8. Summary.

1. The formation of binary compounds of the type ester–acid has been investigated by the freezing-point method. Such compounds have heretofore been assumed to exist, to explain the mechanism of ester hydrolysis as catalyzed by acids, but no conclusive evidence of their presence has been produced. In the present investigation thirteen oxonium compounds of widely differing esters with trichloroacetic acid have been isolated, esters of monobasic acids uniformly yielding equimolecular compounds.

2. Previous papers indicated that oxonium compound formation is in general more evident the more divergent the "acidic strength" of the components employed.[1] Applied to the present case this would demand that combination be most pronounced between *strong* acids and esters of *weak* acids (preferably the alkyl rather than the more "negative" aryl esters). All *three* radicals concerned were varied experimentally as widely as possible and the rule was found to hold throughout the whole range of systems examined.

3. The extent of compound formation varies within wide limits as the above factors are varied. Although decreasing rapidly with decrease in strength of the acid it is still perceptible even with the typical weak acid, acetic acid. We may, therefore, state definitely that *oxonium salt formation is a general phenomenon in systems ester–acid.* These experimental results are in significant agreement with the fact that acceleration of ester hydrolysis is a general property of acids and also decreases with decrease in strength of the acid.

4. The results obtained in this paper are in entire agreement with the "intermediate compound formation" theory as an explanation of acid catalysis of ester hydrolysis. The formation of addition compounds of the type ester–acid as the first step in the mechanism of the reaction may now be regarded as experimentally established.

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

THE THERMAL DECOMPOSITION OF SYMMETRICAL DIARYLHYDRAZINES.[2]

BY JULIUS STIEGLITZ AND HELEN TREDWAY GRAHAM.[3]

Received June 28, 1916.

In the thermal decomposition of hydrazobenzene, azobenzene and aniline are formed according to the equation

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

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[1] Kendall and Gibbons, THIS JOURNAL, 37, 149 (1915).

[2] After the completion of the work reported in this paper and after the original

As shown in previous papers[4] from this laboratory, there are several possible courses which the reaction might take to give these products, the study of which seemed to us of special interest from the point of view of the theory of organic chemistry. One of these involves a preliminary dissociation of the hydrazobenzene into phenyl imide and aniline, the azobenzene being the product of a secondary polymerization of the phenyl imide:[5]

writing of the same, a report by Wieland on the same subject (*Ber.*, **48**, 1098 (1915)) came to hand, in which Wieland arrived at the same conclusion as we had, namely, that one must abandon for symmetrical diaryl hydrazines the theory of Stieglitz and Curme (*Ber.*, **46**, 911 (1913)) and THIS JOURNAL, **35**, 1143 (1913)), which ascribed the *monomolecular* character of the decomposition of hydrazobenzenes into aryl amines and azobenzenes, involving two molecules of hydrazobenzene, to a measurably slow decomposition of the hydrazobenzene into aryl imide $\mathrm{PhN}<$ and amine, followed by the fast polymerization of aryl imide to azobenzene. The monomolecular character of the reaction, discovered by Stieglitz and Curme, is not called into question. We should like to point out here that Dr. Curme, in his paper (THIS JOURNAL, **35**, 1152, footnote 3 (1912)), stated that the critical experiment of the identification of the three possible azo compounds, which the theory would demand for the decomposition of hydrazines $(\mathrm{Aryl}_1)\mathrm{HN.NH}(\mathrm{Aryl}_2)$ would be made as soon as time permitted. As Dr. Curme left for Europe at that time, the work was continued from this point by Miss Tredway the same autumn and, working with methylhydrazobenzene, we found already, Nov. 10 and Dec. 8, 1913, and with bromohydrazobenzene on Jan. 10, 1914, that only one azobenzene is formed in each case—a result recognized at once as incompatible with the theory of Stieglitz and Curme. In consideration of Curme's reservation, we thought it best to make a much more elaborate investigation of the reaction, with a view to securing results for a positive basis of a revised theory before publishing our findings. We recognize now that an immediate preliminary publication would have been wiser; but we are glad to welcome the fact that in a large measure we are now in essential agreement with the findings of our brilliant German colleague. However, while not denying the possibility of Wieland's new hypothesis (his original one (*Ann.*, **392**, 133 (1912)) was disposed of by the discovery by Stieglitz and Curme of the monomolecular character of the reaction), we have developed an alternative hypothesis which we consider of special significance and worthy of more extended investigation, because the reaction under discussion is only a typical case of that large and well-known class of reactions, in which products of an intermediate stage of oxidation are converted under the influence of heat into mixtures of products of lower and higher stages of oxidation. The hypothesis may also be extended to all kinds of oxidation-reduction reactions. In conclusion, we are glad to welcome the fact that Wieland and Reverdy (*Loc. cit.*, p. 1112), by substituting triphenylhydrazine for hydrazobenzene, have actually realized experimentally a thermal decomposition proceeding exactly along the lines of the theory of Stieglitz and Curme, to wit: $(C_6H_5)_2N.NH(C_6H_5) \longrightarrow C_6H_5.N + (C_6H_5)_2NH$ (a slow reaction) and $2C_6H_5.N \longrightarrow C_6H_5N : NC_6H_5$ (a fast reaction)—showing that the fundamental assumptions of the theory of Stieglitz and Curme were and are essentially sound, in spite of the fact that the dissociation of hydrazobenzene itself follows another course.—J. STIEGLITZ.

[3] The work presented in this article formed the basis of a dissertation submitted by Miss Tredway to the University of Chicago in August, 1915, in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[4] Stieglitz and Curme, *Ber.*, **46**, 911 (1913); Curme, THIS JOURNAL, **35**, 1143 (1913).

[5] See Curme, *Loc. cit.*, in regard to an analogous dissociation into phenyl amide, C_6H_5NH.

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

$$2C_6H_5N: \longrightarrow C_6H_5N : NC_6H_5 \qquad (3)$$

Similar dissociation into unsaturated, reactive radicals had been quite commonly assumed in organic chemistry; the reaction in question seemed to be available for a particularly simple and decisive experimental test of the question by determination of the velocity of the decomposition reaction at a given temperature. A reaction proceeding according to Equations 2 and 3 would be a reaction of the *first order* for the measurably slow reaction (2), the union of phenyl imide radicals according to (3) following with a presumably far greater speed. In such a case, the velocity of the action at a constant temperature should satisfy the equations

$$\frac{dx}{dt} = K_{\text{mono}} (a - x) \qquad (4)$$

and

$$K_{\text{mono}} = \frac{1}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2}. \qquad (5)$$

The symbols have their usual significance.

On the other hand, if the reaction were one of intermolecular oxidation and reduction as expressed in Equation 1, and were due to the high reducing tension of the hydrogen attached to the nitrogen in hydrazobenzene,[1] we would have at a constant temperature a reaction of the *second order*, taking place with a velocity

$$\frac{dx}{dt} = K_{\text{di}} (a - x)^2, \qquad (6)$$

from which we find

$$K_{\text{di}} = \frac{1}{t_2 - t_1} \cdot \frac{x_2 - x_1}{(a - x_2)(a - x_1)}. \qquad (7)$$

In the first paper on this problem, the question was considered whether such an intermolecular oxidation and reduction could not also be a reaction of the first order, involving a preliminary dissociation of hydrazobenzene into azobenzene and hydrogen

$$C_6H_5NH.NHC_6H_5 \longrightarrow C_6H_5N : NC_6H_5 + H_2 \qquad (8)$$

followed by the reduction

$$C_6H_5NH.NHC_6H_5 + H_2 \longrightarrow 2C_6H_5NH_2. \qquad (9)$$

Inasmuch as the hydrogen had to have a very high reducing tension, and since it could not be considered to have this when it was once liberated as free hydrogen—which does not reduce hydrazobenzene—it was concluded that it could have this high reducing tension only while it was in unstable union with the nitrogen of the hydroazobenzene. Consequently it could be effective only when a second molecule of hydrazo-

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[1] Wieland, *Ann.*, **392**, 133 (1912); cf. Stieglitz and Curme, *Loc. cit.*

benzene actually met or collided with the first molecule. That would involve dynamically a true dimolecular reaction proceeding according to Equations 6 and 7.

