

THE STOICHIOMETRY OF THE REACTION OF
BENZENEDIAZONIUM CHLORIDE WITH ETHANOL

by

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A Thesis Submitted to the faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
UNIVERSITY OF ARIZONA

1957



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ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. A. E. Kelley for his continual assistance and guidance throughout the course of this research.

AN ABSTRACT

In the reaction of benzenediazonium chloride with ethanol it is generally agreed that the main product formed is phenetole. However some discrepancy has been reported as to the amount of oxidation-reduction taking place. Some workers have reported 10% yields of the oxidation product, acetaldehyde, while others find only 3% of the reduction product, benzene. For the reaction to proceed stoichiometrically they should be formed in equivalent amounts.

By kinetics studies and analysis of the products of the reaction, it was found that benzene and acetaldehyde are formed in equivalent amounts, generally about 3%. The benzene was determined spectrophotometrically, and the acetaldehyde gravimetrically as the 2,4-dinitrophenylhydrazone. When oxygen was added to the ethanol, the products were still found in approximately equivalent amounts, and the kinetics were the same. With the effect of higher temperatures upon the amount of aldehyde, only minor differences were noted.

The experimental results indicate that the oxidation-reduction portion of the reaction proceeds stoichiometrically according to the equation



and that the reported 10% oxidation is in error, probably due to impurities in the diazonium salt in those instances.

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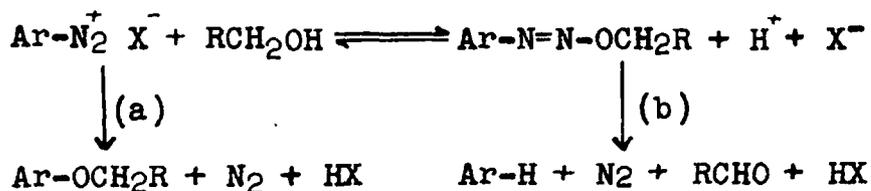
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INTRODUCTION

The reaction of diazonium salts with ethanol has been the cause of much disagreement. In 1864 Griess (1) found benzene and acetaldehyde as the products of the reaction of benzenediazonium nitrate or sulfate with ethanol. This reaction came to be used as a means for replacement of the diazonium group by hydrogen, even though evidence appeared soon afterwards that the diazonium group was replaced by the ether grouping.

In 1887 Remsen and Orndorff (2) showed Griess to be in error by explaining that the reaction actually gave mostly phenetole contaminated with a little benzene. Hantzsch and Jochem (3) in 1901 using benzenediazonium chloride with ethanol confirmed the findings of Remsen and Orndorff, but the oxidation-reduction reaction was still given by some authors as the principal course of the reaction even as late as 1949.

It is now thought that the reaction follows the scheme



with process (a) proceeding through an S_N2 displacement of the diazonium group, while (b) involves a homolytic fission of the bonds to produce radicals which lead ultimately to the hydrocarbon and aldehyde. The position of the equilibrium varies; a diazonium salt with an inorganic acid shifts the equilibrium to the ionic side, whereas an acetate anion, by decreasing the acidity, displaces it toward the covalent form.

In 1930 Hodgson and Kershaw (4), using benzenediazonium sulfate with ethanol, found a 9.3-9.5% yield of acetaldehyde, measured as the p-nitrophenylhydrazone derivative. Huisgen and Nakaten (5) confirmed the results of Hodgson and Kershaw by using benzenediazonium chloride with ethanol and measuring the acetaldehyde formed as either the 2,4-dinitrophenylhydrazone or 4-nitrophenylhydrazone, finding 9.5-11% of the oxidation product. However, A. E. Kelley (6) in 1956, using benzenediazonium chloride with ethanol, found only 3% reduction by measuring the ultraviolet spectrum of benzene with a Cary Automatic Recording Spectrophotometer.

