[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

Chemical Constitution and Reactivity. I. Phenyldiazonium Chloride and its Mono Substituted Derivatives

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In this investigation an attempt has been made to throw some light on the relationship between chemical constitution and reactivity by making an exhaustive study of the reactions which occur when aromatic diazo compounds decompose in aqueous solutions. As a first step an accurate, simple and automatic apparatus was designed for measuring and recording evolved nitrogen.[1] By use of this apparatus, aqueous solutions of phenyldiazonium chloride,[2] and twenty-four of its mono substituted derivatives have been investigated.

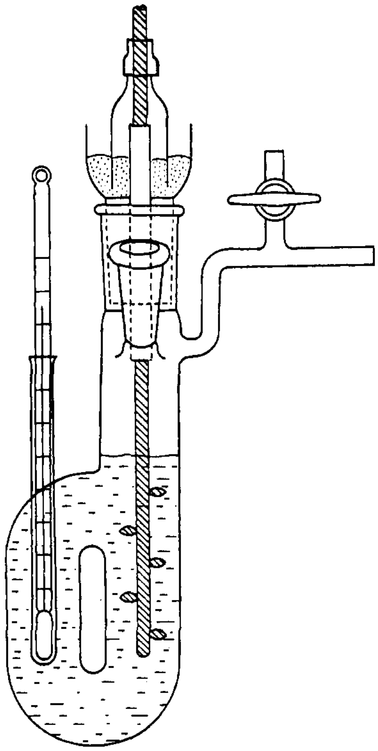

Fig. 1.—Reaction cell.

The experiments were carried out at constant temperature, within ±0.05°, in the dark in an 80-cc. glass cell of special construction, Fig. 1, equipped with an efficient stirrer to prevent supersaturation of the solution with nitrogen. The volume of the gas evolved from the reaction cell was continuously measured and recorded by means of the previously described apparatus.[1]

Effect of Temperature.—Freshly distilled aniline was diazotized at 0° in aqueous solution, using 2.2 molar equivalents of hydrochloric acid and 1.0 molar equivalent of sodium nitrite. The solution was diluted to 0.1 molar concentration with ice water, immediately added to the reaction cell and brought to the experimental temperature. The rate of decomposition was determined over a wide temperature range. The values of the reaction velocity constants are given in Table I. The accuracy of the method of measurement has been described previously.[1]

TABLE I

EFFECT OF TEMPERATURE ON THE REACTION VELOCITY OF DECOMPOSITION OF PHENYLDIAZONIUM CHLORIDE SOLUTION OF CONCN. 0.1 MOLAR AND pH 1.6–1.8

Temp., °C.	k (sec.$^{-1}$) $\times 10^5$
5	0.15
25	4.10
35.2	20.0
50	140.0

The data in Table I are linear when plotted as ln k *vs.* $1/T$, thus satisfying the Arrhenius equation

$$\ln k = \ln Z - (E/RT) \qquad (1)$$

The heat of activation for the reaction has been calculated from these data and found to be 27,200 cal./g. mole.

Effect of Concentration.—The effect of concentration on the reaction velocity was studied over a very wide range. In this series the solutions were prepared from crystalline phenyldiazonium chloride, synthesized as follows.

Aniline hydrochloride, 6.475 g., was suspended in 25 cc. of glacial acetic acid and cooled in an ice-bath to 10°; 10 cc. of octyl nitrite was added rapidly and the solution simultaneously cooled externally to about 5°. The solution was carefully examined for any undissolved and unreacted particles of aniline hydrochloride and these were broken up carefully. The solution was spotted against 5% sodium carbonate solution, and octyl nitrite was added dropwise as long as the spot test was red. As much as 15 cc. of octyl nitrite was necessary in some preparations. When the diazotization was complete, 125 cc. of ether was added in a steady stream, whereupon the product precipitated out as an oil. This was allowed to settle for two minutes and the excess ether decanted until there remained a volume of ether approximately equal to that of the oily precipitate. Then, 200 cc. of acetone was added as rapidly as possible and the solution stirred vigorously, whereupon the product came out as a thick slurry of

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(1) Crossley, Kienle and Benbrook, *Ind. Eng. Chem., Anal. Ed.*, **12**, 216 (1940).

(2) In this paper, the term "phenyldiazonium chloride" will be used rather than phenyldiazochloride, although it is recognized that the nitrogens may be tri-valent under some of the conditions imposed.

coarse crystals. The product was filtered, washed by resuspension twice in acetone and twice in ether. It was dried in air until free of ether and then in a desiccator until free of moisture. The yield was 3.5 g. All reasonable safety precautions were taken because of the highly explosive nature of the product.