The measurements of the velocities of the decomposition of hydrazobenzene, *p*-methylhydrazobenzene and *p*-hydrazotoluene by Curme showed unquestionably that the velocities followed the monomolecular law expressed in Equations 4 and 5: although some falling off of the constant was observed in the course of the decomposition of 75% of the substance in a given experiment,[1] the *initial velocities* in a range of concentrations from 0.054 to 0.22 molar, were uniformly the same[2]—a relation which, according to the best authorities, is a critical test for the order of a reaction. Furthermore, calculations of K_{di} according to Equation 7 showed a very wide variation during the course of a single determination, and an enormous variation with a change of the initial concentration.[3] Calculations likewise made very improbable the occurrence of parallel mono- and dimolecular decomposition reactions. The conclusion was therefore drawn that the thermal decomposition of hydrazobenzene is a reaction of the first order, and it was thought that the occurrence of an intermediate dissociation of hydrazobenzene, for instance, into phenyl imide and aniline according to

$$C_6H_5NH.NHC_6H_5 \longrightarrow C_6H_5N: + C_6H_5NH_2$$

had been demonstrated. This was the main question the investigation was intended to settle.

Wieland,[4] in discussing these results, proposed the explanation, that the reaction measured was the slow decomposition of the hydrazine into azobenzene and *atomic* hydrogen and that this was followed by the immeasurably fast reduction of another molecule of hydrazobenzene by the liberated hydrogen. One of us had already considered the alternative possibility,[5] as shown above, that azobenzene and *ordinary* hydrogen are formed in a slow reaction and could not reconcile the assumption with the known facts: (1) that hydrogen does not appear to reduce hydrazobenzene under the conditions of the experiment, let alone reduce it with immeasurable speed; and (2) that no indications of the presence of free hydrogen were ever observed in Curme's experiments, carried out in sealed tubes. Both of these facts, it may be remarked here, were confirmed by careful experiments made in the course of the present investigation.

The problem at issue seemed settled therefore in favor of the disso-

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[1] For instance, in 0.2 molal solution of hydrazobenzene, at 140.55°, $10^5 \times K_{mono} =$ 157, 159, 159, 156, 153, 149, 144.

[2] Curme, *Loc. cit.*, tables, pp. 1158–9.

[3] For the 0.2 molal solution, $10^4 \times K_{di} = 86$; and for 0.05, $10^4 \times K_{di} = 370$.

[4] *Die Hydrazine*, p. 51 (1913).

[5] Stieglitz and Curme, *Ber.*, **46**, 914 (1913).

ciation theory (Equations 2 and 3), by the unquestioned order (monomolecular) of the reaction and by the experimental fact that a reduction of hydrazobenzene required a higher reducing tension than that possessed by free hydrogen.[1] But the whole problem was opened again for further investigation by the following observations: in the decomposition of hydrazines with two different aryl groups—such as *p*-methyl hydrazobenzene, $C_6H_5NH.NHC_6H_4CH_3$—a preliminary dissociation into phenyl imide radicals and anilines should yield ultimately three azo compounds, $C_6H_5N : NC_6H_5$, $C_6H_5N : NC_6H_4CH_3$ and $CH_3C_6H_4N : NC_6H_4CH_3$, and two anilines, $CH_3C_6H_4NH_2$ and $C_6H_5NH_2$, presumably in unequal proportions, since the decompositions

$$CH_3C_6H_4NH.NHC_6H_5 \longrightarrow CH_3C_6H_4N: + C_6H_5NH_2 \qquad (10)$$

and

$$CH_3C_6H_4NH.NHC_6H_5 \longrightarrow C_6H_5N: + CH_3C_6H_4NH_2 \qquad (11)$$

would almost certainly not be equally favored. As a matter of fact, Dr. Curme's experimental data[2] showed that in the decomposition of *p*-methylhydrazobenzene, just about twice as much toluidine is formed as aniline. A reduction by way of Equations 8 and 9 would demand equal molar proportions of the two anilines. This result therefore agreed perfectly with the main conclusion drawn in favor of the dissociation theory. It was planned[3] to confirm the conclusion by identifying the three azo compounds which should be formed under these conditions, but Dr. Curme's departure for Europe necessitated the postponement of this examination. It was at this point that the present investigation was taken up, with the unexpected but convincing result that in the thermal decomposition of *p*-methyl-hydrazobenzene and of *p*-bromohydrazobenzene, only a *single azo compound* is produced—the one corresponding to the hydrazo compound used. Thus from methylhydrazobenzene, $C_6H_5NH.NHC_6H_4CH_3$, only methylazobenzene, $C_6H_5N: NC_6H_4CH_3$, is obtained; from *p*-bromohydrazobenzene, $C_6H_5NH.NHC_6H_4Br$, only bromoazobenzene, $C_6H_5N: NC_6H_4Br$, is produced.

This conclusion was amply confirmed by careful determinations of the proportions of anilines, $C_6H_5NH_2$ and $XC_6H_4NH_2$, formed in the thermal decomposition: by the use of more elaborate and accurate methods than that used by Curme, it was found that the proportion is 1 : 1, as required for a direct reduction of a molecule of the hydrazobenzene, $XC_6H_4NH.NHC_6H_5$.

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[1] Since then the actual existence and great reactivity of *atomic* hydrogen as compared with ordinary hydrogen has been demonstrated by Langmuir (THIS JOURNAL, 36, 1708 (1914) and 37, 417 (1915)).

[2] Curme, THIS JOURNAL, 35, 1171 (1913).

[3] Curme, *Loc. cit.*, p. 1152, footnote 3.

These results are irreconcilable[1] with the theory of a preliminary dissociation into phenyl imide radicals,[2] as expressed in Equations 3 and 4, and thus the whole problem of the mechanism of the reaction was reopened.

The following facts were next established:

(1) For concentrations ranging from 0.2 to 0.05 molar, the reaction is actually one of the first order, as found by Curme. The main experimental part of Curme's work was thus fully confirmed.

(2) In very dilute solutions (0.01 to 0.005 molar), the reaction is no longer clearly one of the first order; in individual experiments fairly good constants for a second order reaction (Equation 7) are obtained, but the constants for different concentrations do not agree at all with one another. The order of the reaction, therefore, in very dilute solutions is uncertain and probably neither wholly of the first nor of the second order.

(3) In a sealed tube charged with an alcoholic solution of an excess (relative to the hydrogen) of bromohydrazobenzene in an atmosphere of hydrogen, and heated for two hours at 145°, the temperature at which the decomposition reaction was studied, no absorption of hydrogen of any moment was discernible. There is, therefore, no direct reduction with immeasurable speed. The action

$$C_6H_5NH.NHC_6H_5 + H_2 \longrightarrow 2C_6H_5NH_2$$

must therefore be considered excluded in the theory of the thermal decomposition of arylhydrazines.

(4) In extremely dilute solutions (0.01 molar), a little permanent gas is formed, but it fails to respond to the tests for hydrogen, made both with palladium and oxygen, and with oxygen in an explosion pipet[3] (see the experimental part). The absence of hydrogen, taken in conjunction with its failure to react when used with hydrazobenzene, shows that ordinary hydrogen cannot be considered an intermediate product in the thermal decomposition of the arylhydrazines.

(5) The molecular weight of *p*-bromohydrazobenzene was determined in boiling absolute alcohol solution and found to be that of the simple

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[1] See Wieland, *Ber.*, 48, 1098 (1915) and the introductory note to this article.

[2] A dissociation of this type, however, was found by Wieland and Reverdy (*Ber.*, 48, 1112 (1915)) to occur in the case of triphenylhydrazine, $(C_6H_5)_2N.NHC_6H_5$.

[3] As the exact nature of this permanent gas, especially as to the question of its containing hydrogen, seemed of particular theoretical significance (see below), Mr. E. N. Roberts in the autumn of 1915 kindly undertook its re-examination He confirmed the finding of Mrs. Graham that it contains no hydrogen and further established the fact that aside from the presence of the small amount of oxygen and nitrogen left as air in the tube sealed under 18 mm. pressure, a very large proportion of nitrogen is present (at least 75% of the total volume in excess of the air nitrogen). The nitrogen was converted into ammonia by sparking it with hydrogen over sulfuric acid, and the ammonia determined both by titration and by nesslerizing.—J. S.

molecule, $C_6H_5NH.NHC_6H_4Br$. The simple explanation[1] of a reaction of the first order between two molecules of hydrazobenzene as being due to a dimolecular form is thus excluded. The monomolecular form being found at 78°, there should be no polymerization at 140° and 150°, the temperatures at which the experiments were conducted. The possibility that in a reversible reaction

$$2C_6H_5NH.NHC_6H_5 \rightleftarrows (C_6H_5NH.NHC_6H_5)_2 \qquad (12)$$

small quantities of a dimolecular form are present and decomposed, would clearly lead to "constants" varying with the concentration,[2] and this possibility is therefore also excluded.

