreases the equivalent concentration of hydrazobenzene therefore by twice the number of equivalents.

[5] These values, A_1, were determined by direct titration with iodine, the remainder of the values in the columns A_t calculated as indicated in the text.

used; then under V the total volume of its solution in absolute alcohol at 15°; and under v the volume of solution that was put into each tube. The time t is given in minutes in the first column under T; the grams of 0.1 N bromine solution consumed by the aniline formed is given in the second column under B; the equivalent concentration of hydrazobenzene, calculated as indicated in the above equation, is given in the third column under A_t; in the fourth column is the velocity constant, $K_{mono.}$, for a monomolecular reaction; in the fifth, sixth and seventh columns are the results of a duplicate determination carried out under the same conditions, and with the same time intervals; and in the last column is the average value of the velocity constant $K_{mono.}$.

Experiments to Determin the Cause of the Falling Off of the Constant.

In order to investigate the unexpected retardation of the reaction, as it nears completion (see theoretical part), velocity determinations were run with hydrazobenzene solutions, to which had been added amounts of aniline and azobenzene. It is noticed that there is no effect of these substances on the velocity, within the limits of observational error.

Three solutions of initial concentrations of hydrazobenzene, approximately 0.1 molar, were made. To two of these solutions was added sufficient aniline to make them 0.05 and 0.1 molar, with respect to aniline.

TABLE VIII.

1 gram hydrazobenzene. V = 50 cc., v = 5 cc. Temp. = 140.35° ± 0.05°.

	A (0.233 g. aniline).		B (0.466 g. aniline).		
T.	I.	10^5 Kmono.	I.	10^5 Kmono.	Av. 10^5 Kmono.
60	9.67	...	9.69	...	...
	9.67	...	9.71	...	...
180	8.02	156	8.04	156	156
240	7.37	151	7.35	154	152
300	6.73	151	6.72	153	152
420	5.71	146	..	...	146
540	4.94	140	..	...	140
720	3.84	140	..	...	140
					Av. 148

TABLE IX.

1 gram hydrazobenzene. V = 50 cc., v = 5 cc. Temp. = 140.35° ± 0.05°.
0.450 gram azobenzene.

T.	I.	10^5 Kmono.
60	9.90 9.88	...
180	8.26	150
240	7.51	153
300	6.91	149
		Av. 151

To the third solution was added sufficient azobenzene to make it 0.05 molar with respect to that substance. From each of these solutions a series of tubes was filled. The course of the reaction was followed in the usual manner by analyses of the contents of the tubes after known time intervals. In the preceding tables (VIII–IX) the data given and the symbols have the same significance as described for Tables I–III. In addition, the amount of aniline (or azobenzene, as the case may be) added is stated. The calculation of $K_{\text{dimol.}}$ has been omitted:

In order to investigate the effect of the *solvent* as a possible cause of the disturbing reaction, a duplicate series of velocity determinations was run with hydrazobenzene, dissolved in pure thiophene-free benzene, dried over sodium. The analytical method was the same as usual, for the benzene caused no serious interference with the analysis. However, the end point with this method was not as sharp as when alcohol was used. Just as was always noticed before, toward the end of the reaction a coloration of the titration mixture occurred, when an excess of acid was not present, thereby indicating the presence of an, as yet, unidentified product of the reaction. In the benzene medium, the velocity of decomposition is much slower, as it requires a temperature of 155° to give approximately the same velocity that obtains in an alcohol medium at 140°.

Aside from the effect on the speed of decomposition, the benzene medium seems to have no further influence on the nature of the reaction, for the same retardation of the reaction occurs as it nears completion.

TABLE X.

1 gram hydrazobenzene. $V = 50$ cc., $v = 5$ cc. Temp. = 155.35° ± 0.05°.