According to the stoichiometry of the reaction the amount of the reduction product, benzene, should equal the amount of oxidation product, acetaldehyde. Several possibilities could account for the discrepancy between the above observations:

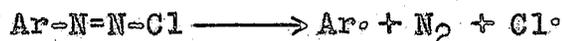
(a) Some of the benzene formed could be used up

in the formation of biaryls or aze compounds, thus lowering the benzene yield:

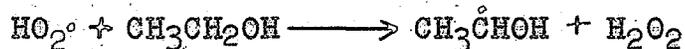


- (b) Acetaldehyde may be formed by alternative reactions such as air oxidation, or in free radical chain reactions where benzene is produced only in the initial step.

Initiation



Propagation



Etc.

Although the reaction has been repeatedly shown to be of first order, Hodgson and Kershaw did not run kinetics on the reaction from which they separated their aldehyde. They merely mixed the two reactants together and "warmed the mixture". Huisgen and Nakaten ran kinetics on their reactions, and found them to be of first order, but they ran no kinetics on the mixture from which they precipitated the aldehyde, and only mentioned that they were mixed at room temperature. Kelley measured his benzene on the same reactions in which he determined first order kinetics.

The purpose of this research is to measure both the acetaldehyde and benzene, as well as other products of the reaction between benzenediazonium chloride and ethanol, while the kinetics is followed by the evolution of nitrogen. The reaction can also be run at several temperatures to see if a variation in temperature might be connected with the higher yields of acetaldehyde. The reaction can then be run either under an atmosphere of nitrogen or in the presence of oxygen, depending on which seems more relevant to the initial results observed.

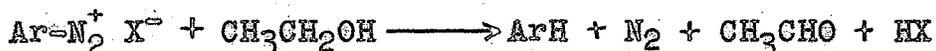
DISCUSSION

The kinetic results of the reaction of benzene-diazonium chloride with ethanol are reported in Table 1. It should be noted that the rate constants at 25° and 30° agree very well with the results of Kelley (6) who found

<u>Temp.</u>	<u>K x 10⁴ sec.⁻¹</u>
25.15°	0.96, 0.95
30°	2.03

and Pray (7), who found a rate constant of 2.05×10^{-4} sec.⁻¹ at 30°. It should also be noted in Table I the results of the kinetics at 30.1°, one reaction with oxygen present and the other without, agree very well, showing that the oxygen added had no measurable effect on the rate of the reaction.

The experimental results also agree with Kelley as to the amount of benzene found at 25°, and also showed that the amount of acetaldehyde was generally equivalent to the amount of benzene. This being true indicates that the reaction does proceed stoichiometrically according to the equation



Huisgen and Nakaten (5) reported a 9.5-11.0% reduction to take place, as measured by the amount of aldehyde produced at "room temperature". The experimental results of approximately 3.0% acetaldehyde found in this

research is in disagreement with their results. Since all precautions were taken to exclude oxygen from all our reagents and reaction, a possible source of the discrepancy could have been due to their allowing some oxygen to enter their system. Running the reaction after first introducing oxygen into our ethanol, we again found the 3% yield.

As an alternative explanation of their 10% yield of aldehyde, it should be pointed out that in their description of the preparation of their diazonium salt, they first obtained an oil which they crystallized and then reprecipitated from ethanol to get a salt of "95% activity". The diazonium salt used in this work was obtained as a crystalline compound, which according to the nitrogen evolved, was of approximate 100% purity. The actual amount of nitrogen was continually found to be around 98%, but upon addition of the ethanol to the diazonium salt the system was open to the atmosphere for approximately 1 minute and this could easily involve a 2% loss of nitrogen. It is believed that their impure diazonium salt caused their high determination of aldehyde.

Since Hodgson and Kershaw obtained a high yield of acetaldehyde by "warming the mixture", a reaction was run at 70°. The results as shown in Table I do not agree with their findings. The same explanation of the diazonium salt being impure may be offered, but it should be pointed out that their work was done on benzenediazonium hydrogen

sulfate, while this work was with the chloride salt.

Whereas Kelley found chlorobenzene present only in 0.1 - 0.4%, it should be noted that in this work it was found to be present in appreciably larger quantities.