We are thus called upon to reconcile the fact that the thermal decomposition of hydrazines in solutions of moderate concentration (0.05 to 0.2 molar) is certainly one of the first order—indicating a decomposition of only a *single molecule*—with the fact that no ordinary decomposition product of the single molecule, namely neither phenyl imide,[3] $C_6H_5N:$, nor hydrogen, H_2, can be formed as an intermediate product, and with the further fact that a *second* molecule of the hydrazobenzene is nevertheless reduced at great speed in some way as the result of the decomposition of the first molecule. We have, in a word, a dimolecular reaction of the first order. Two possible explanations of this set of facts suggest themselves as the most plausible ones. The first of these[4] is that the monomolecular reaction, whose velocity we have measured, is a decomposition of the hydrazobenzenes into azobenzene and *atomic* hydrogen. Langmuir[5] has recently proved that atomic hydrogen is capable of existence, and is *vastly more reactive* than ordinary or molecular hydrogen. The high reducing tension of the hydrogen which, as we have seen, is neces-

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[1] This explanation was apparently not considered by Wieland.

[2] If C_{di} and C_{mon} represent the respective concentrations of the dimolecular and monomolecular forms at any moment of equilibrium, we have $C_{di} = K_{eq} \times C_{mon}^2$. For a reaction, which might be of the first order for the polymerized form,

$$\frac{dx}{dt} = K_{vel} \times C_{di}$$

we would have by substitution

$$\frac{dx}{dt} = K_{vel} \times K_{eq} \times C_{mon}^2.$$

Consequently, if the main amount of hydrazobenzene is present in the monomolecular form—as has been proved by our experimental work—the order of the reaction would still appear as of the second order, even if the small amounts of the dimolecular form were the reacting component. Only if K_{eq} were quite large and by far the greater part of the substance were present in the associated form, would the reaction appear as one of the first order, the dependence of the associated molecules on the nonassociated ones involving only a small error, which could be within the limits of the experimental error.

[3] Or phenyl amide, C_6H_5NH—.

[4] Wieland, "Die Hydrazine," p. 51 (1913); and *Ber.*, 48, 1098 (1915)

[5] THIS JOURNAL, 36, 1708 (1914); 37, 417 (1915).

sary for the reduction of a second molecule of hydrazobenzene may reside and be maintained therefore not only in hydrazobenzene itself, but also in atomic hydrogen sufficiently long for the latter to reach and reduce the second molecule of hydrazobenzene. We would have,

$$C_6H_5NH.NHC_6H_5 \longrightarrow C_6H_5N : NC_6H_5 + 2H \qquad (13)$$

and

$$C_6H_5NH.NHC_6H_5 + 2\dot{H} \longrightarrow 2C_6H_5NH_2.$$

This is an important modification of a possible monomolecular reaction given by Stieglitz and Curme in their first paper, in which the formation of ordinary hydrogen, H_2, was considered.[1] The present view was first advanced by Wieland.[2] It would overcome the objections to the original interpretation raised by Stieglitz and Curme—objections which without this modification would still exist. The modification consists in the assumption that the hydrogen is *atomic* hydrogen of a proved much higher degree of activity than that possessed by ordinary hydrogen.

Now, while we consider this explanation of the thermal decomposition of hydrazobenzenes a possible one, there are certain objections to it, which should be pointed out. In the first place, it should require *time* for the atomic hydrogen to *diffuse* through the solution to the second molecule of hydrazobenzene and reduce it; and instantaneous reduction is therefore out of the question. In the second place, in this process of diffusion, two separate atoms of hydrogen would have to move toward the same hydrazobenzene molecule—*the directing cause for which coincidence it would be hard to find.* And, finally, in this irregular diffusion it is certainly to be expected that a measurable part at least of the atomic hydrogen would, by a collision of the atoms, form ordinary *unreactive* hydrogen, especially in view of the original *proximity* of the two atoms, in leaving the mother hydrazone molecule, compared with the distance to a further molecule of hydrazine. As emphasized above, in solutions of moderate concentration no indications of the formation of any permanent gas at all were obtained; and in dilute solutions (0.01 molar), where a little permanent gas was obtained, it failed to respond to any test for hydrogen.[3] These considerations, and especially the last one, it seems to us, make the alternative hypothesis which we will now present, more likely to be the correct interpretation of the reaction.

This interpretation, based on the electron theory of valence, has interested us in particular because one of us has long suspected the possibility of oxidation and reduction in solution occurring by a transfer of electrons from molecule to molecule, *without the necessity of a collision* (or approach to within molecular distances) *between the respective mole-*

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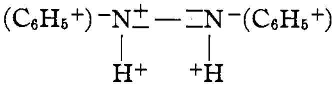
[1] *Loc. cit.*

[2] *Die Hydrazine,* p. 51 (1913).

[3] See footnote 3, p. 1741.

cules. The present case is, we believe, the first instance where evidence of such an action has been recognized in solution in a simple thermal reaction.[1] According to the electron theory of valence, hydrazobenzene, in common with hydrazines in general, has the structure[2]



$$(C_6H_5^+)^-\underset{\underset{H^+}{|}}{N^{+}_{-}}-{}^{-}_{-}\underset{\underset{^+H}{|}}{N}{}^-(C_6H_5^+)$$

When it forms azobenzene and aniline, two electrons are discharged by the nitrogen of the one (reducing or oxidized) molecule, producing azobenzene, $(C_6H_5^+)^-N^{+}_{-} = {}^{-}_{+}N^-(^+C_6H_5)$ or $(C_6H_5^+)^-N^{+}_{+} = {}^{-}_{-}N^-(^+C_6H_5)$, and releasing, as a consequence, two positively charged hydrogen atoms or ions. On the other hand, the nitrogen of the second (reduced) molecule absorbs two electrons to form aniline, in which the nitrogen is unquestionably wholly negative,[3] $(C_6H_5^+)N\equiv(H^+)_3$, as in ammonia; the absorption of two electrons must disrupt the union of the nitrogen atoms in this second molecule of hydrazobenzene, and give to the two negative radicals or ions $C_6H_5NH^-$ formed the power to absorb two positively charged hydrogen atoms or ions (see the equations below). Now, it is easily conceivable that the two electrons discharged by the reducing (oxidized) molecule should pass with very great speed through the solution to the positive valence of the nitrogen in the second molecule; electrons have, of course, at a given temperature, normally, velocities perhaps forty times as great as hydrogen atoms, at the same temperature; and moreover, on account of their volume being, let us say, 1800 times as small as that of the hydrogen atom, they would meet with an enormously smaller resistence in a liquid medium than hydrogen atoms would. Electrons are known indeed to pass even through the interstices of atoms. The two electrons in question could therefore reach the second molecule of hydrazobenzene with a sufficient speed to be negligible; charging the nitrogen of this molecule wholly negatively, they would sunder the molecule, and the negative phenyl amide radicals would unite with two positive hydrogen atoms, derived either from the medium surrounding them or from the oxidized hydrazobenzene molecule. The *actual* reduction[4] would consist in the absorption of the two electrons—the union with the

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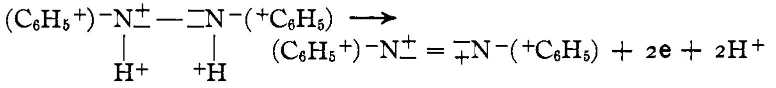
[1] Bodenstein (*Z. physik Chem.*, 85, 330 (1913)) has treated photochemical effects from a similar point of view. The work of Lind (*J. Phys. Chem.*, 16, 494 (1912)) on the influence of radioactive rays on the oxidation of hydrogen by halogens and the work of H. S. Taylor (THIS JOURNAL, 37, 24 (1915)) are also suggestive in this connection. C. A. Kraus (THIS JOURNAL, 36, 864 (1914)) proved the independent existence of electrons in the colored solutions of the alkali metals in ammonia.

[2] Only the essential charges are indicated.

[3] In regard to its first three valences.

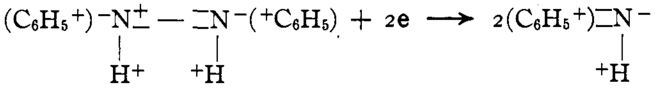
[4] A well-known conception. See, for instance, Stieglitz, "Qualitative Analysis," Vol. I, pp. 251–298 (1911).

positive hydrogen is a simple ionic union of anions and cations. We can express this interpretation[1] in the following equations:



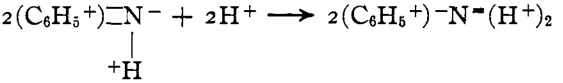
$$(C_6H_5^+)^-N^{\pm} - {}^{\mp}N^-(^+C_6H_5) \longrightarrow (C_6H_5^+)^-N^{\pm} = {}^{\mp}N^-(^+C_6H_5) + 2e + 2H^+ \quad (15)$$

which would be a slow decomposition reaction, whose velocity is measured;



$$(C_6H_5^+)^-N^{\pm} - {}^{\mp}N^-(^+C_6H_5) + 2e \longrightarrow 2(C_6H_5^+){}^{\mp}N^- \quad (16)$$

and



$$2(C_6H_5^+){}^{\mp}N^- + 2H^+ \longrightarrow 2(C_6H_5^+)^-N^{=}(H^+)_2 \quad (17)$$

which would be exceedingly fast reactions, following the first slow decomposition reaction.