The product was stored in a desiccator. In the dry state, no measurable decomposition occurred. The evolved nitrogen per gram remained constant. Each aliquot was weighed out and dissolved immediately prior to use.

In order to justify the comparison of data obtained by use of crystalline diazonium chloride with those obtained by use of diazonium chloride solutions prepared by direct diazotization, two decomposition experiments, identical except as regards the method of preparation, were run. No difference in the rate data was found.

Separate experiments were carried out at concentrations ranging from a water–diazo ratio of 1280:1 (moles) to an extremely concentrated solution wherein the ratio was 2.36:1 (moles). It was observed that for all concentration ratios the reaction followed the first order law. Data showing both the mono- and bimolecular treatments of the most concentrated solution investigated illustrate this point (Fig. 2). The reaction, therefore, appears to be truly monomolecular.

The principal reaction products in the decomposition of phenyldiazonium chloride in water are usually considered to be phenol, nitrogen and hydrochloric acid. By analysis of the residues in the concentration series of experiments, it was found however, that the percentage yield of phenol is a function of the dilution. In the most concentrated experiments carried out, where the water–diazo ratio was 2.36:1 (moles), the percentage yield of phenol was 24.3%. On the other hand, in the most dilute experiment, the corresponding yield of phenol was 95.2%.

The reaction velocity constants and phenol yield obtained for the various concentrations studied are given in Table II.

TABLE II

EFFECT OF CONCENTRATION ON THE REACTION VELOCITY CONSTANT AND YIELD OF PHENOL IN DECOMPOSITION OF PHENYLDIAZONIUM CHLORIDE SOLUTIONS, TEMP. 35°

Moles H_2O/moles diazo	k (sec.$^{-1}$) × 10^5	% yield of phenol
2.36	26.2	24.3
3.11	26.8	30.0
3.54	25.6	27.1
3.94	26.7	31.4
7.93	. .	37.0
11.89	25.3	40.0
23.80	24.5	48.7
31.70	23.9	58.5
47.58	23.4	59.3
79.30	21.9	78.0
158.60	21.2	88.0
317.20	. .	90.8
634.40	. .	94.6
1268.00	19.2	95.2

An attempt was made to determine qualitatively what products other than phenol are present after decomposition has occurred. In the concentrated solutions monochlorobenzene, benzene, and biphenyl were identified, monochlorobenzene appearing in greatest quantity. The formation of monochlorobenzene has been observed by Hantzsch.[3]

Deuterium Oxide as Solvent.—Two runs were made under identical conditions except that in the first run the diazonium chloride was dissolved in water, whereas in the second run the solvent was deuterium oxide. The reaction velocity constants were essentially the same, *i. e.*, 0.00025 sec.$^{-1}$ and 0.00024 sec.$^{-1}$, respectively.

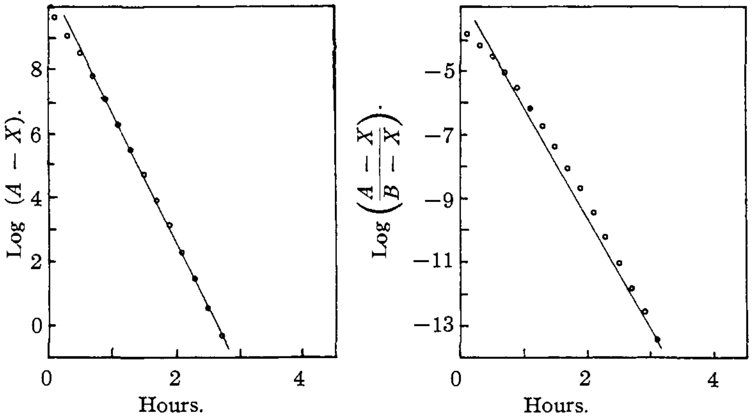

Fig. 2.—Comparison of unimolecular and bimolecular plots. Ratio of diazo to water 1:2.36 moles.

Effect of pH on the Reaction.—A series of experiments was run in which phenyldiazonium chloride was dissolved in different strengths of concentrated hydrochloric acid. In changing the normality of the hydrochloric acid from 0.1 to 12 *N*, only a slight change in the value of the reaction velocity constant is noticed (see Table III). It is interesting to note that the change in

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(3) Hantzsch, *Ber.*, **33**, 2534 (1900).

reaction velocity is small even though Hantzsch[3] has found that in concentrated hydrochloric acid solution the yield of monochlorobenzene increases to 60%.

