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## **NOTE TO USERS**

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THE MECHANISM  
OF THE  
DECOMPOSITION  
OF DIAZONIUM SALTS  
IN HYDROXYLIC SOLVENTS

by  
Norman Bell Godfrey

A Thesis  
Presented to the Faculty of  
The Rice Institute  
in Partial Fulfillment of the  
Requirements for the  
Degree  
of  
Doctor of Philosophy

The Rice Institute  
Houston, Texas  
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I

INTRODUCTION



## I

### INTRODUCTION

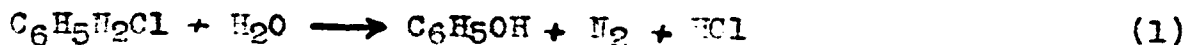
The aromatic diazonium salts are among the most reactive and versatile of the organic compounds. The first diazonium salts were reported by Peter Griess<sup>1</sup> in 1866, and they have been studied continually by numerous workers down to the present time. This paper deals with one of the many classes of reactions undergone by these compounds, namely the decomposition in hydroxylic solvents. The term "hydroxylic solvents" is to be understood as including the alcohols, the carboxylic acids, and water. An attempt will be made to show that the reaction mechanism in all three cases is essentially the same.

The aromatic diazonium salts, of which benzenediazonium chloride is a typical example, are ionic substances, and as such may be expected to dissolve only in relatively polar solvents. In fact, Pray<sup>2</sup> reported that benzenediazonium chloride is insoluble in twenty-five common organic solvents and that, with a few exceptions, the only substances in which it is appreciably soluble are alcohols and carboxylic acids of low molecular weight, and water. These solutions

are all unstable; as soon as the salt is dissolved it begins to break down with the evolution of nitrogen gas. The other products obtained depend on the particular solvent used.

The exceptional solvents mentioned by Pray are furfuryl alcohol, pyridine, quinoline, arsenic trichloride, phosphorus oxychloride, and selenium oxychloride. The course of the decomposition in these solvents is entirely different than in the hydroxylic solvents, and nitrogen is not evolved from solutions in the first three.

In water solution, the principal product is phenol. However, a certain amount of p-hydroxybiphenyl is usually formed by the reaction of the diazonium salt with some of the phenol. These reactions may be formulated as:

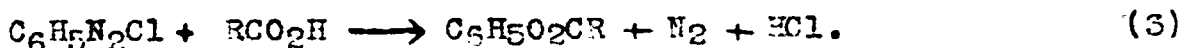


Other products are found in varying proportions depending on the concentration. The decompositions are found to follow first-order kinetics, and the specific reaction rates are essentially constant, except at very high concentrations.<sup>3</sup> However, a large change in the initial concentration of benzenediazonium chloride may markedly change the nature of the reaction products. In an experiment employing a very concentrated solution,

Crossley, Kienle and Benbrook<sup>3</sup> found only a 23% yield of phenol. Chlorobenzene, benzene and diphenyl were identified among the other products.

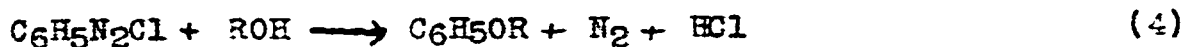
The presence of excess chloride ion in the solution has little or no effect on the rate, but may also change the relative proportions of the products. Blumberger<sup>4</sup> found a significant increase in the yield of chlorobenzene when sodium chloride and hydrochloric acid were added in large excess to a decomposing benzenediazonium chloride solution.

In carboxylic acid solutions the principal product is the corresponding phenyl ester:



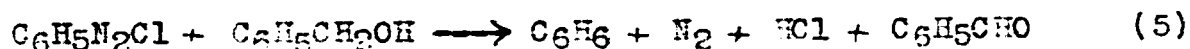
Pray<sup>2</sup> studied the kinetics of the decomposition in formic, acetic, propionic, and butyric acids and found that this reaction is also first order. Furthermore, the reaction rate constants at 30°C varied over a range of only 27% from the smallest (in formic acid) to the largest (in butyric acid). No correlation is possible between the rate constants and the ionization constants of the acids.

In alcoholic solutions, the principal product from the decomposition of benzenediazonium chloride is the phenyl alkyl ether:



Here also, the reaction is first order, is independent of

starting concentration, and is unaffected by the presence of hydrochloric acid or metallic chlorides.<sup>2</sup> Furthermore, the rates in general vary only slightly with the nature of the alcohol. Benzyl alcohol shows the greatest deviation from the rates found with the other alcohols. This may be associated with the fact that a side reaction becomes predominant in this case, involving the oxidation of benzyl alcohol to benzaldehyde, according to the equation



With amyl alcohol which also has an abnormally low rate, there was also noticed some benzene formation.

Some of Pray's results have been converted to specific reaction rate constants in reciprocal seconds and are given in Table 1.

Table 1

Rates of Decomposition of Benzenediazonium Chloride in Hydroxylic Solvents

	$k \times 10^4 \text{ (sec}^{-1}\text{)}$	
	30°	40°
<u>Alcohols</u>		
methyl	2.05	8.71
ethyl	2.05	8.37
n-propyl	2.00	7.84
iso-propyl	2.65	11.05
n-butyl	1.92	7.72
iso-butyl	2.07	7.94
amyl	1.78	--
benzyl	--	5.87
<u>Acids</u>		
formic	.714	2.81
acetic	.718	3.15
propionic	.725	3.15
butyric	.883	3.91
water	.959	4.11

In most of these values, the accuracy of the experimental results does not justify the third significant figure.

Another interesting observation made by Pray<sup>2</sup> is that in mixtures of methanol and water, the rate constants show a linear dependence on the mole fraction. Apparently, therefore, the reaction is a non-selective one. He also determined the rate constants in a series of mixtures of ethanol and ethyl ether, and found that they increase linearly with the mole fraction of ether.

Waring and Abrams<sup>5</sup> measured the rate constants for the decomposition in isoamyl alcohol and active amyl alcohol, and found that they lie in the same range as those for the alcohols employed by Pray. They also found that very little effect on the rate is obtained by changing the composition in mixtures of t-amyl alcohol and ethanol, and of pentanol-2 and ethanol. (Pure t-amyl alcohol and pentanol-2 were found to have too little solvent power for benzenediazonium chloride to serve for kinetic studies.) These authors state that the presence of added metallic salts or of reaction products in the solution have no effect on the kinetics.

It is a striking fact that in all the solvents listed, the overall variation in reaction rate constants is less than fourfold. A simple calculation based on the Arrhenius equation indicates that a difference in activation energy of less than 1 K cal would be sufficient

to account for this much variation. No correlation can be shown between rate constants and various physical properties of the solvent such as dielectric constant, viscosity, surface tension, and dipole moment.<sup>2,5</sup>

The effect of changing the nature of the negative ion associated with the benzenediazonium ion was studied by Cain,<sup>6</sup> who found that the chloride, acid sulfate, nitrate, and oxalate all decompose in water solution at essentially the same rate. His values for the rate constants at 50° in solutions of these four salts show an average deviation of 1.3% from the mean.

So far as the author is aware, no similar kinetic studies have hitherto been made with the purpose of determining the effect of varying the anion of a diazonium salt on the rates of decomposition in acids or alcohols.

An abundance of experimental data is available on the kinetics of decomposition of aqueous solutions of diazonium salts having substituents in the benzene ring.<sup>3,7</sup> The order of the various common substituents in their effect on the first-order rate constants is rather unusual, as will now be shown.

Hammett<sup>8</sup> has prepared a table of "substituent constants" for a number of substituents which are related to their quantitative effect on a large series of reactions of benzene derivatives (or on certain equilibrium constants, such as ionization constants of aromatic acids). The

value of the substituent constant  $\sigma$  is defined by the equation,

$$\log k = \log k^0 + \rho\sigma \quad (6)$$

where  $k$  is the reaction rate constant for a particular reaction in a series of reactions which differ only in the nature or position of a substituent in the benzene ring,  $k^0$  is the rate constant for the unsubstituted reactant and  $\rho$  is a constant which depends on the reaction series under consideration. Thus a linear relationship exists between  $\log k$  and  $\sigma$  for a particular reaction series.

Within fairly close limits, this relation holds good for 52 different series of reaction rate constants or equilibrium constants. From the results of Crossley, Kienle, and Benbrook<sup>3</sup> a table has been prepared (Table 2) showing the order of effect of several substituents on the rates of decomposition of substituted benzenediazonium chlorides in water solution at 30°C, and the corresponding order of the same substituents taken from Hammett's table.