It should be observed that such an action would produce local potential differences in small elements of space; for instance, if H^+ were liberated at the end of one such element and $^-OC_2H_5$ at the other end when H^+, derived from the solvent, is absorbed by the second molecule of hydrazobenzene, we would have for a small time interval, a local potential difference. The same situation would result if the positive hydrogen finally absorbed were the H^+ given off by the first (oxidized) molecule of hydrazobenzene; since the electrons are considered to reach the second (reduced) hydrazobenzene molecule with far greater speed than the H^+, we would have local polarization in which in the small element of space, the hydrogen would be positive, the phenyl amide, $C_6H_5HN^-$, would be negative. Such potential differences would be distributed exceedingly irregularly, that is, in all directions, and would neutralize each other with greatest rapidity by irregularly distributed currents or combinations of ions in the elements of space. It is evident, further, that such a transfer of electrons would become much more difficult in solutions of extreme dilution,

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[1] This electronic interpretation lends itself equally well to the decomposition of triphenylhydrazine into diphenylamine and azobenzene by way of an intermediate dissociation into diphenylamine and the phenyl imide radical C_6H_5N, as postulated by the theory of Stieglitz and Curme and realized by Wieland and Reverdy (*Loc. cit*). In this case the primary action is one of *intramolecular* oxidation-reduction, instead of an intermolecular one as for hydrazobenzene.

$$(C_6H_5^+)_2{}^{=}N^{+} - {}^{-}NH^{=}{}^{+}(C_6H_5^+) \longrightarrow (C_6H_5^+)_2{}^{=}N^{-} + N^{-}(C_6H_5^+) + H^+$$

is the initial action, two electrons, designated by **heavy** type for the corresponding negative charges, passing from the phenyl amide nitrogen atom to the diphenylamide nitrogen atom to make the latter wholly negative. As a result, the union between the nitrogen atoms is rendered and H^+ is also lost by the one nitrogen atom, and either transferred directly to the ion $(C_6H_5)_2N^-$ or it takes the place of a hydrogen ion absorbed by the latter from the solution. The union of two phenylimide radicals to form azobenzene completes the action.

and that as a result the simple order of the action could be changed. This might account for the change in the order of the reaction, when we use very dilute solutions (0.01 molar), from a simple monomolecular one to an indefinite one. In particular, we would recall in this connection the fact that Bodenstein found that the combination of chlorine with hydrogen under the influence of alpha particles is *independent of the concentration of the reducing hydrogen down to a certain limiting concentration of hydrogen.* In the instance we are discussing, we may say that the velocity of the action seems to be independent of the concentration of the molecules of hydrazobenzene down to a certain limiting concentration—which makes the action essentially monomolecular down to that limit.

We recognize the hypothetical character of this theory,[1] but are proposing it not only as an attractive working hypothesis for the case under consideration, but as opening up a problem in the field of the dynamics of oxidation and reduction that has long interested one of us. The theory seems to us to have advantages over the first theory involving atomic hydrogen in that it gives a reasonable explanation of an almost instantaneous reduction of the second molecule of hydrazobenzene, unhampered by the necessity of instantaneous diffusion of such large atoms as hydrogen through an obstructing liquid, in that it gives a reasonable explana-

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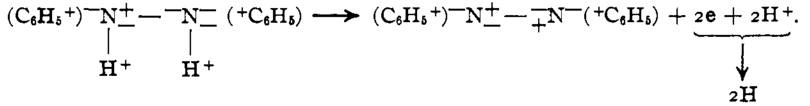
[1] The alternative hypothesis that *atomic* hydrogen is first released by the reducing molecule of hydrazobenzene (Wleland's later theory), when analyzed from the electronic point of view, simply signifies that the two electrons discharged by the nitrogen of this reducing molecule of hydrazobenzene are *first absorbed* by the two positive hydrogen atoms held by the nitrogen, instead of passing directly, as free electrons, from one molecule of hydrazobenzene to the other:



$$(C_6H_5{}^+)^-\underset{\underset{\textstyle H^+}{|}}{N}{}^{+}_{-}-{}^{-}\underset{\underset{\textstyle H^+}{|}}{N}{}^{-}_{-}\ (^+C_6H_5)\longrightarrow(C_6H_5{}^+)^-N{}^{+}_{-}-{}^{-}_{+}N^-(^+C_6H_5)+\underbrace{2e+2H^+}_{\downarrow\ 2H}.$$

The two atoms of hydrogen would then pass through the solution (without any evident directive force) to the second molecule of hydrazobenzene and would there lose the two electrons to a nitrogen atom of the latter and be absorbed as positive hydrogen atoms. The difference between the two theories is then essentially the question whether we must assume the formation of an *intermediate product,* atomic hydrogen, *as the carrier of the electrons,* or whether we must assume the direct transfer of the electrons. Since the independent existence of electrons as atoms and molecules has been amply demonstrated, it seems to us the question raised is not only a reasonable one, but indeed one of fundamental interest. Further investigation of the actual relations seems, therefore, highly desirable; this will include among other methods of attack, attempts to detect any possible (perhaps momentary) conductivity in the solutions in which the decomposition is proceeding, as well as further investigation of the gas formed in extreme dilution. In conclusion, it should be said that this whole problem, *mutatis mutandis,* will be investigated in connection with other well-known cases of oxidation-reduction, especially also of compounds of an intermediate stage of oxidation, both in organic and especially also in well-known inorganic reactions.—J. S.

tion of the fact that no free hydrogen has been observed in the study of the decomposition; and in introducing a directive force (due to the positive charge on the nitrogen of the oxidizing molecule of hydrazobenzene) for the migration of two particles (electrons), to the same molecule.[1]

Experimental Part.[2]

By Helen Tredway Graham.

1. Preparation and Analysis of the Hydrazo Compounds.—The three hydrazo compounds used in this investigation—*p*-methylhydrazobenzene, *p*-bromohydrazobenzene, and 2,4-dichlorohydrazobenzene—were prepared by reduction of the corresponding azo compound with zinc dust in alkaline alcoholic solution. The azo compounds themselves were made by the method of Mills[3] from nitrosobenzene and the substituted aniline. The *p*-methylhydrazobenzene was identical in every respect with that described and used by Curme.[4] In preparing the halogen hydrazo compounds, a pink impurity was noticed, the nature of which was not investigated, but which could be removed only by several recrystallizations of the azo compounds before reduction.

p-Bromohydrazobenzene, *p*-$BrC_6H_4NH.NHC_6H_5$, made by reduction of pure *p*-bromoazobenzene (m. p. 89°), and twice recrystallized from alcohol containing a few grams of zinc dust and several drops of concentrated ammonium hydroxide solution, was obtained as shiny, white plates

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[1] A third interpretation of this characteristic monomolecular oxidation and reduction reaction, involving ultimately two molecules of hydrazobenzene, is found in a combination of the two theories that have been presented. That is, the first, measurably slow reaction, may consist in the loss of two electrons by the reducing molecule of hydrazobenzene to a *single* one of the hydrogen atoms H^+ which it loses—making it a *negative* hydrogen atom H^-, of even greater reducing power than atomic hydrogen. Negative hydrogen has been assumed by Fry (*Z. physik. Chem.*, **76**, 385 (1911) and later papers in This Journal) to exist in certain organic compounds, and it certainly exists and shows its tremendous reducing power in the salts of hydrogen, such as sodium, potassium or calcium hydrides. The detailed application of the idea of the formation of negative hydrogen to the interpretation of the reaction we are investigating is not necessary, as it is indicated sufficiently clearly by our previous discussion. It would, it seems to us, have the advantage over Wieland's theory of the formation of atomic hydrogen, that we would have only a single atom of hydrogen moving to the second molecule of hydrazobenzene to reduce it, which would be guided moreover by the electrical attraction between its negative charge and the positive charge on the nitrogen. It should, however, lead still more easily and almost inevitably to the formation of some ordinary hydrogen H_2 by collision with a hydrogen ion and for this reason we believe our theory of a direct transfer of electrons is most likely to be found to be the correct interpretation of the reaction.

[2] I take pleasure in using this opportunity of thanking my young collaborator, Mrs. Graham, to whose skill and perseverance the experimental part of this investigation is wholly due.—J. S.