T.	I. A.	I. B.	Av. 10^5 K_{mono}.
60	9.82	9.68	...
180	8.29	8.23	138
240	7.57	7.62	139
300	7.01	7.05	136
420	6.08	5.89	135
540	5.18	5.18	131
720	4.11	4.11	127
900	3.43	3.40	125
			Av. 133

To investigate further into the nature of the apparent decrease in velocity of the reaction as it nears completion, a search was made for *benzidine* among the products of the reaction, on the theory that water, carbon dioxide, or some such faintly acidic substance might cause such a rearrangement (see footnote, p. 1147). To make this test, a portion of the solution was heated at 140° for several hours, and the excess of hydrazobenzene removed by oxidation with iodine in presence of an excess of aniline. The alcohol, azobenzene and iodine were removed by steam distillation in acid solution, and the volume reduced to about 15 cc. One gram of solid ammonium sulfate was added, and the solution allowed to stand. A slight, flocculent, dark-colored precipitate was noticed; it was filtered out and treated with chlorine water, but gave no color change. As little as 0.0005 g. of benzidine gave a considerable precipitate under these conditions, and on treatment with chlorine water gave a distinct red coloration to the liquid. The experiment was repeated four times with the heated hydrazobenzene solution, but in no case was any trace of benzidine noticed.

To determin whether hydrazobenzene can be formed reversibly from aniline and azobenzene (p. 1148), a series of tubes, containing each aportion of an alcoholic solution, 0.2 molar with respect to aniline and 0.1 molar in respect to azobenzene was heated at 140° for various intervals of time, and on removal from the thermostat was analyzed as usual for hydrazobenzene. In no case could any absorption of iodine be noticed above a minimal amount consumed, owing to the standing of the alcoholic iodine solution in the presence of the not inconsiderable amount of aniline. This absorption, moreover, was as great in a tube that had not been heated as in one that had been heated for twenty-four hours.

II. Decomposition of *p*-Methyl Hydrazobenzene.

The *p*-methylhydrazobenzene used in this work was prepared by the reduction of *p*-methylazobenzene with zinc dust and sodium hydroxide in alcoholic solution.[1] The *p*-methyl azobenzene was prepared according to the method of Mills[2] from nitrosobenzene and *p*-toluidine. The crude *p*-methylhydrazobenzene, after two recrystallizations from 95% alcohol, gave a product, perfectly colorless, having a constant melting point of 91°. It was dried and preserved in sealed bulbs, as was the hydrazobenzene. The pure product was assayed as was the hydrazobenzene, and showed a reducing power very closely approximating that demanded by theory:

	Wt. sample. Gram.	0.1 *N* I.	Per cent. found.
1	0.2007	20.26	100.0
2	0.2014	20.22	99.6

It was noticed that this substance is much more sensitive to acid than is the hydrazobenzene. When 0.2 g. of it is oxidized with iodine in a volume of about 50 cc. the acid formed in the oxidation causes 3 to 4% of the substance to undergo the semidine (or similar) rearrangement before the oxidation is completed. It is necessary then to add aniline to the sample being analyzed, which prevents this loss entirely, if a slight excess is used.

However, in the velocity determination it was found that the titrations could not be carried out in alkalin solution, for also in the decom-

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[1] Jacobson and Lischke, *Ann.*, 303, 369 (1898).

[2] *J. Chem. Soc.*, 67, 929 (1895).

position of *p*-methylhydrazobenzene some disturbing reaction goes on, which forms a compound, giving a black coloration with iodine in alkalin solution. To avoid, as far as possible, both difficulties, an amount of 0.1 *N* aniline solution, in absolute alcohol, was added to the titration mixture, which would be insufficient by 2.0 cc. to neutralize the hydriodic acid formed in the oxidation. The volume of the titration mixture being considered constant, this enables the titrations to be carried on under a condition of constant minimal acidity. In this way, with the pure substance, consistently 98.5% of the *p*-methylhydrazobenzene could be accounted for. If then in all analyses 98.5% of the undecomposed hydrazo compound is found, the correction factor will cancel out of the expression for the monomolecular velocity constant, and so the numerical value of the constant is not changed. That the reaction is monomolecular cannot be doubted, for this slight correction could not possibly change the apparent order of the reaction.

From a preliminary experiment, an approximate value of the velocity constant was obtained, and by using this value the proportion of the hydrazo compound and of aniline present in a tube at any time, *t*, could be calculated. Thus from a consideration of the amount of hydriodic acid which would be formed, and the aniline (or *p*-toluidine) which already was present in the solution, the proper amount of 0.1 *N* aniline solution was added to the titration mixture, and the analysis performed as usual.

