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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

## THE DECOMPOSITION OF DIAZOBENZENE CHLORIDE IN WATER SOLUTION<sup>1</sup>

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### Introduction

The kinetics of the decomposition of the diazo bodies in water solution have been studied rather extensively by various investigators, *viz.*, Hausser and Muller,<sup>2</sup> Hantzsch<sup>3</sup> and Cain and Nicoll.<sup>4</sup>

More recently Pray,<sup>5</sup> Yamamoto<sup>6</sup> and Blumberger<sup>7</sup> have continued investigations on these same decompositions. An examination of the data of these various individuals will show that the addition of those substances which hydrolyze alkaline give larger velocity constants but that there is a diminished evolution of nitrogen. This is claimed to be due to the so-called coupling reactions which are supposed to take place in the presence of hydroxyl ion in preference to the simple decomposition. Blumberger states that there is a maximum in the curve of reaction rate plotted against hydroxyl ion increase.

It is the purpose of the present paper to show that the decreased evolution of nitrogen is not due to the so-called coupling reactions and that the maximum in the curve of reaction rate against hydroxyl ion is not attributable simply to this ion.

**Materials and Apparatus.**—Ordinary aniline was redistilled several times; only that portion which boiled constantly at 183.5° was taken for the subsequent experiments. The other chemicals were of C. P. grade and no further attempts at purification were made.

<sup>1</sup> This paper is constructed from a thesis submitted by Bartholdt C. Hadler to the Faculty of Holy Cross College in partial fulfillment of the requirements for the degree of Master of Science.

<sup>2</sup> Hausser and Muller, *Bull. soc. chim.*, [3] 7, 721 (1892); *Compt. rend.*, 114, 549, 669, 760, 1438; *Bull. soc. chim.*, [9] 353 (1893).

<sup>3</sup> Hantzsch, *Ber.*, 33, 2517 ff. (1900).

<sup>4</sup> Cain and Nicoll, *J. Chem. Soc.*, 81, 1412 (1901); 83, 206, 470 (1903); *Ber.*, 38, 2511 (1905).

<sup>5</sup> Pray, *J. Phys. Chem.*, 30, 1417, 1477 (1926).

<sup>6</sup> Yamamoto, *J. Soc. Chem. Ind. Japan*, 32, 352 (1929).

<sup>7</sup> Blumberger, *Rec. trav. chim.*, 49, 276 (1930).

The reaction vessel consisted of a large test-tube about 15 cm. long and 2.5 cm. in diameter to which had been sealed a capillary side arm. The latter communicated with the water-jacketed gas-measuring buret which was maintained at the same temperature as the thermostat by circulating water from the latter through the former. The aniline hydrochloride was diazotized below  $5^{\circ}$  and upon completion of this process the solution was placed in the reaction vessel. After adding that substance whose effect we wished to investigate, a mercury-sealed stirrer was fitted into place and rotated at a constant speed. The gas-measuring buret could be adjusted and read accurately to within 0.1 cc., which, in the early stages of the reaction, leads to an error of 3 or 4%. All of the experiments were conducted at  $30 \pm 0.01^{\circ}$ . The volume of nitrogen evolved was recorded at thirty-minute intervals. These gas volumes were reduced to standard conditions and the reaction velocity constants were calculated according to the graphical method of Guggenheim,<sup>8</sup> which is supposed to overcome uncertainties in the value of  $A$  in the ordinary unimolecular equation.

### Experimental

The following experiment is selected as being typical of this decomposition. In this table, as in all following tables, the first column contains the time in minutes; the second column, the corrected amount of nitrogen evolved; the third column, the value of  $v-v_0$ ; the fourth column, the  $\log_{10}$  of  $v-v_0$ ; the fifth column, the same value as read from the graph; and the last column gives the value of  $0.4343 K \times 10^4$ .