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

[4] Curme, *Loc. cit.*, p. 1166.

melting at 101–101.5°.[1] Once dry, *p*-bromohydrazobenzene is very stable at ordinary temperatures; a sample was left exposed to the air of the laboratory for two weeks before it showed the slightest discoloration or change in melting point. For the determination of its purity the substance was oxidized in absolute alcohol with 0.1 *N* iodine solution. The solutions were made up and the analysis carried out exactly as described by Curme for hydrazobenzene,[2] except that we found it necessary to allow the iodine to act on the bromohydrazobenzene for an hour instead of ten minutes before acidifying the mixture and titrating the excess of iodine with thiosulfate. A weighed amount of 0.1 *N* iodine solution was first introduced into a glass-stoppered Erlenmeyer flask, and to it was added alcoholic aniline solution (approximately 0.1 *N*), sufficient to give an excess of 2–3 cc. over the amount required to neutralize the hydriodic acid to be formed in the subsequent oxidation. The weighed sample of *p*-bromohydrazobenzene was then dissolved in absolute alcohol and transferred with rinsing to the flask containing the iodine. The whole mixture was allowed to stand one hour, was then acidified with 10 cc. 6 *N*-sulfuric acid, and diluted to approximately 500 cc. with water. Bright yellow crystals of bromoazobenzene were thus precipitated. Standard 0.1 *N* thiosulfate solution was then run in until the fading of the brown color of the iodine indicated the approach of the end point, and starch indicator (10 cc.) was added, producing a greenish black discoloration. The thiosulfate solution was then introduced drop by drop until the bright yellow color of the azo compound was just restored. Blank experiments showed that the factor of the iodine solution was not materially affected by the presence of the aniline solution or by evaporation during the hour it was allowed to stand.

0.2001 and 0.2092 g. subst. required 15.24 and 15.92 g. 0.1 *N* iodine. Theory: 15.23 and 15.90 g.

2,4-Dichloroazobenzene, $Cl_2C_6H_3N:NC_6H_5$.—The preparation and purification of this substance offers much more difficulty than that of the other azo compounds employed. 2,4-Dichloroaniline was dissolved in glacial acetic acid, and nitrosobenzene added to the warm solution, which was refluxed for an hour. Cooling precipitated a black crystalline mass, which was collected on a filter, washed with 50% alcohol, dried thoroughly by suction, and extracted with ligroin (b. p. 30–50°). The ligroin solution was filtered from black insoluble particles and evaporated to dry-

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[1] Janovsky and Erb (*Ber.*, 20, 364 (1887)), who reduced *p*-bromoazobenzene with ammonium hydrosulfide in alcoholic solution, give the melting point of the hydrazo product as 115°; this method of reduction was tried and gave a product with the melting point, 101–101.5°, given above. Janovsky and Erb also give an incorrect melting point, 85°, for *p*-bromoazobenzene (*Ber.*, 19, 2155 (1886)).

[2] *Loc. cit.*, p. 1155.

ness. The product was then recrystallized from 95% alcohol several times, until it had a constant melting point of 105°, and a brilliant orange color. The best yield of crude dichloroazobenzene obtained was 45%, and recrystallization to the required purity reduces the yield to 10–20%. Addition of water to the acetic acid solution filtered from the black mass, and to the wash liquid, precipitated fine light green needles which were very soluble in alcohol, melted at 137°, and on recrystallization from dilute alcohol, melted at 139°. Mixed with acetodichloroanilide (white rhombohedrous melting at 143°), they melted at 100°, which proved that they were not acetodichloroanilide. No further attempt was made to determine the nature of the green product.

2,4-Dichlorohydrazobenzene, $Cl_2C_6H_3NH.NHC_6H_5$.—The azo compound can be reduced almost quantitatively to 2,4-dichlorohydrazobenzene by treatment with zinc dust in ammoniacal alcoholic solution, filtration from the zinc dust in an atmosphere of carbon dioxide, and precipitation of the hydrazo compound with warm, air-free water. The oil which first separates out, crystallizes on cooling. The product so obtained, even after several recrystallizations, invariably contained a trace of pink impurity similar to the one observed occasionally in the preparation of *p*-bromohydrazobenzene. As dichlorohydrazobenzene very easily becomes contaminated with some dichloroazobenzene by oxidation, material which was pinkish yellow in color, melted at 73.5–74°, and analyzed 95–96% pure, was used in the velocity experiments. A very small amount of pure dichlorohydrazobenzene was obtained by reduction of the purest dichloroazobenzene, the pink impurity being removed from the hydrazo compound by fractional precipitation with warm water. The slight amount of impurity present was entirely precipitated by a quantity of water insufficient to precipitate all the hydrazo compound; and as the solution was carefully protected from the air, the addition of more water to the filtrate precipitated almost colorless plates of dichlorohydrazobenzene, which melted at 74.5°, and analyzed 99.7% pure. Dichlorohydrazobenzene is so easily oxidized that it was found necessary to allow only ten minutes for the action of the iodine. In the analyses of this substance, no aniline was used to neutralize the hydriodic acid formed; but instead, the oxidation was carried out in the presence of sufficient acid ammonium carbonate to neutralize the acid formed in the oxidation, and in the presence of carbonic acid, liberated by the addition of acid ammonium carbonate to a measured quantity of hydrochloric acid. This method of neutralization was developed in connection with the work on the ratio of the two amines formed in the decomposition of *p*-bromohydrazobenzene and was found quite as satisfactory as the use of aniline.

0.1395 g. subst. required 10.99 g. 0.1 *N* iodine. Calculated, 11.02 g.

2. Thermal Decomposition Products of **Asymmetrical Hydrazobenzenes.**[1]—In order to find out whether a mixture of azobenzene and its mono- and di-substituted derivatives could be separated into its components on the basis of their different solubilities in alcohol, 0.5 g. azobenzene, 0.5 g. *p*-methylazobenzene, and 0.5 g. *p*-azotoluene were thoroughly powdered and mixed, and the mixture extracted with 15 cc. 95% alcohol at 0°. The yellow crystals obtained by the evaporation of the alcohol melted at 46–47°, while the part which did not dissolve in the alcohol melted at 59–61°. A second extraction with 10 cc. alcohol at 0° left a residue which melted at 117–137°, while evaporation of the alcohol yielded crystals melting at 47–48°. The melting points of azobenzene, *p*-methylazobenzene, and *p*-azotoluene are 69°, 70° and 144°, respectively. It is therefore clear that, even without completing the separation, fractionation with alcohol at 0° would very easily distinguish between a mixture of the three azo compounds and *p*-methylazobenzene alone.

p-Methylhydrazobenzene (1.7 g. in 10 cc. absolute alcohol) was then heated for fifteen hours at 125°, in tubes which had been sealed off at a pressure of 15 mm. The solution was allowed to evaporate in the air, after dilute hydrochloric acid had been added to acid reaction with litmus, for the purpose of neutralizing the amines formed by the decomposition. Orange-colored crystals appeared, which were transferred to a filter with water, and washed with water till they were free from acid. When dry, they melted at 70°. They were extracted three times with 10 cc. alcohol at 0°, and the residues and the crystals from evaporation of the alcohol melted uniformly at 70°, alone and when mixed with a known sample of *p*-methylazobenzene. An independent experiment showed that under the conditions used, *p*-azotoluene would not have been acted upon by the aniline present, the reaction

$$CH_3C_6H_4N : NC_6H_4CH_3 + C_6H_5NH_2 \longrightarrow CH_3C_6H_4N : NC_6H_5 + CH_3C_6H_4NH_2,$$

being thus excluded. Therefore, no *p*-azotoluene was formed in the decomposition of *p*-methylhydrazobenzene.[2] Exactly the same results were obtained when the products of the decomposition in 0.2 molal solution were examined.

The experiment was then repeated with 2.8 g. *p*-bromohydrazobenzene in 10 cc. absolute alcohol and perfectly analogous results were obtained.[3] Fractionation with alcohol had no effect on the melting point of the product, the various fractions melted uniformly at 89°, the melting point of

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[1] See the theoretical part.

[2] This result was obtained Nov. 10 and Dec. 8, 1913 (see the introductory footnote to this article).

[3] Jan. 10, 1914.

p-bromoazobenzene, whether tested alone or mixed with a known sample of *p*-bromoazobenzene.

Dichlorohydrazobenzene (2 g., 95–96% pure), treated in the same way, yielded on cooling a mass of bright orange needles, which were separated by filtration from the red alcoholic solution, and extracted three times with alcohol. The melting point of the needles was 100°, and this was raised to 103° by the mixing of the crystals with pure dichloroazobenzene (m. p. 105°). The residues from the extractions melted at 105°, as did the crystals obtained by evaporation of the alcoholic filtrates from the last two extractions. Evaporation of the acidified alcoholic solution, and of the alcohol used in the first extraction, gave orange-colored crystals melting below 100°. In no case did admixture of dichloroazobenzene lower the melting point still further, and the impurities which caused the low melting point could hardly have included tetrachloroazobenzene (m. p. 161°), which is but little soluble in alcohol.[1] The more insoluble fractions always had the melting point of 2,4-dichloroazobenzene.