In the manner described for hydrazobenzene, with the above mentioned modifications, an examination was made of the rate of decomposition of *p*-methylhydrazobenzene in alcoholic solutions for initial concentration approximately 0.2, 0.1 and 0.05 molar, respectively. From the quantities of the hydrazo compound left after the various time intervals the calculation of the velocity constant[1] was made as before.

TABLE XI.

2.10 grams *p*-methylhydrazobenzene. V = 50 cc., v = 5 cc. Temp. 125.30° ± 0.05°.

	A.		B.		
T.	I.	10^5 $K_{mono.}$	I.	10^5 $K_{mono.}$	Av. 10^5 $K_{mono.}$
60	18.77	...	18.83	...	...
180	15.71	148	15.73	150	149
240	14.40	147	14.46	147	147
300	13.18	147	13.12	150	148
420	11.13	145	11.18	145	145
540	9.44	143	9.50	143	143
720	7.60	137	7.59	138	138
900	6.18	132	6.21	132	132
					Av. 143

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[1] We have here two parallel decompositions of methyl-hydrazobenzene, aniline being formed in the one, toluidine in the other. The velocity equations show that $K_{mono.}$, as calculated, represents the sum of the corresponding velocity coefficients $K_{anil.}$ and $K_{tol.}$.

TABLE XII.

1.05 grams p-methylhydrazobenzene. $V = 50$ cc., $v = 5$ cc. Temp. = 125.30 ± 0.05°.

	A.		B.		
T.	I.	10^5 $K_{mono.}$	I.	10^5 $K_{mono.}$	Av. 10^5 $K_{mono.}$
60	9.27	...	9.22	...	...
180	7.66	159	7.71	148	153
240	7.01	155	6.96	156	155
300	6.45	151	6.49	146	148
420	5.40	150	5.41	148	149
540	4.59	147	4.60	145	146
720	3.70	139	3.69	141	140
900	3.00	134	2.97	135	134
					Av. 146

TABLE XIII.

0.53 gram p-methylhydrazobenzene. $V = 50$ cc., $v = 5$ cc. Temp. = 125.30° ± 0.05.°

	A.		B.		
T.	I.	10^5 $K_{mono.}$	I.	10^5 $K_{mono.}$	Av. 10^5 $K_{mono.}$
60	4.54	...	4.51	...	...
180	3.69	(173)	3.74	156	156
240	3.41	159	3.42	154	156
300	3.12	156	3.16	148	152
420	2.65	149	2.64	149	149
540	2.25	146	2.23	147	146
720	1.79	141	1.81	138	139
900	1.43	138	1.43	134	136
					Av. 148

An attempt was made to prepare the theoretically possible electromer of p-methylhydrazobenzene (see p. 1152) by reduction of the azo compound prepared from nitrosotoluene and aniline by the Mills[1] synthesis. The product thus obtained was then closely compared with the p-methyl

TABLE XIV.

1.05 grams p-methylhydrazobenzene.[2] $V = 50$ cc., $v = 5$ cc. Temp. = 125.30° ± 0.05.°

T.	I.	10^5 $K_{mono.}$
60	9.24	...
180	7.64	158
240	6.97	157
300	6.37	155
420	5.36	151
540	4.59	146
720	3.65	141
900	3.01	133
		Av. 149

[1] *Loc. cit.*

[2] The sample prepared from p-nitrosotoluene and aniline was used in this determination—designated as the β-form.

hydrazobenzene, previously described. For the sake of convenience, these two forms may be designated as "α" and "β," respectively, in the order of preparation, although no difference was found between them. The melting points of the two forms are the same, 91°,[1] and a melting point of a mixture of the two shows no depression. A velocity determination was also run with the "β" form, which shows that the rate of decomposition of the two forms is the same. The preparation of tubes and the method of analysis were the same as described before.

Decomposition Products of *p*-Methyl Hydrazobenzene.