Table 2

Effect of Substituents in Benzenediazonium Chloride on  
Rate of Decomposition

<u>Substituent</u>	<u>Serial no. in order of decreasing k</u>	<u>Serial no. in order of increasing <math>\sigma</math></u>
m-CH <sub>3</sub>	1.	3
m-OCH <sub>3</sub>	2	6
m-C <sub>6</sub> H <sub>5</sub>	3	7
none	4	4
m-CO <sub>2</sub> H	5	9
p-CO <sub>2</sub> H	6	12
p-CH <sub>3</sub>	7	2
p-C <sub>6</sub> H <sub>5</sub>	8	5
m-Cl	9	10
p-NO <sub>2</sub>	10	13
p-Cl	11	8
m-NO <sub>2</sub>	12	11
p-OCH <sub>3</sub>	13	1

A striking difference in the two orders is at once apparent. If the meta-substituents are considered as a group, it is seen that their order in the second column parallels the order of increasing  $\sigma$  values, without exception. The positions of the para-substituents, however, appear to be entirely random with respect to their  $\sigma$  values. In one case the normal order is completely overturned, and para-methoxyl, which has the highest  $\sigma$  value, appears at the bottom of the list in order of reaction rates. Apparently there is something peculiar about this particular series of reactions which sets it apart from those correlated by Hammett.

Ortho-substituents were omitted from Hammett's table because steric hindrance and other effects prevent the quantitative prediction of their influence on reactions.



The order of their influence on the decomposition of substituted benzenediazonium chlorides in water, however, closely parallels that of the para-substituents. Of the substituents listed, only carboxyl is out of line with this order. O-methoxybenzenediazonium chloride reacts by a different mechanism which is autocatalytic in its kinetics and results in complex tarry products. 4,5-benzoxadiazole-1,2,3 has been postulated by the authors as an intermediate.<sup>9</sup>

To summarize some of the experimental observations with which any successful theory of the mechanism of the decomposition of diazonium salts in hydroxylic solvents must be compatible:

- 1) In all cases the kinetics are first order, or at least pseudo first order (since the order with respect to a solvent in great excess cannot be determined directly by kinetic measurements), and are independent of starting concentration.

- 2) The extreme range of variation in the rate constants for all the hydroxylic solvents studied is very narrow--about fourfold. In other words, the reaction rates are nearly independent of the nature of the solvent.

- 3) The reaction rates are independent of the nature of the anion for different benzenediazonium salts in water solution.

- 4) The presence of added salts or acid with a common anion has no effect on the rate of decomposition of the

diazonium salt.

5) The rate constants in mixed solvents vary linearly with the mole fraction of one of the constituents of the binary mixture.

In addition, the complete theory would explain the effect of substituents in the ring. It should also attempt to account for such solvent effects as are observed.

## II

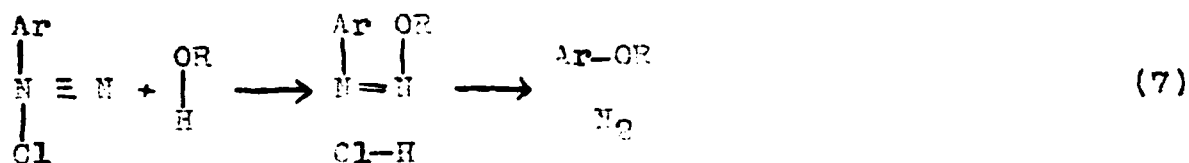
### THEORETICAL PART

## II

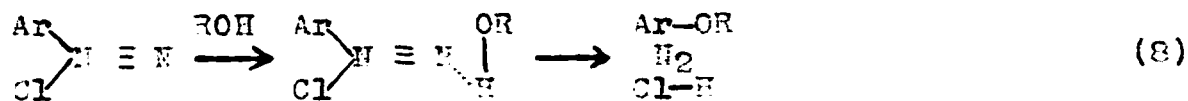
### THEORETICAL PART

#### A. Proposed Mechanisms

An early attempt to formulate the mechanism of the reaction of diazonium salts with alcohols was made by Hantzsch<sup>10</sup> in the following form:



He later revised this formulation as follows:<sup>10-</sup>



The essential difference is in the structure of the postulated intermediate, apparently involving some sort of hydrogen bond between a nitrogen atom of the diazonium group and the oxygen atom of the alcohol. The syn-diazo ether has been eliminated from the picture.

Pray<sup>2</sup> points out two serious objections to the first of Hantzsch's mechanisms. The essence of the first is that no matter which step is assumed to be the rate-determining one, its rate should depend to a high degree on the nature of the alcohol. The other is that the presence of excess chloride ion would be expected to affect the rate. Pray claims that it does not, but this

statement appears to be based on his rate studies in water,<sup>11</sup> not in alcohols. He offers no alternative mechanism.

In any case, the configurations required by Hantzsch's formulas are incompatible with modern theories of structural chemistry.

In the light of current theories of electronic structure and reaction mechanisms, several possibilities present themselves:

1) A bimolecular nucleophilic displacement of nitrogen by a solvent molecule. This would imply as the rate-determining step, the reaction,

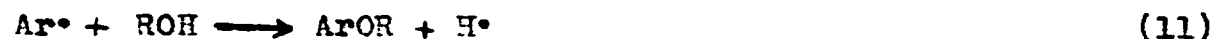


where Ar is an aromatic group and R may be acyl, alkyl, or H. This mechanism is similar to the S<sub>N</sub>2 mechanism of Gleave, Hughes and Ingold,<sup>12</sup> but the kinetics would be pseudo first order rather than second order.

2) A free radical mechanism, involving the unimolecular decomposition of a covalent diazo form of the compound as the rate-determining step,



followed by the rapid reaction of the aryl radical with the solvent,

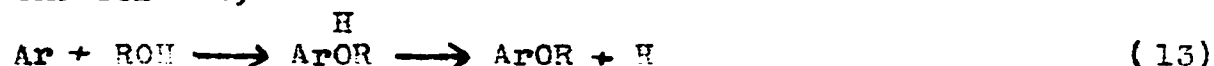


3) A first order nucleophilic displacement, or S<sub>N</sub>1 mechanism. This has as its rate-determining step the

unimolecular decomposition of the aryldiazonium ion,



followed by the rapid reaction of the aryl cation with the solvent,



This is the mechanism favored by the author as offering the best explanation for the observed facts in all the decompositions in hydroxylic solvents under discussion.

4) An intramolecular decomposition of some intermediate compound formed from the diazonium salt and the solvent. This is called the  $S_N1$  mechanism in the Hughes and Ingold terminology.<sup>13</sup> The decomposition of the syn-diazo ether originally proposed by Hantzsch<sup>10</sup> would be of this type. A somewhat more attractive alternative would be the rapid reversible formation of the conjugate acid of the diazo ether, which might be present only in very low concentration, followed by its slow intramolecular decomposition:



These four mechanisms will now be discussed at length.

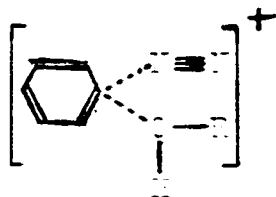
### B. Discussion

1) The possibility of a bimolecular nucleophilic displacement of  $N_2$  from the aryl diazonium ion by a molecule of the solvent cannot be ruled out on the basis of the observed first-order kinetics alone. Since the solvent is always in great excess, its concentration is essentially constant. The rate law, therefore, has the form

$$dN_2/dt = k(ArN_2^+)(ROH) = k'(ArN_2^+) \quad (15)$$

Unfortunately, the effect of varying  $(ROH)$  cannot be determined because no inert solvent is available. Even if there were such a solvent, the data obtained would be unreliable because of the change in the nature of the reaction medium which would inevitably result.