In the determination of the ratio of the two amines formed in the decomposition, the method of precipitation of their hydrochlorides[2] was used, with subsequent bromination with 0.1 *N* potassium bromate solution.[3] Of the three hydrazo compounds studied, *p*-bromohydrazobenzene was most suitable for this purpose, since the two amines from *p*-methylhydrazobenzene have nearly the same molecular weight, and since dichloroaniline is only very slightly basic.[4] A 0.2 molal solution (10 cc.) of bromohydrazobenzene in alcohol was heated at 145° in evacuated tubes for 12 hours; after the tubes had been cooled, their contents were introduced into a distilling flask containing 15 cc. 0.1 *N* HCl, 0.3 g. acid ammonium carbonate, and an excess of 0.1 *N* iodine solution. The oxidation of the undecomposed hydrazo compound by the iodine was thus carried out in the presence of carbonic acid and ammonium acid carbonate, *i. e.*, in a very slightly alkaline medium, and rearrangement of the hydrazo compound under the influence of acid therefore avoided. The mixture was allowed to stand for ten minutes before it was acidified with 20 cc. of 6 *N* sulfuric acid. It was then distilled with steam until the azo compound had all passed over, and the further distillate was colorless. Sodium hydroxide (20 cc. of a 10 *N* solution) was added to the mixture in the distilling flask, and 100 cc. of the liquid were distilled from the alkaline solution into dilute hydrochloric acid. This solution of the amine hydrochlorides was evaporated down to about 25 cc. by dry air drawn through

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[1] Zincke, *Ber.*, 34, 2855 (1901).

[2] Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

[3] Curme, *Loc. cit.*, p. 1162. Cf. also p. 1169 for the less direct method there described in the study of the proportion of the two amines from *p*-methylhydrazobenzene, and the results obtained.

[4] Witt, *Ber.*, 7, 1602 (1874).

it at reduced pressure at 55°; it was then transferred to a separatory funnel, made alkaline with 33% potassium hydroxide solution, and extracted with alcohol-free chloroform until the aqueous layer gave no color with chloride of lime.[1] The chloroform solution was filtered through a cotton plug in the stem of a funnel into a weighed beaker; sodium-dried ether (2 cc.), saturated with hydrogen chloride gas, was added to the chloroform to convert the amines into the hydrochlorides, and partly precipitated them as such; the liquid was evaporated by dry air drawn over the beaker. The hydrochlorides were then dried to constant weight in vacuum over calcium chloride, extracted with 2–3 cc. ligroin to remove any organic impurities, and again weighed to constant weight. The product thus obtained was almost colorless, and was analyzed by bromination as follows: A weighed portion of the mixed hydrochlorides was dissolved in a small amount of water in an Erlenmeyer flask, and 10 cc. 10% potassium bromide solution added to the solution. A definite amount of standard 0.1 *N* potassium bromate was run in from a buret, the flask closed by means of a paraffined cork holding a calcium chloride tube containing glass beads moistened with potassium iodide solution, and the mixture kept in a water bath at 50° for fifteen minutes. White tribromoaniline was precipitated out, and the solution was colored yellow by the excess of free bromine. Potassium iodide (10 cc. of a 10% solution) was rinsed through the glass beads, the mixture was cooled, and the end point determined with 0.1 *N* thiosulfate solution and starch indicator. Blank experiments with known amounts of aniline, bromoaniline, bromoazobenzene, and bromohydrazobenzene, corresponding to the amounts present in 10 cc. of a 0.2 molal solution of bromohydrazobenzene after 12 hours' heating, showed that the ratio of amines could be determined by this method with an accuracy of 0.4%.[2] But as there are undoubt-

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[1] Ten drops of half-saturated chloride of lime solution will produce a distinct brown color in 3 cc. of a slightly alkaline solution of *p*-bromoaniline containing as little as 2 milligrams of the amine. The ordinary test for aniline can therefore be used to test for both amines in question.

[2] If we put: x = millimols of aniline hydrochloride used,
y = millimols of bromoaniline hydrochloride used,
g = weight of mixed hydrochlorides used,
c = volume, in cc., of 0.1 *N* bromate used,

then we have:

$$\begin{aligned} 0.1295\,x + 0.2085\,y &= g \\ 60\,x + 40\,y &= c \end{aligned}$$

(Cf. Curme, *Loc. cit.*)

A mixture of 0.0728 g. aniline and 0.1449 g. bromoaniline with 0.15 g. bromohydrazobenzene and 0.40 g. bromoazobenzene was run through the entire process, beginning with the oxidation of the hydrazo compound by 0.1 *N* iodine solution. 0.0613 g. of the mixed hydrochlorides required 17.90 cc. 0.1 *N* $KBrO_3$. These analytical data give 48.49 molar % aniline, while there was actually present in the original mixture of amines, 48.14% aniline.

edly present in the decomposed hydrazo solution, products of benzidine or similar rearrangements which are somewhat volatile with steam from basic but not from acid solution, the error in an actual determination may be larger. In any case, however, it is well within the necessary limit of accuracy. The following results were obtained in two experiments carried out as described:

Gram amine hydrochlorides.	Cc. 0.1 *N* $KBrO_3$.	Molar percentages.	
		Aniline.	Bromoaniline.
0.0627	18.58	50.2	49.8
0.0673	19.63	48.4	51.6

The above experiments establish the fact that there is only one azo compound, the asymmetrical one, found in the thermal decomposition products of asymmetrical hydrazobenzenes; and the further fact that the two amines are found in equimolecular proportions. The interpretation of the reaction involving the formation of phenyl imide radicals must therefore be incorrect.[1]

3. The Velocity of Decomposition of *p*-Bromohydrazobenzene and 2,4-Dichlorohydrazobenzene.—In order to justify the assumption that *p*-bromo- and 2,4-dichlorohydrazobenzene would resemble the hydrazo compounds studied by Curme, and give velocity constants according to the law for a monomolecular reaction (see Equation 5). determinations of the velocity of decomposition were carried out with *p*-bromohydrazobenzene and dichlorohydrazobenzene in alcoholic solution. Curme's apparatus and methods[2] were used, the tubes containing the solution being sealed off in a freezing mixture at a pressure of 10–20 mm. The whole number of tubes was then heated to 70–80° in a small oil bath and plunged simultaneously into the thermostat at 145°. On removal from the thermostat after a definite time interval, each tube was plunged into the bath at 70–80° for thirty seconds, cooled to ordinary temperatures by water, and analyzed as soon as convenient. Essentially the same method of analysis was employed as in assaying the pure bromohydrazobenzene, except that no aniline was used. The reason for this change was that in neutral or alkaline solution, a dark discoloration[3] which interfered with the sharpness of the end point, appeared on oxidation of the decomposed hydrazo solution. This was entirely avoided by carrying out the oxidation in slightly acid solution, and accordingly, the acid formed by the decomposition was not neutralized by the addition of aniline nor of acid ammonium carbonate. On the other hand, since aniline is formed by the decomposition, it was found necessary, after the decomposition had been allowed to proceed for some time, to add a small

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[1] See Wieland, *Ber.*, 48, 1104 (1915) and the theoretical part of this article.

[2] Curme, *Loc. cit.*, p. 1156.

[3] According to Wieland (*Ber.*, 48, 1104) this is due to some semidine formed when hydrazobenzenes are heated in alcohol solution.

amount of 0.1 *N* HCl solution to the iodine solution before introducing the hydrazo solution, in order to have the oxidation mixture acid, and thus obtain a sharp end point.

The results for *p*-bromohydrazobenzene in 0.2 and 0.05 molal solutions are found in Table I. The first column gives the time in minutes during which the tube was heated, the second and fourth the number of grams of 0.1 *N* iodine solution required for 5 cc. of the hydrazo solution in two separate experiments, the third and fifth the values of the corresponding constants for a monomolecular reaction, calculated from these data and the above equation, and the sixth column the average value of $\mathbf{K}_{mono}$. For the sake of comparison, in the last column is given the velocity constant for a dimolecular reaction, calculated from the data given in the fourth column and Equation 7.

It will be noticed that the "constant" for bromohydrazobenzene, while not showing the inclination to droop exhibited by the "constants" for Curme's substances, varies slightly from concentration to concentration. As the first determinations in 0.2 and 0.05 molar concentrations were run simultaneously, the difference in the constant for the two concentrations cannot be ascribed to an unobserved change of temperature of the thermostat.