A qualitative test was first made for the two aromatic amines, which theoretically could be formed from the breaking down of the unsymmetrical *p*-methylhydrazobenzene molecule. A portion of the reaction mixture was oxidized with an excess of 0.1 *N* iodine solution, the solution acidified, and distilled with steam to remove iodine, alcohol and azo bodies. The residue was made alkalin and again distilled with steam, and the distillate tested for (1) aniline and (2) *p*-toluidine. Aniline[2] was identified by the formation of a purple coloration, when calcium hypochlorite solution was added to some of the distillate, made faintly alkalin with sodium hydroxide. *p*-Toluidine[3] was identified by the formation of a red coloration, when a portion of the distillate was boiled with a few drops of ferric chloride in dilute hydrochloric acid solution.

By a modification of the method used to determin aniline (see p. 1162), it was found possible to obtain an indirect analysis for the proportion of aniline and *p*-toluidine formed. It was found that in warm solutions bromine destroys *p*-toluidine, with consumption of an indefinit amount of the former. However, at 0° bromine reacts quantitatively with *p*-toluidine forming 1,5-brom-3-methylaniline according to the equation:

$$CH_3C_6H_4NH_2 + 2Br_2 \longrightarrow CH_3C_6H_2Br_2NH_2 + 2HBr.$$

From pure samples of *p*-toluidine a product with the correct melting point, 73°, is precipitated, and the proper amount of bromine is consumed, when the reaction mixture is kept cooled to 0°.

Since potassium bromate will not liberate bromine freely from acidulated bromide solutions at 0°, it was necessary to use an aqueous bromine solution. This solution was made up as follows: 8.5 g. bromine, 50 g. potassium bromide, 1000 g. water. It was standardized against 0.1 *N* thiosulfate solution with acid potassium iodide and starch indicator. When a glass-stoppered weight buret was used in the titration, no great loss from volatilization of the bromine was noticed. The other solutions

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[1] The melting point given by Jacobson and Lischke, *Ann.*, **303**, 369 (1898), is 86–87°.

[2] *Compt. rend.*, **67**, 398 (1868).

[3] Biehringer and Busch, *Chem. Ztg.*, **26**, 1128 (1902).

used were the same as described in the analysis for aniline. In the analysis of a sample of the velocity mixture, the unchanged hydrazo compound was first oxidized with iodine. However, to prevent the formation of certain amounts of semidine, a 0.1 *N* ammonium carbonate solution was used to destroy the acid formed in the oxidation, just as aniline had been used before. This was found to have the same effect and introduced no substance which would absorb bromine on the later stage of the analysis. After the oxidation the alcohol, iodine and azo compounds were removed by distillation in acid solution, and then the two amines were distilled into an acid solution. The acid distillate was then cooled in a freezing mixture until ice separated out; a known quantity of standard bromine water was then added and the mixture allowed to stand for ten minutes. Potassium iodide solution (10 cc.) was then added and the solution was titrated with 0.1 *N* sodium thiosulfate solution and starch indicator. Alone, as little as 0.05 g. of aniline or *p*-toluidine could be estimated by this method within 1.0%. With a known mixed sample, however, the accuracy was not greater than 5%.

To secure the necessary data, a number of tubes, each containing the same amount of the *p*-methylhydrazobenzene solution, was placed in the bath simultaneously. After one hour two tubes were withdrawn, one of which was analyzed (as described above) for bromine-absorbing power, the other of which was analyzed for *p*-methylhydrazobenzene, with excess of aniline present. After a suitable interval, two other tubes were withdrawn, and again analyzed for bromine-absorbing power. If we use the known velocity constant, $K_{mono.}$, the amount of *p*-methylhydrazobenzene that has suffered decomposition at this time can be calculated.