The theory of the nucleophilic displacement mechanism involves the concept of a transition state in which the entering group may be considered as forming an incipient bond before the leaving group has completely broken its bond at the point of attachment. The transition state in the reaction of the benzenediazonium ion with a hydroxylic solvent by this mechanism could be formulated as:



The concentration of molecules in the transition state, though small, has a definite value and is related to the

concentration of the diazonium ions by the equation,

$$C^{\ddagger}/C_d = K^{\ddagger} \quad (16)$$

where  $C^{\ddagger}$  is the concentration of molecules in the transition state and  $C_d$  is the concentration of the diazonium ions. The free energy of activation, which is the free energy of formation of the transition state, is given by

$$\Delta F^{\ddagger} = -RT \ln K^{\ddagger} \quad (17)$$

According to the transition state theory,<sup>14</sup> the rate constant for any reaction passing through such a transition state is given by

$$k = K^{\ddagger} \underline{k} T/h \quad (18)$$

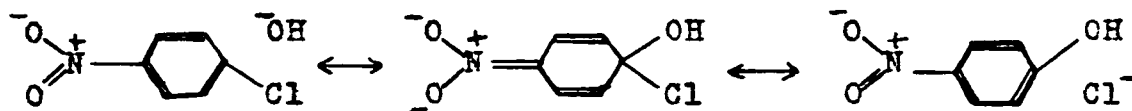
where  $\underline{k}$  is Boltzmann's constant and  $h$  is Planck's constant.

It seems evident that  $\Delta F^{\ddagger}$ , and hence  $k$ , would depend on the structure of the transition state, consequently would vary markedly with the nature of the solvent.

Some less theoretical and more direct evidence against the nucleophilic displacement by solvent is available in the effect of substituents on other nucleophilic displacement reactions. The hydrolysis of aryl chlorides is believed to proceed by a nucleophilic displacement mechanism. The conversion of chlorobenzene to phenol requires high temperatures and the use of concentrated alkali. The presence of a p-nitro group in the molecule makes the reaction go much more readily. This may be attributed to lowering of the activation



energy by resonance in the transition state:

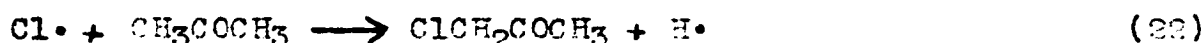
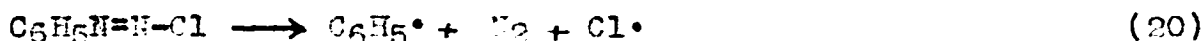


The introduction of other nitro groups in the ortho-positions further increases the reactivity, until in 1,3,5-trinitro-2-chlorobenzene a substance as reactive as an acyl chloride is obtained.<sup>15</sup>

In sharp contrast to this accelerating influence of the nitro group on a typical bimolecular nucleophilic displacement is its strong retarding influence on the decomposition of diazonium salts. It therefore appears improbable that the latter reaction is a bimolecular nucleophilic displacement.

2) The free radical mechanism involving the decomposition of a covalent diazo form of benzene diazonium chloride was advanced by Hey and Waters<sup>16</sup> to account for the observations of Pray<sup>2</sup> on the decomposition in alcoholic solutions. Waters<sup>17</sup> considers these to be of the same type as the reactions which occur during the decomposition of solid benzenediazonium chloride in contact with other organic liquids including acetone, ethyl acetate, acetonitrile, and ether. He postulates a "tautomeric rearrangement" to the diazo form accompanying the process of solution in these relatively nonpolar solvents, which have a slight though definite solvent power for benzenediazonium chloride. This is followed by a homopolar

dissociation into nitrogen gas, phenyl radicals, and atomic chlorine. The last two species, being extremely reactive, attack the solvent. The final products are those which result from the action of phenyl radicals, which abstract hydrogen from the solvent, and chlorine atoms, which displace hydrogen from it. The sequence of reactions with acetone, for example, is depicted by the following equations:



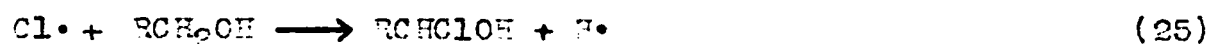
This mechanism accounts for the major products of the reaction, benzene and chloroacetone. The fate of the atomic hydrogen set free according to Equation 22 is not accounted for by Waters, but it may presumably perpetuate itself by chain collisions, eventually combining with another radical to form benzene, acetone, hydrogen chloride or hydrogen gas. Chlorobenzene might be expected among the products and, in fact, is often found in small yield. It need not be assumed that the phenyl radical and the chlorine atom formed in the second step would immediately combine, because each of these would react at once with the closest molecule, which would probably be a solvent molecule.

By analogy with this type of reaction, Waters

considers that the decomposition in alcohols would take place entirely via the covalent diazo chloride. The phenyl radical is then supposed to react with an alcohol molecule by one of two mechanisms:



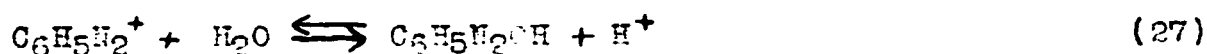
It is uncertain whether the hydrogen atom displaced according to Equation 24 is the one attached to hydrogen or another one. The formation of aldehyde which accompanies benzene formation is accounted for by the equations



However, with benzenediazonium chloride and most alcohols in which it dissolves, ether formation (Equation 23) is overwhelmingly predominant over the reaction which leads to benzene and aldehyde (Equations 24 to 26). During the ether-forming reaction, the chlorine atoms formed simultaneously with the phenyl radicals are supposed to react quantitatively with the hydrogen atoms to give hydrogen chloride.

To the author, Waters' analogy between the reactions of the type of the one with acetone, and those with alcohols does not seem justified. In the first place, nearly all of Waters' reactions were carried out in the presence of calcium carbonate to keep the solutions nearly neutral. It is probable that these conditions would

favor a free radical type of mechanism whereas the acid conditions prevailing in Pray's reactions with alcohols might tend to prevent it. A certain concentration of water would be built up due to the neutralization of the calcium carbonate, and in a neutral solution the hydrolysis of benzenediazonium chloride is known to occur with the production of benzenediazo hydroxide:<sup>18</sup>



This was found by Hey and Waters<sup>19</sup> and by Waters<sup>20</sup> to react with many organic liquids by a free radical mechanism.

In the second place, energy considerations make Equation 23 appear unlikely. Pauling's table of bond energies<sup>21</sup> indicates for the O-H bond an energy of 110.2 Kcal/mole, for the C-H bond an energy of 87.3 Kcal/mole, and for the C-O bond an energy of 70.0 Kcal/mole. Equation 23 involves the breaking of an O-H bond in preference to a C-H bond of lower energy, and the formation of a C-O bond of lower energy than that of the O-H bond.

In the third place, the fact that the rate constant is independent of the initial concentration of benzenediazonium chloride or of the presence of excess chloride ion is incompatible with Waters' mechanism. Davidson and Eantzschen<sup>22</sup> found that benzenediazonium chloride in ethanol solution is a moderately strong electrolyte, comparable to lithium chloride and sodium iodide. The latter salt is 48% dissociated in N/16 alcoholic solution

at 25°C.<sup>23</sup> Waters seems to have ignored completely the effects of this dissociation. If his mechanism is correct, we must consider the equilibrium constant of the reaction:



which we may call K. The rate law would then be given by

$$d\text{N}_2/\text{dt} = k(\text{C}_6\text{H}_5\text{N}_2\text{Cl}) = (k/K)(\text{C}_6\text{H}_5\text{N}_2^+)(\text{Cl}^-) \quad (29)$$

Since chloride ion is not consumed in the reaction, the observed kinetics would be first order but the rate constant would be dependent on the initial concentration of benzenediazonium chloride. This prediction is not in accordance with the results of Pray,<sup>2</sup> who found that changing the starting concentration by a factor of two did not change the rate constant. In addition, the dielectric constant of the solvent would be expected to have a marked influence on the ionization constant K and hence on the apparent unimolecular rate constant  $(k/K)(\text{Cl}^-)$ , since ions appear only on one side of Equation 28.