Table III

Effect of Acid Concentration on the Reaction Velocity Constant in Decomposition of Phenyldiazonium Chloride Solution, 0.1 Molar, Temp. 35°

HCl concn., N	k (sec.$^{-1}$) × 10^5
0.1	20.0
5.0	23.5
10.0	24.1
12.0	22.6

Several solutions of phenyldiazonium chloride were brought to different *p*H values by the addition of sodium hydroxide solution. Each sample was held at a temperature of 35°. When the *p*H was brought to a value of 11.2 (Fig. 3), it dropped within a period of forty minutes to a *p*H of 2. However, when the original *p*H was 11.6 or more, the *p*H value remained above 10. This series was followed by another in which buffered samples were studied at various *p*H's to cover the range 3 to 11.8. The data obtained showing the percentage nitrogen evolved, together with the *p*H changes which occur in spite of the buffering, are given in Fig. 4.

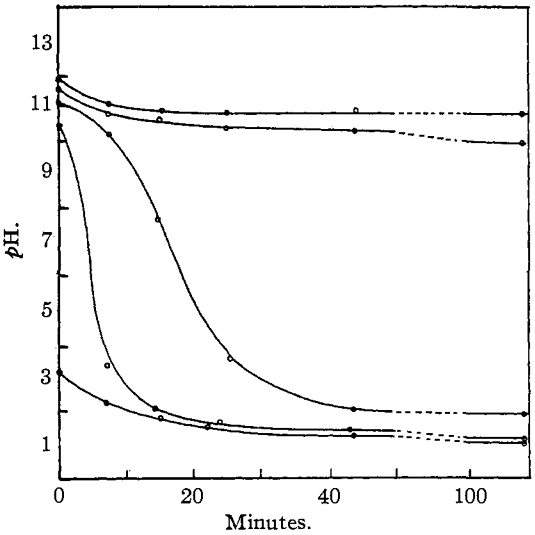

Fig. 3.—*p*H *vs.* time plot, phenyl diazo chloride solution, T = 35°, concn. = 0.1 molar.

Mono-substituted Derivatives of Phenyldiazonium Chloride.—A temperature study was made on the ortho, meta, and para methyl, methoxy, phenyl, hydroxy, chloro, carboxy, sulfo, and nitro phenyldiazonium chlorides. The amines from which the diazonium salts were prepared were Eastman Kodak Co. c. p. chemicals, except for *m*-aminobiphenyl, which was synthesized by the method of Fichter and Sulzberger.[4] The Eastman samples were further purified in our laboratory.

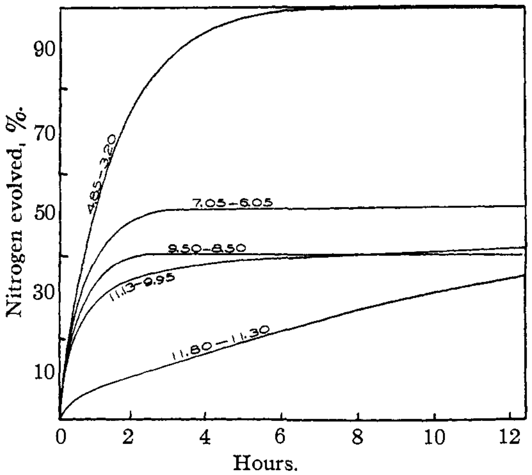

Fig. 4.—Per cent. nitrogen evolved *versus* time at *p*H values indicated, T = 35°, 0.1 M solution.

The amines were dissolved in water by the use of 2.20 molar equivalents of hydrochloric acid, iced to zero and diazotized by use of a normal solution of sodium nitrite and then diluted to 0.1 molar concentration of diazonium chloride and 0.02 molar concentration of hydrochloric acid. In general, the completely diazotized solutions were perfectly clear, but whenever a cloudiness occurred as a result of the formation of diazoamino compound, the cold solution was filtered before use. Prior to the decomposition experiments, the *p*H of each solution was checked with the glass electrode and used if between 1.60 and 1.80.