TABLE I  
EXPERIMENTAL RESULTS

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343 K \times 10^4$
30	4.0	4.0	0.602	0.607	
60	7.3	3.3	.519	.536	
90	10.4	3.1	.491	.465	
120	13.1	2.7	.431	.393	23.8
150	15.3	2.2	.342	.323	
180	17.0	1.7	.230	.250	
210	18.4	1.4	.146	.178	

The value 23.8 was obtained from the straight-line plot of  $\log_{10} v-v_0$  against the time. This value agrees very well with the value 24.0 as found by Pray for this same decomposition.<sup>9</sup>

It has been stated by Pray and others that any substance which exerts a dehydrating effect will retard the velocity of decomposition. He observed this in his study of the effect of sulfuric acid on this decomposition. We give in the following table the effect of sulfuric acid on this decomposition mainly because we will need the constant for subsequent discussion. The sulfuric acid was added to the diazotized aniline hydrochloride in the molar ratio of fifteen to one.

The tabulated data show definitely that there is a decrease in the reaction velocity constant in the presence of sulfuric acid. Blumberger attributes

<sup>8</sup> Guggenheim, *Phil. Mag.*, 2, 538 (1926).

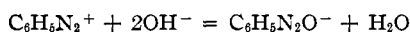
<sup>9</sup> Pray, Ref. 5, p. 1481.

TABLE II  
RESULTS IN PRESENCE OF SULFURIC ACID

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343 K \times 10^4$
60	6.6	6.6			
90	9.6	3.0	0.477	0.477	
120	12.1	2.5	.398	.417	
150	14.4	2.3	.362	.357	
180	16.3	1.9	.279	.296	20.1
210	18.1	1.8	.255	.235	
240	19.5	1.4	.146	.175	
270	20.8	1.3	.114	.115	

this decrease to the formation of a  $C_6H_5N_2SO_4$  ion. If this is true it seems strange that Pray did not observe the decrease on the addition of potassium sulfate. We cannot, therefore, attribute this decrease simply to the formation of a sulfate ion, and it appears that the dehydrating effect is the proper cause of the decrease.

It is known that the diazonium salt is amphoteric. Consequently there is an equilibrium relation as follows



Also large quantities of the  $C_6H_5N_2O$  ion cannot exist in the presence of sodium or potassium ion, for the solubility product is exceeded and precipitation takes place. We should expect, therefore, that if certain salts which hydrolyze alkaline or if alkalis are added to the diazo compound, this precipitate of diazotate will follow with a consequent effect on the decomposition rate of the diazo body. Varying amounts of salts or alkalis added will have differing effects according to the above equilibrium. On the other hand, acid or neutral salts should not affect the reaction rate. This can easily be seen by an examination of the data of Pray.

In the following table we give the effect of monosodium dihydrogen phosphate. Since this substance hydrolyzes acidic, we would not, according to the above argument, expect any effect on the reaction rate. The data show this to be the case.

TABLE III  
RESULTS WITH MONOSODIUM PHOSPHATE

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343 K \times 10^4$
30	3.5	3.5			
60	7.1	3.6	0.556	0.560	
90	10.3	3.2	.505	.492	
120	13.0	2.7	.431	.420	
150	15.2	2.2	.342	.351	23.3
180	17.2	2.0	.301	.279	
210	18.7	1.5	.176	.210	
240	20.1	1.4	.146	.140	

A comparison of this table with Table I will show an almost exact similarity in the amounts of nitrogen liberated at the various points of time. Of necessity then the constants agree with one another very well. Therefore, in spite of the fact that the molar ratio of salt added to the diazo salt is in this case nine to one, there appears no effect on the decomposition rate.

Although secondary sodium phosphate hydrolyzes faintly basic, yet in sufficient quantity (in this case, nine moles of phosphate to one of diazo compound) the  $P_H$  of the diazo solution can be changed enough to cause an apparent increase in the reaction rate, as the following table shows.