In his book, The Chemistry of Free Radicals<sup>17b</sup> (p.16), Waters predicts that solvents as polar as ethyl alcohol should favor the type of reaction involving ionic fission of covalent bonds as opposed to free radical formation. Nevertheless, he holds the opinion that reactions of diazonium salts dissolved in acetic acid "are, like the majority of those in water, reactions of diazonium cations,  $(\text{ArN}_2^+)$ , and not those of neutral radicals or of unionized  $\text{ArN}_2\text{Cl}$  molecules." (p. 162)

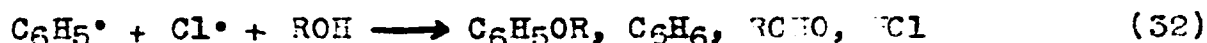
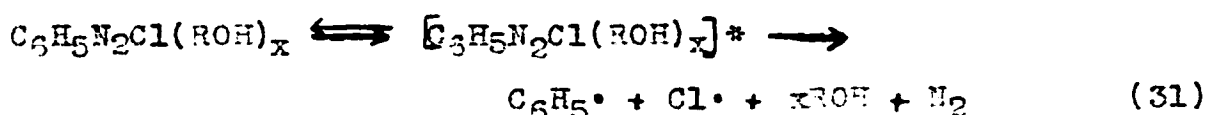
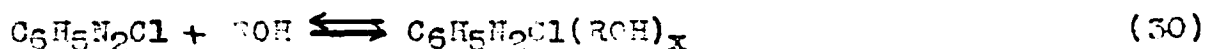
Since acetic acid has a far lower dielectric constant than that of ethyl alcohol (7.1 as compared with 25.0), this view seems inconsistent with his free radical mechanism for the decomposition in alcohols.

Finally, perhaps the most serious objection to the free radical mechanism consists in its logical consequence that diazonium salts differing only in the nature of the anion should decompose at different rates. This follows from the variation in the energy required to dissociate an N-X bond that would necessarily accompany a change in the group X. A still stronger argument against the free radical mechanism would be at hand if the rate of decomposition of a diazonium salt incapable of assuming a covalent form were measured and found identical with that of the corresponding diazonium chloride.

The mechanism proposed by Waring and Abrams<sup>5</sup> also involves the assumption that phenyl free radicals are the reactive species in the decomposition of benzenediazonium chloride in alcohols. Their modification of Waters' hypothesis consists in the postulation of a solvated complex between benzenediazonium chloride and an unspecified number of solvent molecules. Its structure is described as "a favorable distribution of a number of solvent molecules, achieved by chance, around the reactant in order to lower the activation energy sufficiently to permit reaction. This favorable arrangement may depend

on some fixed set of geometrical conditions. These conditions may have to be such as to permit the attacking molecule to approach sufficiently close for reaction to take place. Or, they may be such that once exact geometrical arrangement is obtained, the forces involved between the surrounding solvent molecules and the reactant may cause electronic disturbances which lead to the decomposition of the latter.

Their formulation of the mechanism is as follows:



Here  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}(\text{ROH})_x]^*$  represents the activated complex, whose decomposition constitutes the rate-determining step.

This mechanism is subject to the same criticisms as Waters' mechanism, and also to an additional one, that the geometrical arrangement of the described solvated complex would almost certainly have a large effect on its stability, and would depend on the structure of the alcohol.

Waring and Abrams attach great significance to the fact that when  $\log PZ$  is plotted against  $E_a$  for the various decompositions in hydroxylic solvents, the points for the alcohols fall on one straight line, and those for the acids and water on another parallel one. This

is, of course, a necessary consequence of the fact that the reaction rate constants fall into two groups which vary only slightly within themselves, as can readily be seen from the logarithmic form of the Arrhenius equation,

$$\log k = \log(PZ) - E_a/RT \quad (33)$$

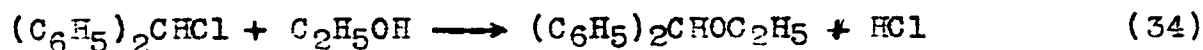
It is difficult to explain why the activation energy,  $E_a$ , and the collision constant,  $PZ$ , should vary from one reaction to another in such a way that  $k$  remains practically constant.<sup>5,17b</sup> It is far simpler to attribute this effect to inaccurate values for the activation energies due to experimental error in determining the rate constants.

3) The  $S_N1$  mechanism (Equations 12 and 13) is favored by Waters<sup>24</sup> as the explanation for the course of decomposition of aqueous benzenediazonium salt solutions. Other authors,<sup>4,25</sup> although agreeing that the benzenediazonium ion is probably involved in the rate-determining step, have apparently been reluctant to postulate even the transient existence of the phenyl cation which results from its decomposition. This reluctance probably stems from the fact that it seems to be impossible to produce the phenyl cation by conventional means, such as the hydrolysis of phenyl halides.

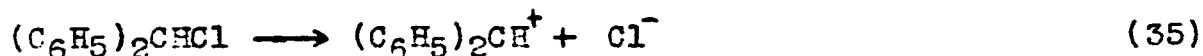
All other accepted examples of the  $S_N1$  mechanism permit the stabilization of the carbonium ion intermediate by resonance among various electronic structures



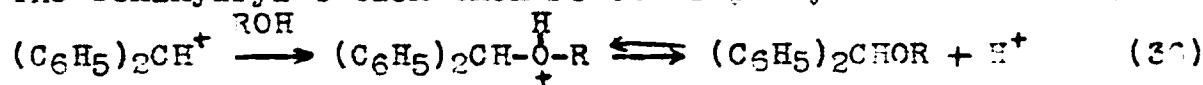
of equivalent energy. The consequent lowering of the potential energy of the carbonium ion serves to lower the activation energy so that the reaction can proceed. A typical example is the reaction of benzhydryl chloride in ethyl alcohol to produce benzhydryl ethyl ether:<sup>26</sup>



This reaction proceeds at a rate which is independent of the concentration of ethylate ion and is a true first order, or  $\text{S}_{\text{N}}1$  reaction. The rate-determining step is the dissociation of the benzhydryl chloride, assisted by the solvating power of the alcohol for the chloride ion which is produced:



The benzhydryl cation then reacts rapidly with the solvent:



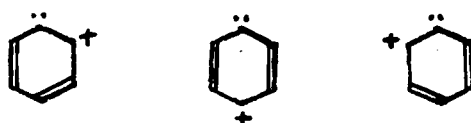
The chief factor which favors the  $\text{S}_{\text{N}}1$  mechanism over the  $\text{S}_{\text{N}}2$  in this case is the strong resonance in the carbonium ion among various structures having the positive charge residing on the ortho- and para- positions of the two benzene rings, such as:



It is a principle of the resonance theory that in order for such resonance to occur, the central carbon atom,

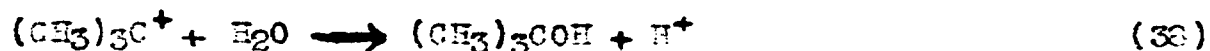
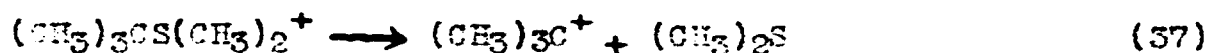
the hydrogen attached to it, and the two benzene rings must all lie in the same plane.

For the phenyl cation produced by the unimolecular decomposition of the benzenediazonium ion, the alternative resonating structures which can be written are of a lower order of stability than the above, since they involve an open sextet of electrons on two of the carbon atoms in the ion:



This means that the reaction of diazonium salts by an  $S_N1$  mechanism has to overcome the difficulty of a carbonium ion intermediate which is stabilized by resonance to a lower degree than those occurring in most other reactions in this category. However, this disadvantage may be compensated for, at least in part, by the simultaneous formation of an extremely stable molecule of nitrogen.

Another reaction, which resembles the diazonium salt decompositions more closely, is the decomposition of dimethyltertiary-butylsulfonium salts in water and aqueous alcohol solutions:<sup>27</sup>



Here the rate-determining step involves the unimolecular decomposition of a positively charged ion to produce a

carbonium ion and a neutral molecule, as in the proposed mechanism for the decomposition of the diazonium salts. It is interesting to note that the reaction rate is moderately increased by increasing the concentration of alcohol in the solution. Thus the solvent effect in this reaction appears to be similar to that found by Pray<sup>2</sup> for ethanol-ether mixtures, in that decreasing polarity of the solvent favors a higher rate of reaction. An explanation for this solvent effect in terms of the Brønsted theory<sup>28</sup> of the effect of the medium upon reaction rate is as follows:

For the formation of a critical complex (or transition state) by the reaction  $A \longrightarrow A^\ddagger$ , the exact equilibrium expression is:

$$K^\ddagger = (A^\ddagger)f_{A^\ddagger}/(A)f_A \quad (39)$$

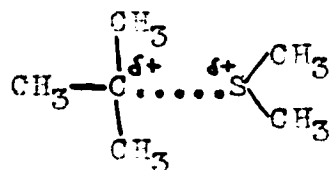
where  $f$  stands for activity coefficient. The specific rate of the overall reaction is (cf. Equation 18)

$$k = (kT/h)K^\ddagger(f_A/f_{A^\ddagger}) \quad (40)$$

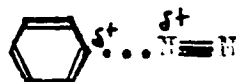
Therefore, the factors which will tend to increase  $k$  will be those which increase the ratio  $f_A/f_{A^\ddagger}$ .