Rate of Decomposition.—On the basis of preliminary experiments, two or more temperatures were selected at which virtually 100% decomposition could be reached for each diazo within a reasonable time (three to thirty-six hours). Each experiment was then carried to completion and the unimolecular reaction velocity constants calculated, careful correction having been made for all such factors as slight changes in room temperature and/or barometric pressure. A linear relationship between log concentration and time was found over 95–96% of the entire reaction for every diazo in the present series, except for the diazo derived from *o*-anisidine. The latter com-

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(4) Fichter and Sulzberger, *Ber.*, **37**, 878 (1904).

pound does not decompose according to the simple unimolecular law but rather with an autocatalytic trend with the production of an "S" curve. This has been found to be characteristic of several other less common mono-substituted derivatives of phenyldiazonium chloride as well as a large number of poly-substituted derivatives. These exceptions will be treated in a subsequent communication.

TABLE IV

VALUES OF k IN DUPLICATE EXPERIMENTS, SUBSTITUTED PHENYLDIAZONIUM CHLORIDE, CONCN. 0.1 M, pH 1.6–1.8

Diazo from	Temp., °C.	k (sec.$^{-1}$) $\times 10^5$
o-Aminophenol	69.7	20.6
	69.7	20.7
o-Toluidine	35.0	96.0
	35.4	95.6
p-Nitroaniline	60.0	3.29
	60.0	3.30
p-Chloroaniline	59.3	1.72
	59.7	1.79

Duplicate experiments check closely as shown in Table IV.

A further test of the accuracy of the present investigation was obtained when experiments on the same diazo were run at more than two temperatures. From the values of ln k at two temperatures, E and ln Z were calculated by equation (1), after which ln k values at other temperatures were calculated. The calculated values of ln k were compared with the experimental values and agreements of the order of magnitude shown in Table V obtained.

All of the individually determined values of k, for simplicity, are given graphically in Fig. 5. The values of E and ln Z calculated by use of equation (1) are shown in Table VI.

It will be observed that the stabilities as measured by k vary greatly, although the values of E are surprisingly of the same order. Insofar as the latter are not equal, however, crossing of lines occurs when the data for each compound are plotted as ln k *vs.* $1/T$. Consequently, when the diazos are listed according to increasing or decreasing stability, one order is obtained at one temperature and a slightly different order may be obtained at another temperature.

TABLE V

COMPARISON OF OBSERVED VALUES OF ln k WITH VALUES CALCULATED FROM E AND ln Z IN TABLE VI. SUBSTITUTED PHENYLDIAZONIUM CHLORIDES; 0.1 M SOLN., pH 1.6–1.8

Substituent	Temp., °C.	ln k Obsd.	ln k Calcd.
o-Cl	82.7	−10.46	−10.48
p-C_6H_5	40.0	−10.98	−10.98
o-C_6H_5	30.0	− 9.01	− 8.98
-H	25.0	−10.10	−10.12
-H	35.2	− 8.52	− 8.59

The authors wish to acknowledge the assistance of a former associate, Dr. E. G. Kelley, during the early stages of the investigation.