TABLE IV  
RESULTS WITH SECONDARY SODIUM PHOSPHATE

Time	Nitrogen evolved	$v - v_0$	$\log v - v_0$	Calcd.	$0.4343 K \times 10^4$
30	3.8	3.8	0.580	0.575	
60	6.1	2.3	.362	.397	
90	7.9	1.8	.255	.219	59.9
120	9.0	1.1	.041	.040	

The amount of nitrogen liberated in this experiment after a lapse of twenty-four hours was less than half of that obtained in the simple decomposition. This confirms Pray's observation but we do not believe it to be due to the so-called coupling reactions. When the phosphate is added to the diazo solution, a brown precipitate appears. This occurs immediately, and so cannot be attributed to the formation of hydroxyazobenzene, for at the beginning of the reaction there is no phenol present with which the diazo compound might combine. Such behavior is explained according to the previous argument.

Concerning the increase in the reaction rate, for which no one has offered an adequate explanation, may we propose that it is a heterogeneous reaction and so catalyzed by the precipitate of the diazotate. We believe this to be so, for one of us has carried out preliminary experiments on this decomposition in the presence of silica gel and suchar and has found the rate to be approximately tripled in the presence of these substances. These experiments are now in the process of completion and we expect to report them in the future.

The addition of hydrogen ion, according to the above-mentioned equilibrium, should cause a shift to the left and a consequent dissolution of the precipitated diazotate. Normal decomposition would be expected to ensue. This is found to be the case, as the following experiments show. Sodium succinate was added to the diazo solution in the molar ratio of nine to one. Precipitation occurred as with the phosphate. We followed the decomposition of this heterogeneous system for two hours and then added sufficient sulfuric acid to redissolve the precipitate.

TABLE V  
 RESULTS WITH SODIUM SUCCINATE

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343 K \times 10$
30	1.3	1.3	0.114		
60	2.7	1.4	.146		
90	3.9	1.2	.079		
120	5.2	1.3	.114		
30	2.5	2.5	.398	0.416	
60	4.9	2.4	.380	.356	
90	6.9	2.0	.301	.296	20.1
120	8.6	1.7	.230	.237	
150	10.1	1.5	.176	.176	
180	11.4	1.3	.114	.114	

The first part of this table shows again decreased nitrogen evolution. The rate appears to be constant within experimental error. The second part of the table shows definitely that the precipitated diazotate will go back into solution and decompose in regular fashion. The constant for this portion of the table is exactly the same as that of Table II.

In the following experiment we added sodium hydroxide in the molar ratio of forty to one in an attempt to reduce the decomposition of the diazo solution to a minimum. After one and one-half hours we added sufficient sulfuric acid to redissolve the precipitate.

 TABLE VI  
 RESULTS OF EXPERIMENT

Time	Nitrogen evolved	$v-v_0$	$\log v-v_0$	Calcd.	$0.4343 K \times 10^4$
90	0.8				
30	5.4	5.4	0.732	0.725	
60	8.4	3.0	.477	.625	
90	11.5	3.1	.491	.521	33.6
120	13.3	2.8	.447	.421	

It will be observed in this experiment that the sodium diazotate decomposes at a very slow rate, for after ninety minutes' time we obtained only 0.8 cc. The constant obtained from these data shows that the reaction is proceeding at a faster rate than the decomposition in Table II. This is due very likely to the large amount of nitrogen liberated in the early stages of the reaction on account of the heat evolved in the neutralization of the alkali. These data show again that the precipitated diazotate can be redissolved and that the resulting decomposition is in order with the simple decomposition.

As a final test the following experiment was performed. In order to overcome the heat effect of the previous experiment, we prepared some solid sodium diazotate by adding sodium hydroxide to the diazo compound around zero degrees. This we filtered off and washed with cold water until it was free from sodium hydroxide. We dried this in a vacuum

desiccator over sulfuric acid. Thirty-two grams of this dried diazotate was suspended in 20 cc. of distilled water and placed in the reaction vessel. We noted the decomposition of this heterogeneous mixture and after two hours' time sufficient dilute hydrochloric acid was added to cause solution.