We will now let A_1 and A_2 represent the *equivalents* of hydrazine present at any two times, t_1 and t_2, in a tube—the amount decomposed in the time interval is then $(A_1 - A_2)$. From equations 18, 19 and 20 (p. 1152) it is seen that one molecule or *two equivalents* of methylhydrazobenzene produce one molecule of the aromatic amine (*i. e.*, either aniline or paratoluidine, as the case may be). $(A_1 — A_2)$ equivalents of the hydrazo compound will therefore produce $(A_1 — A_2)/2$ molecules of amine. A molecule of aniline consuming six equivalents of bromine, if all the amine produced were aniline, the total bromine consumed would be $3\ (A_1 — A_2)$ equivalents; and, a molecule of toluidine consuming only four equivalents of bromine, if only toluidine were formed, $2(A_1 — A_2)$ equivalents of bromine would be consumed. The total possible excess of bromine used over this last amount or $(A_1 — A_2)$ equivalents of bromine is therefore proportional to 100% of aniline and the actual excess of bromine used beyond what would be needed for toluidine is a measure of the proportion of aniline found in the titration of the mixed amine. If we call B_1 and B_2 the grams of 0.1 *N* bromine solution (equivalents of bromine) used in the titration of two samples taken at times t_1 and t_2, then ($B_2 - B_1$) is the bromine actually consumed for the amine obtained from ($A_1 - A_2$) equivalents of hydrazobenzene, and we have:

$$\text{Per cent. aniline in the amine} = \frac{(B_2 - B_1) - 2(A_1 - A_2)}{A_1 - A_2}.$$

Per cent. toluidine in the amine = 100% — % aniline found.

One series each of the so-called "α" and "β" forms of *p*-methyl hydrazobenzene was examined for *p*-toluidine and aniline in this manner. In both cases the initial concentration of the solution was approximately 0.2 molar. The whole number of tubes was heated one hour before the first pair was withdrawn, and analysis was made for bromine-absorbing power and for unchanged *p*-methylhydrazobenzene. After being heated for four hours further, two more tubes were withdrawn, and a duplicate analysis for bromine-absorbing power was made.

In the following summary of results is given in the first column, under A_1, the grams of 0.1 *N* iodine solution consumed by the *p*-methylhydrazobenzene present at the time t_1; in the second column, under B_1, is given the grams of 0.1 *N* bromine solution consumed by the combined amines present at time t_1; in the third column under ($A_1 - A_2$) is given, in equivalents, the calculated amount of *p*-methylhydrazobenzene which should have decomposed by the time t_2, when the final analyses for "bromine consumed" were made; in the fourth column under B_2 is given the weight of 0.1 *N* bromine solution consumed at the time t_2; and in the fifth and sixth columns are given the percentages of aniline and of *p*-toluidine, respectively, which were calculated from the above formula:

	A_1.	B_1.	($A_1 - A_2$).	B_2.	Per cent. anil.	Per cent. Tol.
1...........	19.33	4.55	5.78	18.05	33.5	66.5
				17.96	32.0	68.0
2...........	19.17	4.58	5.73	17.96	33.5	66.5
				18.06	35.0	65.0

Series (1) was carried out with the sample of *p*-methylhydrazobenzene designated as α, and series (2) with that designated as β. It is seen here again that no difference between the two samples is noticeable.

III. Decomposition of *p*-Hydrazotoluene.

The *p*-hydrazotoluene used in this work was prepared by the reduction of *p*-nitrotoluene[1] by the same process, by which hydrazobenzene was prepared from nitrobenzene. The crude substance obtained gave, after two recrystallizations, a product only very slightly tinged with yellow, having a constant melting point of 134°. It was dried and preserved in sealed bulbs and assayed exactly as was the hydrazobenzene and showed a reducing power very close to that demanded by theory:

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[1] Janovsky, *Monatsh. Chem.*, 9, 829 (1888).

Wt. sample. Gram.	0.1 N I.	Per cent. found.
0.1985	18.64	99.6
0.1982	18.70	100.1

This substance is much more sensitive to acid than either of the other two hydrazo compounds studied. When 0.2 g. of it is oxidized with iodine in a volume of about 50 cc., the acid formed in the oxidation causes 8–10% of the substance to undergo the semidine or a similar rearrangement before the oxidation is complete. Here, too, an addition of an excess of the 0.1 N aniline solution is necessary and sufficient to prevent loss in the analysis.