In the particular case under consideration, namely the decomposition of dimethyl-tertiarybutylsulfonium ion, both  $A$  and  $A^\ddagger$  represent singly charged positive ions. In the transition state  $A^\ddagger$ , however, the positive charge may be considered to be less highly concentrated, or dispersed over a larger region. This is due to the stretching of the C-S bond prior to complete dissociation.

the structure of the transition state may be depicted as



Since decreasing the dielectric constant of the medium would be expected to increase the activity of an ion with a more highly dispersed charge proportionately less than that of an ion with a more concentrated charge, the increase in the reaction rate is accounted for. The same arguments would apply equally well to an  $S_N1$  decomposition of a benzenediazonium cation, with the transition state



They would be consistent with the increase in rate of decomposition of benzenediazonium chloride in ethanol solution to which increasing amounts of ether are added.<sup>2</sup>

However, dielectric constant of the medium is not the only determining factor in the rate of decomposition. Methanol has a higher dielectric constant than acetic acid, but its diazonium salt solutions also have a higher rate of decomposition. It is suggested that part of the explanation may lie in differing degrees of solvation of the diazonium ion by the different hydroxylic solvents.

An expected consequence of the  $S_N1$  mechanism is that the formation of the final products should be nonselective with respect to composition of a mixed solvent. Since

the phenyl cation formed in the rate-determining step (Equation 12) is extremely unstable and reactive, it should combine with virtually the first solvent molecule with which it collides. Thus a solution of benzenediazonium chloride in an equimolar mixture of methanol and water would be expected to yield equimolar amounts of phenol and anisole (disregarding side reactions). This prediction has been roughly confirmed (see Experimental Part).

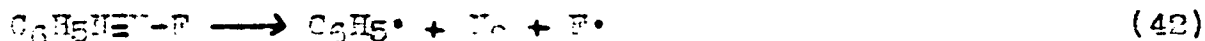
If the rate-determining step were a nucleophilic displacement by a solvent molecule, then the product of the reaction with methanol would be expected to exceed the product of the reaction with water, in about a two-to-one ratio, since this is the approximate ratio of the specific reaction rates in the pure solvents. (See Table 1)

The prediction that the rate of decomposition should be independent of the anion in the benzenediazonium salt has been tested and found to be valid. Benzenediazonium chloride and benzenediazonium fluoborate decompose in methanol at practically an identical rate. In the case of the latter compound, the only way in which the covalent intermediate necessary for the production of free radicals could be formed is by the reaction,



In view of the known stability of the fluoborate ion, such a reaction appears to be unlikely. Even if it occurred rapidly and were followed by a rate-determining

step,



the latter reaction would hardly be expected to proceed at the same rate as the decomposition of a covalent benzenediazo chloride. The bond energies for the two different nitrogen-halogen bonds whose rupture would be involved differ by over 30 Kcal/mole.<sup>21</sup> This single experimental observation, therefore, constitutes very strong evidence that the decomposition in alcohols is a reaction of the diazonium ion and not of a covalent diazo structure.

It was thought advisable to compare the effect of substituents in the benzene ring on the rate of decomposition in water solutions with the effect on the rates in other hydroxylic solvents. Unfortunately, many substituents promote the side reaction with alcohols



at the expense of ether formation.<sup>22</sup> In general, this effect seems to be strongest with those substituents which have the greatest retarding effect on the decomposition in water. A series of experiments was therefore performed in acetic acid, which gives exclusively the desired type of reaction. It was found that p-methyl and p-chloro substituents in benzenediazonium chloride decrease the rate of decomposition in that order, which parallels the order found in water solution. This order is anomalous,

when compared with the order of effects on other common reactions of benzene derivatives (see Table 2). This result is in agreement with the assumption that decomposition in the two solvents proceeds by the same mechanism.

Table 3 lists the results of rate measurements made in this laboratory, together with pertinent results of other workers.

Table 3

<u>Salt</u>	<u>Solvent</u>	<u>Temp.</u>	<u><math>k \times 10^4</math> (sec<sup>-1</sup>)</u>
$C_6H_5NaCl$	$CH_3COH$	30°	0.08
"	"	"	0.05 <sup>2</sup>
$C_6H_5NaBF_4$	"	"	2.03
$C_6H_5NaCl$	$CH_3CO_2H$	"	0.04
"	"	"	0.79 <sup>2</sup>
"	"	50°	10.3
"	"	"	11.4 <sup>2</sup>
"	$H_2O$	"	15.5 <sup>2</sup>
$p-ClC_6H_4NaCl$	$CH_3CO_2H$	"	1.40
"	$H_2O$	"	1.75 <sup>3</sup>
$p-ClC_6H_4NaBF_4$	$CH_3CO_2H$	"	0.017
$p-ClC_6H_4NaCl$	$H_2O$	"	0.045 <sup>3</sup>

An attempt will now be made to show that the qualitative effect of the nature and position of the common substituents can be harmonized with the  $S_N1$  mechanism. From a consideration of the reactions correlated by Hammett<sup>8</sup> it can be deduced that those reactions which involve electrophilic attack on the benzene derivative by a reagent are accelerated by electron-releasing substituents (high  $\sigma$  values) and retarded by electron-withdrawing substituents (low  $\sigma$  values). For such reactions, the sign of the reaction series constant,  $\rho$ , in Equation 6 is negative. A few examples taken at random are the reaction of ethyl iodide with substituted phenolates, the reaction of methyl iodide with substituted dimethylanilines, and the reaction of dinitrochlorobenzene with substituted anilines. In all such reactions, the mechanism of the rate-determining step is such as to be facilitated by an increased availability of electrons at the point of attack by the reagent. Correspondingly, the reaction is hindered by a decreased availability of electrons brought about by the presence of electron-withdrawing substituents in the ring.

In the decomposition of the diazonium ion by an  $S_N1$  mechanism, the C-N bond undergoes unsymmetrical fission, and the nitrogen atom takes both electrons with it. One would expect this process to be facilitated by



the presence of electron-releasing substituents in the ring and hindered by electron-withdrawing substituents. An examination of the meta-substituents listed in Table 2 shows that their order of retarding effect on the decomposition parallels the order of increasing  $\sigma$ , which is also the order of increasing electron-withdrawing effect.

In the meta-substituted benzenediazonium ions, the substituent exerts a purely inductive effect. The anomalous order observed for the para-substituents leads one to suspect that a strong mesomeric or resonance effect may be operating in some of these cases. If the diazonium ion were strongly stabilized by resonance, it could be expected to require a greater activation energy to bring about its decomposition. "Good" resonance structures can be written for the diazonium ion in the case of four of the para-substituents listed in Table 2. These four are (a) p-CH<sub>3</sub>, (b) p-C<sub>6</sub>H<sub>5</sub>, (c) p-Cl, and (d) p-OCCH<sub>3</sub>. The resonance structures (aside from the principal Kekule forms,  $\text{X}-\text{C}_6\text{H}_4-\text{N}^+=\text{N}$  and  $\text{X}-\text{C}_6\text{H}_4-\text{N}^+=\text{N}$ ) in each case) are: (a)  $\text{H}-\text{C}^+=\text{C}_6\text{H}_4-\text{N}^+=\text{N}$  and two similar hyperconjugated structures; (b)  $\text{C}_6\text{H}_5^+=\text{C}_6\text{H}_4-\text{N}^+=\text{N}$  and two similar structures involving an open sextet of electrons in the para and the other ortho position of the C<sub>6</sub>H<sub>5</sub>

group; (c)  $\text{Cl}-\text{C}_6\text{H}_4=\text{N}^+=\text{N}^-$  and (d)  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4=\text{N}^+=\text{N}^-$ .

It is worthy of note that all four of these substituents are associated with a lower rate of decomposition when they are in the para-position than when they are in the meta-position, although the relative  $\sigma$  values would tend to place them in the reverse order. In p-methoxybenzene-diazonium ion, the resonance effect is so strong that this compound has the lowest decomposition rate of any of those considered, whereas the inductive effect of the p-methoxy group as measured by its  $\sigma$  value, if uncomplicated by the resonance effect, would tend to place it at the top of the list.