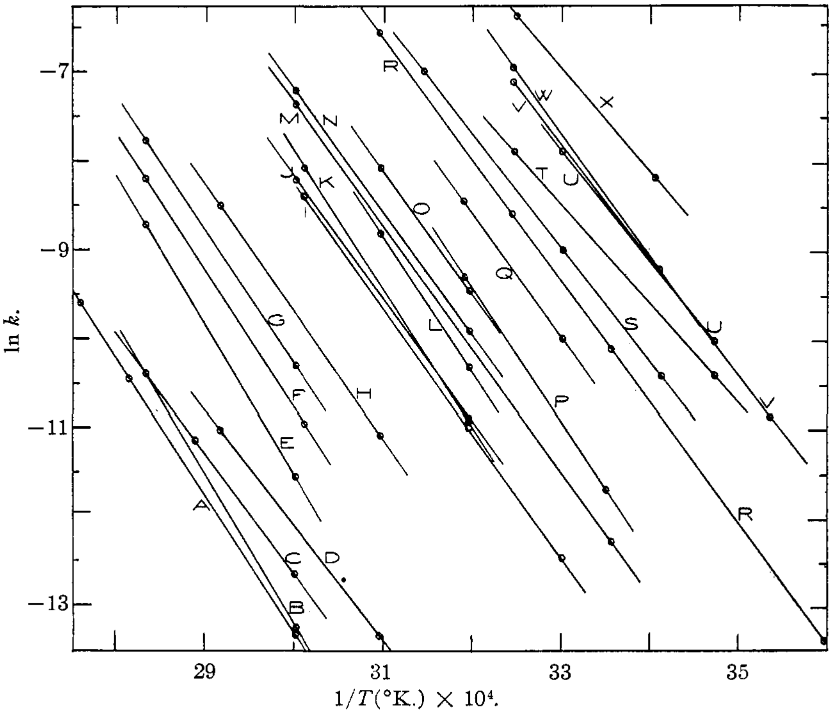

Fig. 5.—ln k *vs.* $1/T$ plots, substituted phenyldiazonium chlorides, 0.1 M solution, pH 1.6–1.8: A, o-chloroaniline; B, p-anisidine; C, o-nitroaniline; D, p-aminophenol; E, m-nitroaniline; F, p-chloroaniline; G, p-nitroaniline; H, o-aminophenol; I, p-aminobiphenyl; J, p-aminobenzene sulfonic acid; K, m-chloroaniline; L, o-aminobenzene sulfonic acid; M, p-toluidine; N, p-aminobenzoic acid; O, m-aminobenzene sulfonic acid; P, o-aminobenzoic acid; Q, m-aminobenzoic acid; R, aniline; S, o-aminobiphenyl; T, m-aminobiphenyl; U, m-anisidine; V, m-toluidine; W, o-toluidine; X, m-aminophenol.

TABLE VI

VALUES OF E AND ln Z FOR THE DECOMPOSITION OF PHENYLDIAZONIUM CHLORIDE AND A NUMBER OF ITS MONO-SUBSTITUTED DERIVATIVES; 0.1 M SOLUTION, pH 1.6–1.8

Diazo compound from	Substituent	E			ln Z		
		Ortho	Meta	Para	Ortho	Meta	Para
Aminophenol	—OH	30,400	26,000	25,600	36.5	36.3	26.5
Anisidine	—OCH$_3$	....	24,600	32,500	..	33.0	35.9
Aminobiphenyl	—C$_6$H$_5$	25,500	22,800	27,600	33.4	29.3	33.5
Toluidine	—CH$_3$	26,200	25,700	27,500	35.8	34.8	34.2
Chloroaniline	—Cl	30,800	30,200	31,600	33.2	37.6	36.9
Aminobenzoic acid	—COOH	29,400	27,100	27,700	37.8	35.1	34.6
Aminobenzene sulfonic	—SO$_3$H	30,300	28,000	27,400	38.9	35.6	33.3
Nitroaniline	—NO$_2$	26,500	33,200	29,800	27.1	38.8	34.7
Aniline	—H	27,200			35.8		

Summary

1. Rate measurements over 96% of the reaction indicate that the decomposition of phenyldiazonium chloride in dilute hydrochloric acid, pH 1.75, is a first order reaction. This is true over the entire range of concentrations studied, *i. e.*, 1280 moles of water:1 mole of diazo to 2.36 moles of water:1 mole of diazo.

2. The heat of activation of the reaction was found to be 27,200 cal./g. mole.

3. The nature of the decomposition products and the reaction velocity are functions of the concentration of the diazonium chloride solution. In very concentrated solution, the phenol yield falls to 24%. Other products formed under these conditions are monochlorobenzene, benzene and biphenyl.

4. The reaction velocity appears to increase very slightly as the concentration of hydrochloric acid is increased, but decreases again above 10 N hydrochloric acid.

5. In deuterium oxide solution the reaction velocity is substantially the same as in water.

6. At initial pH's below 11.2 the pH of the decomposing solution drops slowly to about 2. At initial pH's above 11.6 the pH drops only to about 10.

7. In buffered solutions the percentage of the total nitrogen which is evolved as a gas varies with the pH.

8. Rate measurements of the decomposition of 24 monosubstituted derivatives of phenyldiazonium chloride indicate that with the exception of the *o*-methoxy derivative, the reactions are of the first order. The diazos studied are the ortho, meta and para methyl, methoxy, phenyl, hydroxy, chloro, carboxy, sulfo and nitro phenyldiazonium chloride.

9. The stability of the parent compound, phenyldiazonium chloride, was decreased by *m*-hydroxy, *o*- or *m*-methyl, *m*-methoxy or *o*- or *m*-phenyl substitution. In all other cases studied, the stability was increased.

10. The values of E vary from 22,800 cal./g. mole for *m*-aminobiphenyl diazo to 33,200 for *m*-nitroaniline. The values of ln Z vary from 26.5 for *p*-aminophenol diazo to 38.9 for orthanilic acid diazo.

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