Fortunately, in this case, it was found that in the velocity determinations the titrations could be carried out in alkalin solutions (*i. e.*, with slight excess of aniline), as no interfering color reaction occurred. Only in the tubes where the reaction had run nearly to completion was a slight pink coloration noticed. So in all analyses the excess of acid theoretically formed in the oxidation was calculated. Then an amount of 0.1 N aniline solution, more than sufficient, by 2.0 cc., to neutralize this acid, was added to the titration mixture, and the titration performed as usual.

TABLE XV.

1.10 grams *p*-hydrazotoluene. V = 50 cc., v = 5 cc. Temp. = 110.25° ± 0.05°.

	A.		B.		
T.	I.	10^5 K$_{\text{mono}}$.	I.	10^5 K$_{\text{mono}}$.	Av. 10^5 K$_{\text{mono}}$.
50	9.03	...	9.04	...	...
150	7.58	(175)	7.57	177	(176)
200	7.08	163	7.06	165	164
250	6.42	171	6.41	172	171
350	5.49	166	5.44	169	167
450	4.74	161	4.74	161	161
600	3.93	151	3.88	154	152
750	3.26	145	3.27	145	145

Av. 162

TABLE XVI.

0.55 gram *p*-hydrazotoluene. V = 50 cc., v = 5 cc. Temp. = 110.25° ± 0.05°.

	A.		B.		
T.	I.	10^5 K$_{\text{mono}}$.	I.	10^5 K$_{\text{mono}}$.	Av. 10^5 K$_{\text{mono}}$.
50	4.33	...	4.44	...	...
150	3.67	165	3.75	169	167
200	3.38	165	3.45	170	167
250	3.06	173	3.16	170	171
350	2.67	161	2.69	167	164
450	2.31	157	2.35	159	158
600	1.99	141	1.98	147	144
750	1.64	139	1.58	148	143

Av. 159

The limited solubility of the *p*-hydrazotoluene in absolute alcohol prevented the use of solutions more concentrated than 0.1 molar.

In the manner described for hydrazobenzene, with the above-mentioned modifications, an examination was made of the rate of decomposition of *p*-hydrazotoluene in alcoholic solutions of initial concentration approximately 0.1 and 0.05 molar, respectively.

In conclusion, the author wishes to express his most sincere thanks to Professor Julius Stieglitz, whose fruitful suggestions and inspiring counsel alone have made the successful completion of this investigation possible.

THE QUANTITATIVE SEPARATION OF NITROSUBSTITUTION COMPOUNDS FROM NITROGLYCERIN.[1]

By A. L. Hyde.

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Introduction.

A practical method for separating nitro compounds from nitroglycerin is of considerable importance in the analysis of explosives. A large number of the explosives now manufactured contain both nitroglycerin and one or more nitro compounds. Though a satisfactory determination of nitroglycerin in such mixtures can often be made with the nitrometer, it has been shown that the nitrometer method is not always available.[2] Moreover, an actual separation of the constituents of an unknown mixture is always more satisfactory than an indirect determination because each of the separated products can be tested.

The method here outlined for separating nitro compounds from nitroglycerin is a further development of a method already described.[3] It overcomes some of the difficulties and increases the accuracy of that method. The method depends upon the differences of solubility of nitroglycerin and nitro compounds in carbon bisulfide and mixtures of acetic acid and water. Nitroglycerin is only slightly soluble in carbon bisulfide but is very soluble in glacial acetic acid and decidedly soluble in mixtures of this acid with water. On the other hand, most nitro compounds though not very soluble in carbon bisulfide are more soluble than nitroglycerin, whereas in mixtures of acetic acid and water they are less soluble than nitroglycerin.

Carbon bisulfide and mixtures of acetic acid and water are only slightly miscible. Hence if a mixture consisting of nitroglycerin and a nitro compound be shaken in a separating flask with carbon bisulfide and an acetic acid and water mixture, allowed to stand, and the two layers be separated,

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Storm, C. G., "Effect of the Nitrotoluenes on the Determination of Nitroglycerin by Means of the Nitrometer," *Com. 8th Intern. Congr. Appl. Chem.*, 4, 177.

[3] Hyde, A. L., "Separation of Nitroglycerin from Nitrosubstitution Compounds," *Com. 8th Intern. Congr. Appl. Chem.*, 4, 69.