With  $\text{CO}_2\text{H}$  and  $\text{NO}_2$  substituted in the para-position, resonance structures analogous to the above cannot be written. In the carboxyl compounds, the effect of a change of the substituent from the meta- to the para-position parallels the order of increasing  $\sigma$  values, as expected. In the nitro compounds the order is the reverse. Perhaps the anomalous effect of the p- $\text{NO}_2$  group can be explained by the assumption that its mesomeric effect is strong enough to increase the stability of the resonance structure

$$\text{O}^--\text{N}^+=\text{C}_6\text{H}_4=\text{N}^+=\text{N}^+$$

to a significant degree. Normally, structures of this type are not favored because of the presence of like charges on adjacent atoms.

Let us consider the two remaining substituents

whose effects on aqueous diazonium salt decompositions have been studied by Crossley, Kienle and Benbrook,<sup>3</sup> but which are not included in Hammett's table of  $\sigma$  values. The meta-hydroxyl group causes a faster rate of decomposition than any of the other substituents studied, which would place it ahead of meta-methoxyl in Table 2. Para-hydroxyl, on the other hand, would come just ahead of meta-nitro, near the bottom of the list. This may be associated with the fact that para-hydroxy-benzenediazonium ion resonates between structures analogous to those of the methoxy compound. M-SO<sub>3</sub>H lies between m-CO<sub>2</sub>H and p-CO<sub>2</sub>H in its effect, and p-SO<sub>3</sub>H lies between p-CH<sub>3</sub> and p-C<sub>6</sub>H<sub>5</sub>. The sulfonic acid group, which would not be expected to exert a resonance effect, is therefore quite analogous to the carboxyl group in its effect.

To summarize the arguments in favor of the S<sub>N</sub>1 mechanism for the decomposition of diazonium salts in hydroxylic solvents:

- (a) It explains the first-order kinetics observed.
- (b) It is compatible with the comparatively slight differences in rate observed between the various solvents.
- (c) It explains the independence of rate on the nature of the anion.
- (d) It explains the independence of rate on the concentration of the anion.
- (e) It explains the non-selectivity both in rate

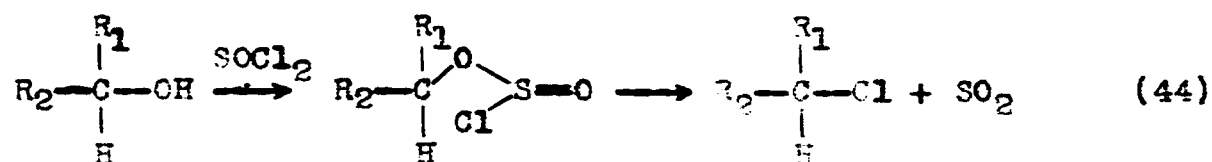
and in composition of products with respect to composition of mixed solvents.

(f) It explains the slight increase in rate accompanying decrease in polarity of the reaction medium on addition of an inert solvent.

(g) It explains many of the effects of the nature and position of substituents in the benzene ring.

Against these favorable arguments must be set the objection that it involves the assumption of an intermediate carbonium ion of relatively high energy. The author believes that the preponderance of evidence forces us to accept this assumption as valid.

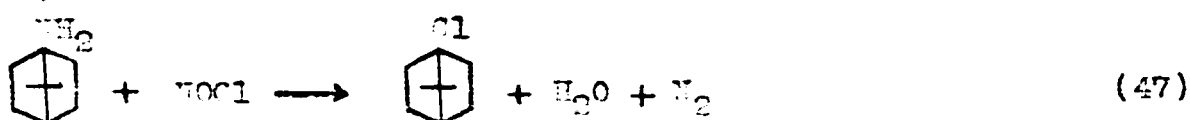
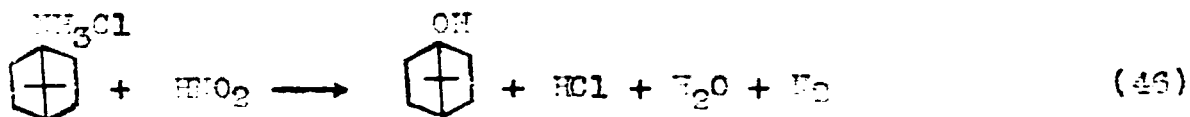
4) The fourth possibility is the internal nucleophilic displacement, or  $S_N1$  mechanism of Hughes and Ingold.<sup>13</sup> Only a few accepted examples of this mechanism are known, and of these the essential details are little understood. The original example is the replacement of the hydroxyl group in an alcohol by chlorine through the action of thionyl chloride in the absence of pyridine:



The second step, involving the unimolecular decomposition of a chlorosulfite, is said to proceed by an  $S_N1$  mechanism. If the alcohol is optically active, its configuration is retained in the final product. This



type bear a close resemblance to some of the reactions of diazonium salts. They are the reaction of 1-amino-apocamphane hydrochloride with nitrous acid to form apocamphanol-1 and of the free amino compound with nitrosyl chloride to form 1-chloroapocamphane.



The first of these reactions is carried out in water solution at 80°, and the second in ether solution at -10°. As the authors point out, the possibility of a mechanism involving nucleophilic attack by H<sub>2</sub>O or HNOCl is ruled out by the structure of the carbon skeleton in these compounds. It is sterically impossible for an attacking molecule to approach the 1-C atom from the rear, as is required by the S<sub>N</sub>2 mechanism.

It was found impossible to displace either the hydroxyl group or the chlorine atom in the products of these reactions, even by the most drastic means. This fact was interpreted by the authors to mean that not only the S<sub>N</sub>2, but also the S<sub>N</sub>1 type of reaction is prevented by the peculiar structure of these compounds. The latter conclusion is justified by the fact that a carbonium ion intermediate in the S<sub>N</sub>1 reaction would be

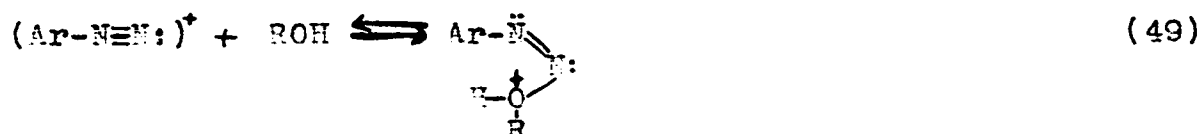
incapable of assuming the planar configuration necessary for resonance stabilization, due to the large amount of strain which would thereby be set up in the bridged ring system. The authors extend this reasoning to apply also to the reactions by which apocamphanol-1 and 1-chloro-apocamphane are formed. Thus they rule out as improbable the sequence of reactions:



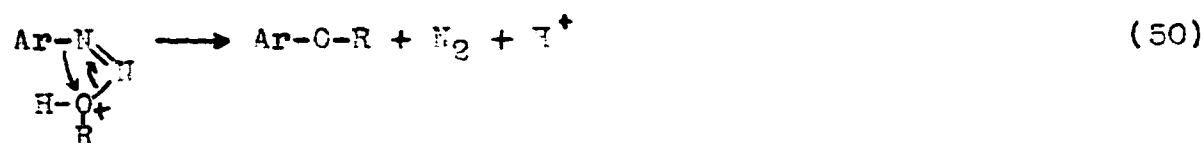
or a similar one for the reaction with nitrosyl chloride. They therefore conclude that the mechanism is probably an internal one, involving the decomposition of some unspecified intermediate in each case. Their objection to the  $\text{S}_{\text{N}}1$  mechanism on the basis of the instability of a non-planar carbonium ion applies equally well to the assumption of an aryl cation intermediate in the diazonium salt decompositions. On the other hand, if this objection can be considered to have been removed by the arguments presented in this paper, then the possibility of an  $\text{S}_{\text{N}}1$  mechanism involving an apocamphyl positive ion still remains open.