TABLE VII  
EXPERIMENTAL RESULTS

Time	Nitrogen evolved	$v - v_0$	$\log v - v_0$	Calcd.	$0.4343 K \times 10^4$
120	1.9	1.9			
60	10.4	10.4			
90	14.9	4.5	0.653	0.673	
120	18.9	4.0	.602	.578	30.1
150	21.7	2.8	.447	.487	
180	24.4	2.7	.431	.396	

The constant of this experiment is in fair agreement with those of Tables I and III, and the data again show that the diazotate which is precipitated in alkaline solution can be redissolved, forming the diazo salt which decomposes normally.

What the decomposing entity is we do not know. The facts at hand will not admit of any ion as the deciding factor. We do know, however, that in the simple decomposition hydrogen ion is formed. This being so, the equilibrium above will shift to the left as the reaction proceeds, or, what amounts to the same thing, the amount of substance undergoing decomposition in solution is increased. Under these conditions the value of  $A$  in the simple unimolecular equation is not known accurately and if sufficient time is allowed to elapse all of the diazo compound would be expected to decompose. The arbitrary method of selecting say twenty-four hours or of taking readings until an apparently constant value occurs cannot give the correct value of  $A$  in the presence of alkalis or of substances which hydrolyze alkaline. Consequently the real reaction rates, under these circumstances, can be obtained only by some method which eliminates such an uncertain value. This has been accomplished in the present paper by selecting the method of Guggenheim.

### Summary

1. The simple decomposition of diazobenzene has been repeated.
2. The decomposition in the presence of sulfuric acid shows that the rate is decreased. This is not due, however, simply to the formation of a diazosulfate ion.
3. The decomposition has also been studied in the presence of alkali and of substances which hydrolyze alkaline.
4. It has been shown that if the  $P_H$  of the solution is in the neighborhood of 7 or greater, a precipitate will form. This precipitate is an alkali diazotate.

5. This precipitate can be redissolved upon the addition of acids and the resulting diazo compound will follow the normal decomposition.

6. The solid diazotate has been prepared and its decomposition noted. The addition of acid to this solid causes it to redissolve and decompose normally.

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## ABSORPTION SPECTRA IN SOLUTION AT LOW TEMPERATURES

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### Introduction

Extended and systematic work on light absorption of carbon compounds in solution has been concerned mainly with the identification and quantitative study of rather broad absorption regions. Each of these can be assigned to a definite electronic transition in the molecule, at least in cases where information on the absorption spectra in the gaseous state is available. The main achievement of this work is the evidence that certain absorption regions, located mostly in the near and middle ultraviolet, can be identified with definite atomic groups like the carbonyl, double bond, benzene ring, etc. Evidence has also been accumulated indicating that, if more than one such light absorbing group is present in a large molecule, the resulting spectrum can be represented in the first approximation as a sum of the component spectra. A more detailed study, by the usual method of quantitative measurement of the light absorption coefficients, has revealed, however, that the summation rule holds only very approximately and that in general the rest of the molecule exerts an influence on the absorption by a given part of it. Such an effect, as has been pointed out frequently, is altogether analogous to the alterations in the chemical properties of a group produced by the rest of the molecule, that are so common in organic chemistry.

The study of the spectral changes in solution is thus of considerable interest, at least in the domain of large and complicated molecules where neither the Raman spectra nor the absorption spectra in the vapor phase are sufficiently simple to offer a promise of a more rapid and direct solution of the problem. An attempt at a closer theoretical treatment of the absorption coefficient data for homologous molecules is complicated, however, by the circumstance that this experimental method records simultaneously the effects of two essentially different phenomena. In addition to alterations in the energy of electronic levels as well as to more or less mechanical changes in vibrational frequencies of an atomic group, resulting in a shift and modification of bands comprising an absorption