TABLE I.

0.2 molal solution of *p*-bromohydrazobenzene. Temperature 145° (uncorrected).

Time.	G. 0.1 *N* I.	$10^5 \times K_{mono}$.	G. 0.1 *N* I.	$10^5 \times K_{mono}$.	Average $10^5 \times K_{mono}$.	K_{di}.
90	16.52	...	16.05	...	...	....
150	14.80	183	14.27	196	190	0.0129
210	13.10	192	12.92	181	187	0.0126
300	10.92	197	10.55	200	199	0.0155
450	7.64	214	7.85	199	207	0.0181
510	7.23	197	6.91	201	199	0.0196
600	6.22	192	5.82	199	196	0.0215
720	...	...	4.14	215	215	0.0285
					199	
	0.05 molal solution of *p*-bromohydrazobenzene.					
90	4.21	...	4.18	...	...	....
150	3.81	167	3.84	(141)	167	0.0353
210	3.41	176	3.41	170	174	0.0450
300	2.91	176	2.89	176	176	0.0509
450	2.23	177	2.27	170	174	0.0559
510	2.05	171	2.09	165	168	0.0570
600	1.83	163	1.77	169	166	0.0639
720	...	...	1.38	176	176	0.0771
					171	

Since the original theory of the reaction had to be abandoned as a result of the study of the products of the decomposition (see the theoretica part), the velocity was next measured in exceedingly dilute solutions in order to determine whether the order of the reaction changes with extreme dilution. For the analytical data, 0.05 *N* and 0.1 *N* solutions of iodine and sodium thiosulfate were used as indicated, and 10 cc. of the hydrazo solution used for each titration. Whereas the results (Table II) show values for a dimolecular reaction constant within experimental error in any one series, the constant in 0.005 molar is practically three times the constant in 0.01 molar concentration. The values of the monomolecular constant fall off decidedly in any series in these very dilute solutions, but the average value for *all* the concentrations used varies only from 199 $\times$ 10_5 in 0.2 molar to 258 $\times$ 10_5 in 0.005 molar; while the average value for the dimolecular constant in 0.2 molar is only one one-hundredth of the constant in 0.005 molar (0.0184 to 1.27).

TABLE II.

0.015 molal solution of *p*-bromohydrazobenzene.

Time.	G. 0.05 *N* I.	K_{di}.	$10^5 \times K_{mono}$.
90	5.02	...	...
150	4.42	0.180	212
210	4.00	0.169	189
300	3.31	0.196	198
450	2.68	0.193	174
510	2.36	0.214	180
600	2.12	0.214	169
720	1.82	0.222	161
		0.198	183

0.01 molal solution of *p*-bromohydrazobenzene.

Time.	G. 0.05 *N* I.	K_{di}.	G. 0.05 *N* I.	K_{di}.	Average K_{di}.	$10^5 \times K_{mono}$.
90	2.90	...	2.70	...	...	...
150	2.45	0.420	2.32	0.404	0.412	253
210	2.16	0.394	2.10	0.353	0.374	209
300	1.80	0.401	1.70	0.415	0.408	220
450	1.49	0.363	1.35	0.412	0.388	193
510	1.29	0.410	1.19	0.448	0.429	195
600	1.16	0.406	1.06	0.449	0.428	183
720	0.87	(0.511)	0.98	0.413	0.413	161
					0.407	202

0.005 molal solution of *p*-bromohydrazobenzene.

Time.	0.05 *N* I.	K_{di}.	G. 0.01 *N* I.	K_{di}.	Average.	$10^5 \times K_{mono}$.
90	1.25	....	6.05	....	....	...
150	0.94	1.76	4.91	1.28	1.52	348
210	0.88	1.12	4.03	1.38	1.25	339
300	0.67	1.32	3.99	(0.81)	1.32	(198)
450	0.58	1.03	2.57	1.25	1.14	238
510	0.47	1.26	2.21	1.37	1.32	240
600	0.36	(1.55)	2.18	1.15	1.15	300
720	0.37	1.21	1.89	1.16	1.19	185
					1.27	258

The order of a reaction is tested more exactly by the constancy or inconstancy of the velocity constant in two solutions of differing initial concentrations, than by its constancy through the course of the reaction in any one solution. An exact expression for the order of a reaction, involving solutions of differing initial concentrations, has been developed by A. A. Noyes:[1]

$$n = 1 + \frac{\ln t_1/t_2}{\ln c_2/c_1},$$

where n is the order of the reaction, and t_1 and t_2 are the time intervals required for the reaction to proceed to equal fractions of the original concentrations, c_1 and c_2.

In order to test the reaction in question by means of this equation, the percentages of decomposition in terms of the concentrations after 90 minutes at 145° were calculated from the data in Tables I and II, and the results plotted. The times required for a given percentage decomposition were found from this graph, and the values substituted in Noyes's equation. Tabulation of the results thus obtained will be found in Table III.

TABLE III.

Initial conc., mols per liter. Av. of two values.	Per cent. decomposed.	Time in minutes.	$n=1+\frac{\ln t_1/t_2}{\ln c_2/c_1}$.	Initial conc., mols per liter. Av. of two values.	Per cent. decomposed.	Time in minutes.	$n=1+\frac{\ln t_1/t_2}{\ln c_2/c_1}$.
0.1617	$33^1/_3$	205	1.10	0.1617	$66^2/_3$	550	1.04
0.0418	$33^1/_3$	235		0.0070	$66^2/_3$	630	
0.1617	50	350	1.11	0.0070	$33^1/_3$	170	0.63
0.0418	50	405		0.0031	$33^1/_3$	125	
0.1617	$66^2/_3$	550	1.11	0.0070	50	350	0.62
0.0418	$66^2/_3$	635		0.0031	50	235	
0.1617	$33^1/_3$	205	0.94	0.0070	$66^2/_3$	630	0.79
0.0070	$33^1/_3$	170		0.0031	$66^2/_3$	525	
0.1617	50	350	1.00				
0.0070	50	350					

From these values of n, there can be no question as to the order of the reaction. The largest values are found for the more concentrated solutions where the velocity constants for a monomolecular reaction are unambiguous; and in these cases, the differences from unity are inconsiderable. Comparison of the two more dilute solutions gives values decidedly below one, which shows that in spite of the constancy of the value of K for a dimolecular reaction in each of these solutions by itself, the reaction is not dimolecular.

A study of the velocity constants of the decomposition of 2,4-dichlorohydrazobenzene (Table IV), shows that with this substance the monomolecular constant, which remains unchanged through a run in 0.1 molal

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[1] Cf. Kremann, *Monatsh.*, **27**, 611 (1906).

solution, falls off[1] toward the end of the run in a concentration (0.05 molar) where the constant for bromohydrazobenzene is still good. The average values of the constant for the chlorohydrazo compound agree very well in the two concentrations. In the third and lowest concentration used (0.01 molar), the monomolecular constant falls off still more decidedly, as would be expected from the results with bromohydrazobenzene, but the dimolecular constant, on the other hand, shows a tendency to rise, which is not the case with the bromohydrazo compound in solutions less than 0.015 molal. Just as before with bromohydrazobenzene, the dimolecular constants for dichlorohydrazobenzene vary greatly from concentration to concentration, and this substance supports the evidence against a dimolecular reaction.

TABLE IV.

	0.1 molal 2,4-dichloro-hydrazobenzene.			0.05 molal 2,4-dichloro-hydrazobenzene.			0.01 molal 2,4-dichloro-hydrazobenzene.		
Time.	G. 0.1 N I required for 5 cc.	$10^5 \times$ K_{mono}.	K_{di}.	G. 0.1 N I required for 5 cc.	$10^5 \times$ K_{mono}.	K_{di}.	G. 0.01 N I required for 10 cc.	$10^5 \times$ K_{mono}.	K_{di}.
60	7.07	...	....	3.89	...	....	13.61	...	...
120	6.08	251	0.0387	3.25	300	0.0846	10.66	(407)	0.678
180	5.08	276	0.0462	2.72	298	0.0922	9.23	324	0.581
240	4.35	270	0.0491	2.37	275	0.0916	7.79	310	0.610
300	3.59	282	0.0571	2.04	269	0.0971	6.67	297	0.637
390	2.87	273	0.0627	1.57	275	0.0151	5.40	280	0.677
480	2.24	274	0.0726	1.28	265	0.1248	4.36	271	0.742
600	1.71	278	0.0854	1.09	236	0.1220	3.49	267	0.789
720	1.15	275	0.0102	1.07	(196)	(0.1027)	1.53	(347)	(1.766)
		272	0.0652		274	0.1039		292	0.673

4. Parallel Determinations of Hydrazo Compound Consumed and Amines Formed.—In Curme's work on hydrazobenzenes, he calculated the velocity constant for the decomposition by means of the increasing amounts of aniline formed, and found that this method of analysis also gave a velocity constant according to the law for a monomolecular reaction, with only a slightly lower value than that obtained from the analytical determinations of the undecomposed hydrazo compound.[2] The method was indirect in that the amount of hydrazobenzene present at any instant of time was *calculated* from the experimentally determined concentration of hydrazo compound at the beginning of the run amd the amount of aniline present at the time considered. In the following experiments on *p*-bromohydrazobenzene, the amounts of hydrazo compound as well as the amounts of amine present, were determined *experi-*

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[1] A part but not all of this droop of $33^1/_3\%$ might be attributed to experimental error. No duplicate determination was made, owing to lack of time and the difficulty of preparing the substance.