An  $\text{S}_{\text{N}}1$  mechanism for the aromatic diazonium salt decompositions in alcoholic solutions would necessitate the formation of an intermediate addition product from the diazonium ion and the solvent. The most probable structure of such an intermediate would be that of the

conjugate acid of a diazo ether. It seems likely that such a reaction would be reversible:

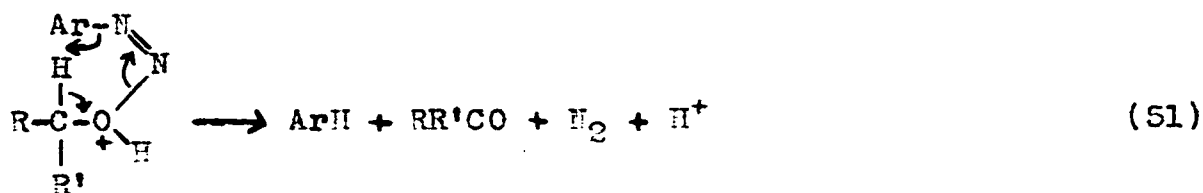


The rate-determining step then might be the decomposition of this complex by an internal mechanism involving electron shifts as follows:



This mechanism is subject to the objections that the ease of formation of the intermediate complex, and also its rate of decomposition, would be expected to vary markedly with the nature of the alcohol.

If ROH is a primary or secondary alcohol, a different mechanism involving a six-membered cyclic ring for the transition state becomes possible. A cyclic shift of three electron pairs could then occur, leading to the formation of an aromatic hydrocarbon, an aldehyde or ketone, and nitrogen.



This mechanism is similar to the one suggested as the explanation for the production of hydrogen chloride, propylene and carbon dioxide in the decomposition of isopropyl chlorocarbonate (Equation 45). It is suggested



by the author as a possible explanation for the well-known deamination reaction with ethyl alcohol, which may compete with successfully or totally override the reaction resulting in ether formation in cases where the  $S_N1$  decomposition of the diazonium ion is slow.

III

EXPERIMENTAL PART

## III

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Experiment 1 Decomposition of Benzenediazonium Chloride  
in a Methanol-Water Solution.

25.9 gm. (.278 mole) of freshly distilled aniline were dissolved in a solution of 116 ml. 6N hydrochloric acid and 100 ml. water. This was cooled in an ice-salt bath and diazotized with a solution of 19.2 gm. (.278 mole) sodium nitrite in 30 ml. water. Addition was carried out at such a rate that the temperature of the reaction mixture did not exceed 5°C, and required 30 minutes. Upon completion of the diazotization as determined by a starch-iodide test, the solution was poured into 412 gm. (12.85 moles) of methanol, an amount equivalent to the water used in and produced by the diazotization reaction. The mixture was then allowed to stand at room temperature (28° to 29°C) for 20 hours. At the end of this time it was made alkaline with an excess of 6N sodium hydroxide. The mixture was then distilled to remove methanol through a column packed with glass helices, until the distillation temperature reached 64.5°, at which time the reflux began to separate into two phases.

The residue was extracted with ether and the ether

solution was dried with anhydrous magnesium sulfate. After distilling off the ether at atmospheric pressure, the residue was distilled at reduced pressure from a modified Claisen flask with a fractionating side arm. The fraction distilling from 70° to 95° at 40mm., consisting chiefly of anisole, was collected and weighed. It amounted to 8.35 gm. (.077 mole), or a 28% yield, based on the total amount of aniline used. A second cut, consisting of impure phenol which did not crystallize completely, distilled at 98° to 103° and weighed 2.4 gm.

The alkaline water layer was acidified to Congo Red with sulfuric acid and extracted with ether. Upon treatment similar to the above, this ether extract yielded 5.5 gm. of phenol, distilling from 97° to 98° at 40 mm. The total amount of phenol, 7.9 gm. (.084 mole) represents a 30% yield, based on total aniline.

Remarks: While the yields obtained leave something to be desired, probably on account of the method of separation used, the amounts of phenol and anisole formed are apparently roughly equivalent.

The remaining experiments were reaction rate measurements carried out on decomposing solutions of diazonium salts in methanol and acetic acid solutions. The reactions were followed by measuring the evolution of nitrogen in a mercury-filled gas buret. The reacting

solution was contained in a cylindrical flask which was surrounded by a jacket through which water from a thermostat was circulated. After leaving this jacket the water was passed through a jacket around the gas buret before returning to the thermostat. The reaction flask was mounted in a shaking machine to eliminate supersaturation effects which are otherwise large.

In the runs at 50° the flask was wrapped with asbestos paper to reduce heat loss, so that the actual temperature of the reacting solution was 49.85°C, only .15° below the thermostat temperature. Temperature control was maintained within limits of  $\pm 0.02^\circ$  and checked by means of a Beckmann thermometer. This was set by comparison with a conventional thermometer calibrated against the ice point, steam point, and sodium sulfate transition point. Changes in atmospheric pressure during a run were compensated for in reading the volumes by means of a manometer connected with the system and with one arm open to the air.

Benzenediazonium chloride was prepared by the method of Smith and Varing.<sup>32</sup> This consists in diazotization by ethyl nitrite of aniline hydrochloride suspended in a one-to-one mixture of dioxane and acetic acid cooled in an ice-salt bath. The ethyl nitrite gas was generated in an apparatus similar to the one described by Semon and Damerell,<sup>33</sup> but on about one fourth the scale. The

aniline hydrochloride was purified from some very impure commercial material by dissolving in water, filtering, heating the filtrate with activated charcoal, filtering again, concentrating the solution by evaporation at reduced pressure while warming in a water bath, and crystallizing in an ice bath. Commercial dioxane was purified according to the instructions of Fieser,<sup>34</sup> except that the use of nitrogen gas was eliminated. The methanol and acetic acid were of a C.P. grade and were not subjected to further purification.

When the method of Smith and Waring<sup>32</sup> was applied to the preparation of para-toluenediazonium chloride, the yield was unsatisfactory, and a very much larger amount of anhydrous dioxane was required to precipitate the product from the reaction mixture. Nevertheless, a sufficient amount for one run was obtained.

Benzenediazonium fluoborate and para-chlorobenzene-diazonium fluoborate were prepared by the Organic Syntheses method,<sup>35</sup> using 40% commercial fluoboric acid to precipitate the salt.

The benzenediazonium chloride and para-toluenediazonium chloride were stored under dioxane in a refrigerator. Before use in an experiment, they were collected by suction filtration on a sintered crucible, washed with dry ether, and freed from ether in a vacuum desiccator. The benzenediazonium fluoborate and para-chlorobenzene-diazonium fluoborate were dried and stored in amber

screw-capped bottles for no more than two days before being used. Of these four substances, only benzene-diazonium chloride appears to be dangerously sensitive. An approximately one-gram amount was accidentally detonated by the author while scooping the dry substance up in a porcelain spatula preparatory to weighing. The porcelain crucible containing it was shattered into tiny pieces.

In Experiments 2 and 3, the procedure for starting the run was as follows: The dried, weighed benzene-diazonium salt (approximately .03 mole) was dissolved in the solvent (58 and 100 ml. of methanol resp.) and the solution was placed in the reaction flask. The shaking machine was started, and the zero of time was taken after three or four minutes. This was to allow the solution to come to thermal and vapor pressure equilibrium. In most of the succeeding experiments, in which calculations were based on the amount of starting material, the solvent (usually 50 ml.) was placed in the reaction flask and shaken for about 5 minutes, with the system vented to the atmosphere from the top of the buret. The diazonium salt was then introduced into the reaction flask from a weighed crucible, the system was immediately closed off and shaking was started. In the longer runs, the shaking machine was stopped between volume readings and started again about

five minutes before each reading.

The rate constants were determined by plotting  $1 - v_t/v_\infty$  against time in minutes on semi-logarithmic graph paper.  $v_\infty$ , the volume of nitrogen evolved when the reaction is essentially complete, was determined in the case of the benzenediazonium salts by allowing the reaction to proceed for about 20 hours before taking the final reading. Since the yield of nitrogen in Experiment 4 was 99.7% of the theoretical  $v_\infty$  was calculated for the succeeding experiments from the weight of diazonium salt, with satisfactory results. In Experiment 10,  $v_\infty$  was checked by passing steam through the jacket of the reaction flask until the volume (under excess pressure) reached a constant value. The system was then brought back to thermostat temperature, and the final volume was noted. It amounted to 97.2% of the calculated value. In Experiments 2, 3, 6 and 7, the points fell on a good straight line for the first 75 to 95% of the reaction. In the other runs, which were slower, experimental points were obtained up to 30 to 50% completion of the reaction. From the slope of the straight lines, the specific reaction rates were calculated by the equation

$$k = -\frac{2.303}{60} \frac{d}{dt} \log \left( 1 - \frac{v_t}{v_\infty} \right)$$

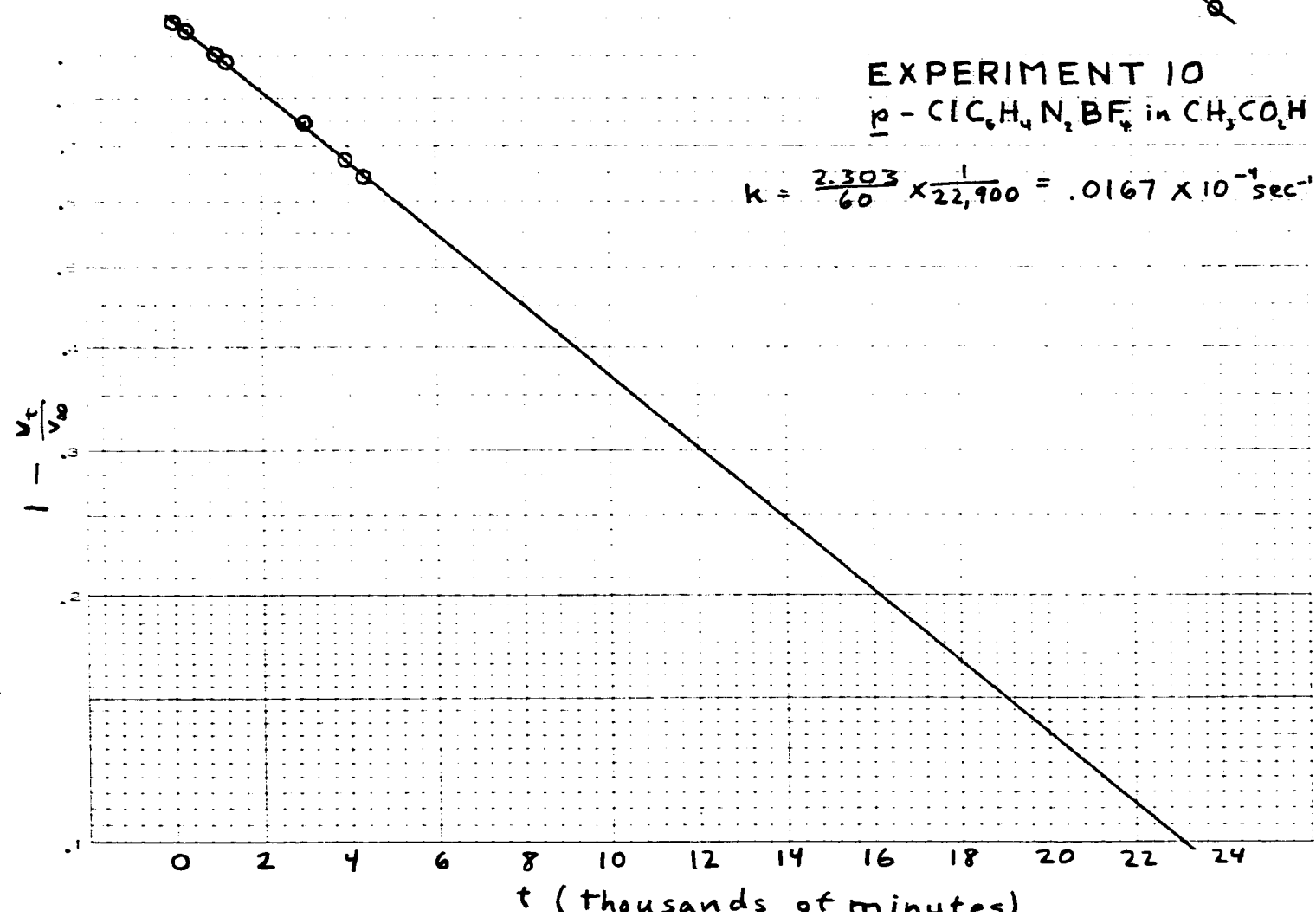
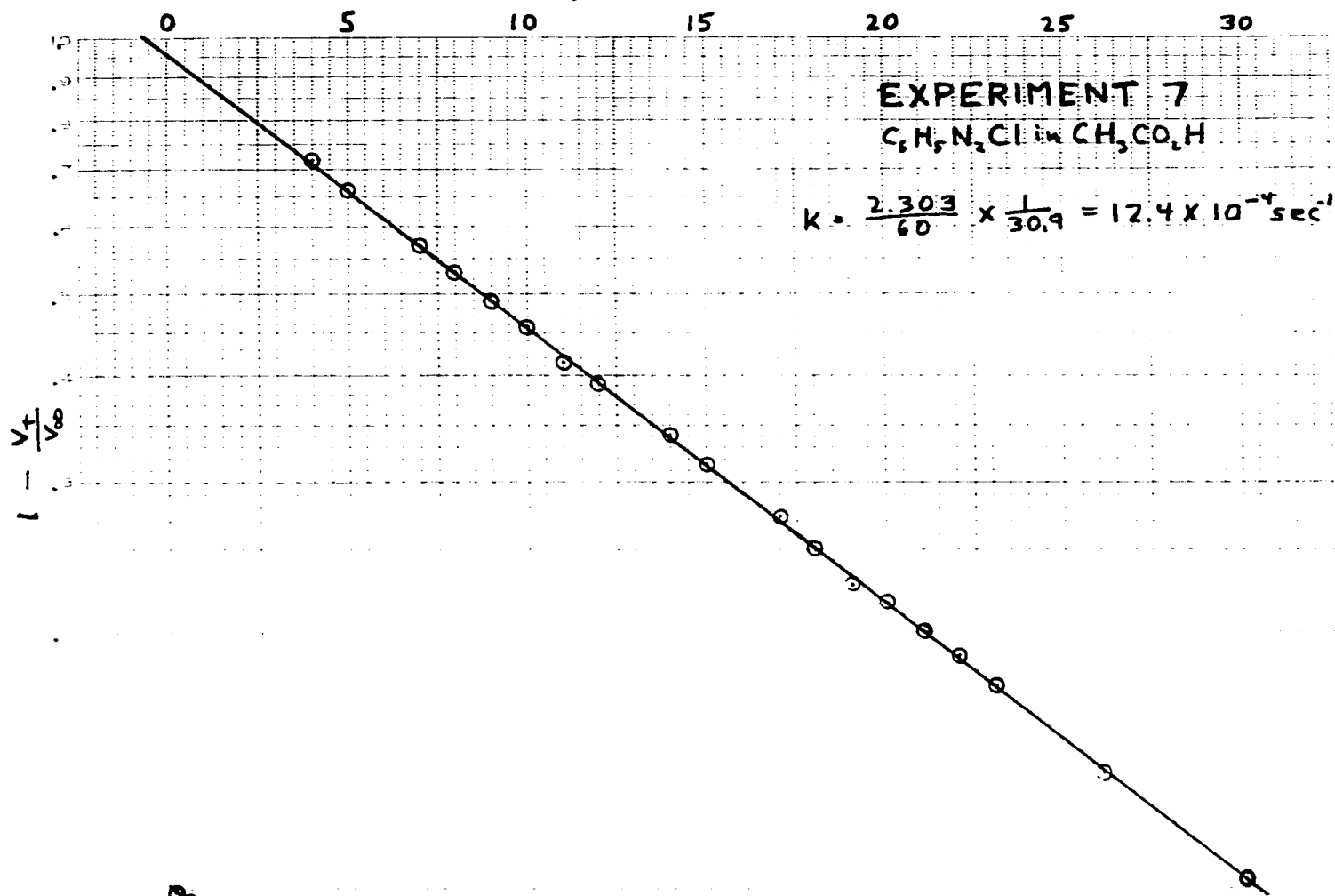
Sample graphs to illustrate the method are included.



## SUMMARY OF RESULTS

<u>Experiment</u>	<u>Salt</u>	<u>Solvent</u>	<u>Temp.</u>	<u><math>k \times 10^4</math> (sec<sup>-1</sup>)</u>
2	$C_6H_5N_2Cl$	$CH_3OH$	$30^\circ$	2.08
3	$C_6H_5N_2BF_4$	"	"	2.03
4	$C_6H_5N_2Cl$	$CH_3CO_2H$	"	.86
5	"	"	"	.83
6	"	"	$50^\circ$	12.1
7	"	"	"	12.4
8	$p\text{-}CH_3C_6H_4N_2Cl$	"	"	1.42
9	$p\text{-}ClC_6H_4N_2BF_4$	"	"	.0171
10	"	"	"	.0167

t (minutes)



IV

ACKNOWLEDGMENTS

## IV

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## V

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