[2] Curme, *Loc. cit.*, p. 1163.

mentally in each case; *i. e.*, four tubes, each containing 5 cc. of the solution, were removed from the thermostat at one time, the contents of two of them analyzed as above for bromohydrazobenzene by oxidation with 0.1 *N* iodine, and the contents of the other two for amines by separation through steam distillation as above, and bromination of the acidified distillate with 0.1 *N* potassium bromate. It has already been shown that the two amines occur in equimolecular proportions; the equation for the bromination is therefore

$$C_6H_5NH_2 + BrC_6H_3NH_2 + 10Br \longrightarrow 2C_6H_2Br_3NH_2 + 5HBr.$$

Since two mols of amine are formed by the decomposition of *two* mols of hydrazo compound, one cc. 0.1 *N* potassium bromate corresponds to 0.00002 mol hydrazo compound.

In Table V we find in the first column the time in minutes during which the tubes were heated, in the second the number of grams of 0.1 *N* iodine required for 10 cc. of solution, and in the third the corresponding number of mols of unchanged hydrazo compound per liter, calculated from consideration of the fact that one cc. 0.1 *N* iodine to 10 cc. solution is equivalent to 0.005 mol hydrazine per liter. In the fourth column is given the number of cubic centimeters of 0.1 *N* potassium bromate solution required for 10 cc. of the hydrazo solution, and in the fifth the number of mols hydrazine decomposed per liter. In the last column are given the sums of the concentrations in the third and fifth columns, *i. e.*, the total concentration of the hydrazo compound, decomposed and undecomposed. If there is no interfering reaction by which bromohydrazobenzene is used up without producing amine,[1] the numbers in the last column should be constant. This is the case within the limit of the experimental error, which is rather wide here, since it is the sum of the possible error in the iodine analysis and the error in the bromate analysis.

TABLE V.

Time.	G. 0.1 *N* I.	Conc. undecomposed hydrazobenzene.	Cc. 0.1 *N* $KBrO_3$.	Conc. decomposed hydrazobenzene.	Total hydrazo conc.
90	8.25	0.04125	4.64	0.00928	0.0505
180	6.82	0.03410	7.23	0.01446	0.0486
270	5.69	0.02845	9.12	0.01824	0.0467
390	4.60	0.02300	12.58	0.02516	0.0482
570	3.40	0.01700	14.71	0.02942	0.0464

Table VI gives, in exactly similar form, the results of duplicate experiments on less concentrated solutions. In neither concentration is there any indication of a secondary reaction which is not negligible, nor is there any difference between the two concentrations.

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[1] According to Wieland's work, published since this was written, small amounts of the hydrazobenzene suffer a semidine rearrangement under the conditions used (Wieland, *Loc. cit.*).

TABLE VI.

Time.	G. 0.01 N I.	Conc. undecomposed hydrazobenzene.	Cc. 0.01 N KBrO$_3$.	Conc. decomposed hydrazobenzene.	Total hydrazo conc.
90	13.63	0.006815	7.86	0.001572	0.00838
180	11.83	0.005915	12.12	0.002424	0.00834
270	9.83	0.004915	15.00	0.003000	0.00791
390	7.65	0.003825	20.81	0.004162	0.00799
570	6.09	0.003045	25.74	0.005148	0.00819
90	13.88	0.006940	7.47	0.001494	0.00843
180	10.76	0.005380	12.92	0.002584	0.00796
270	9.83	0.004915	16.39	0.003278	0.00819
390	7.66	0.003830	21.14	0.004228	0.00806
570	4.82	0.002410	26.50	0.005300	0.00781

5. Gaseous Products of Decomposition.—In order to determine whether any hydrogen could be detected as a product of the thermal decomposition of hydrazobenzenes, an approximately molal solution of *p*-bromohydrazobenzene (10 cc.) was heated for 12 hours at 145° in two tubes which had been sealed off at a pressure of 10 mm. After cooling, the tubes contained a dark blue crystalline mass. When they were opened under a eudiometer filled with water, a very small bubble of permanent gas appeared—perhaps 0.03 cc. from each tube.

Since the solid product of the reaction made it seem possible that the reaction might have gone somewhat differently in this molal solution than in the more dilute solutions used in the velocity experiments, tubes containing 0.05 and 0.01 molal solutions were tested in a similar manner. From a tube containing 5 cc. of either solution with 6.5 cc. free space, which had been sealed off in a freezing mixture at 18 mm., and heated twelve hours at 145°, was obtained 0.7 cc. permanent gas at room temperature. Since the gas contained in 6.5 cc. at 0° and 18 mm. could give only 0.17 cc. at 20° and 760 mm., there must be some gas evolved during the heating, the nature of which was investigated in the following experiment: 50 cc. of 0.01 molal solution of bromohydrazobenzene were sealed off at 18 mm. in a bomb-tube of 125 cc. capacity, and heated for 10 hours at 145°. The tube was then opened under an inverted buret filled with water, and the gas transferred to a gas buret, and tested for hydrogen by passage over palladium black at 95°, after the oxygen present had been removed with pyrogallol. The volume of gas obtained from the tube was 4.6 cc. which was decreased to 4.35 cc. by the pyrogallol absorption. Treatment with palladium black reduced this volume only 0.05 cc.; and a subsequent attempt to explode the gas with the electric spark after admitting 12 cc. of air had no effect whatever. It is therefore certain that the gas obtained is not hydrogen, and that it can contain at most very small quantities of hydrogen, if any; and the small amount of oxygen shows that it cannot have been residual air due to imperfect evacuation of the tube. There remains the possibility of some slight secondary decomposition of the hydrazo compound which involves evolution of nitrogen.[1]

6. Effect of Molecular Hydrogen on Hydrazobenzene.—To exclude the possibility that molecular hydrogen might react with hydrazobenzenes under the conditions of the experiments, an approximately 0.5 molal solution (5 cc.) was sealed off in a tube suspended in ice, with a stream of hydrogen at atmospheric pressure passing through it. The tube was then heated for two hours at 145°, cooled, and opened under a eudiometer. The volume of permanent gas obtained over water at 20° was 18.9 cc., while the volume of the tube above the solution was 17.15 cc.; 18.9 cc. at 20° corresponds to 18.2 cc. at 10°, which is about the temperature at which the tube was sealed off. Roughly, therefore, 1 cc. excess gas was found, and no appreciable amount of hydrogen was consumed by the hydrazo compound.

7. Molecular Weight in Alcoholic Solution.—There still remained the possibility that association of the hydrazo compound might account for the fact that the decomposition appeared as a monomolecular reaction, and that the decomposition of these complex molecules was the reaction of which the velocity was measured. The molecular weight of *p*-bromohydrazobenzene in absolute alcohol was therefore determined, and the evidence obtained was decisively against any association, as Table VII shows. McCoy's boiling point apparatus was used. In the following tabulation of the results, the first column contains the observed change in boiling point (Δ'), the second the corresponding volume (V) of solution in which the given weight (W) of substance was dissolved, and the last column the molecular weight calculated from these data by means of the equation:

$$\text{Molecular weight} = \frac{W \times T}{\Delta \times V},$$

where T = 1560 for alcohol.[2] The concentration of the solution at the beginning of the experiment was approximately 0.2 molar.

TABLE VII.

W = grams *p*-bromohydrazobenzene taken = 0.8403.

Δ	0.185°	0.173	0.175	0.170	0.172	0.161	0.161	
Vol. in cc	25.7	26.9	27.6	28.3	29.7	32.7	33.0	
Mol. wt	276	282	271	272	257	249	247	Av., 265
					Calculated for $C_6H_5NH.NHC_6H_4Br$			263

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[1] These conclusions have been fully comfirned since by E. N. Roberts in this laboratory (see footnote 3, p. 1741).

[2] McCoy, *Am. Chem. J.*, **23**, 353 (1900).