TABLE I
RATE CONSTANTS AND THE YIELDS OF PRODUCTS IN THE
REACTION OF BENZENEDIAZONIUM CHLORIDE WITH ETHANOL
 concentration of diazonium salt 0.1 M

Reaction	Temp. in °C	K x 10 ⁴ in sec ⁻¹	Yield in % of Theoretical				
			ArH	ArCl	ArOEt	CH ₃ CHO	N ₂
3	25.1	0.97	2.9	2.9	84.3	2.1	97.4
1	30.1	1.98	3.5	2.4	81.8		
4 ^a	30.1	2.00	3.3	2.4	80.3	2.0	98.3
4 ^a	30.1	2.00	4.9	4.4	84.9	2.7	99.2
2	36.3	4.66	2.5	2.6	80.9	2.1	98.1
5	70	- ^b	4.8	5.5	76.5	3.2	-

a The ethanol was saturated with oxygen prior to mixing with the diazonium salt.

b Too fast to measure.

EXPERIMENTAL

Materials. The ether used was Mallinckrodt Analytical Reagent, one pound cans, freshly opened, which show a negative test for peroxides. The acetone was Baker's Analyzed Reagent meeting A.C.S. specifications. The ethanol was absolute, which was further purified by the process of Lund and Bjerrum (8a) to remove the water, then distilled under nitrogen, and the first 10% of distillate discarded. The purified ethanol was stored in glass stoppered bottles under an atmosphere of nitrogen. The dioxane was purified according to the procedure in Fieser's "Experiments in Organic Chemistry" (8b), and was kept in glass stoppered bottles under nitrogen.

The aniline used was E. and A. Tested Purity Reagent distilled through a modified Widmer column. Aniline hydrochloride was prepared by running freshly prepared anhydrous hydrogen chloride into an ether-aniline solution under a dry atmosphere. The aniline hydrochloride was filtered, washed with acetone and four times with ether, and stored in a vacuum desiccator overnight. Ethyl nitrite was prepared by the method in "Organic Synthesis" (9). The ethyl nitrite was not stored but passed directly into a flask containing aniline hydrochloride in a mixture of dioxane and acetic

acid* to prepare benzenediazonium chloride by the method of Smith and Waring (10). The diazonium salt was placed in test tubes (no more than 5 grams per tube) capped with two way stopcocks, and alternately evacuated and flushed with nitrogen. The material was then stored in a nitrogen atmosphere at Dry Ice temperature.

Apparatus. For runs 1-4 the apparatus used was a modification of that described by Cooper (11). The gas buret was jacketed, and in order to maintain it at the same temperature as the reaction vessel, water was circulated from the bath to the jacket. Since ethanol was used in the reaction vessel, it was also used in the gas buret to simplify the correction for vapor pressure.

For reaction 5 the apparatus consisted of a 300 ml. 3-neck round-bottom flask with ground glass joints. One neck contained a dropping funnel with pressure equalizing side arm, the center neck a cold finger condenser filled with a CHCl_3 - CCl_4 -Dry Ice mixture, and the third neck a ground glass stopper.

All spectra were taken on a Beckmann Model D.U. Spectrophotometer, in 3 matched 1 cm. silica cells.

Fractionations were done through a Todd column, and

*The dioxane and aniline-HCl were mixed first and then acetic acid added to prevent the formation of a large lump of solid.

final distillations were through a micro condenser.

Preparation of standard curves. Standard solutions of freshly distilled benzene, phenetole, and chlorobenzene were made and run on the Spectrophotometer, plotting the wave length as abscissa and absorbance as ordinate, at the various concentrations. A plot of absorbance versus concentrations at the wave lengths of the peaks gave linear results, indicating Beer's law is obeyed in the concentration range used.

Preparation of aldehyde reagent. Methone was tried as a possible reagent using the method of DeTar and Turetsky (12). Since no precipitate was obtained, various proportions of water, 2 N hydrochloric acid and ethanol were used to try to induce precipitation, and when this failed the use of methone was discarded.

Various mixtures of 2,4-dinitrophenylhydrazine were tried before a suitable reagent was found. The reagent was a 500 ml. solution of 1.25 g. of 2,4-dinitrophenylhydrazine, 85 ml. concentrated hydrochloric acid, and the remainder 24% ethanol. Adding 50 ml. (62.5×10^{-5} moles) of this reagent to 10 ml. of a known aldehyde solution, we obtained a precipitate weighing 0.0184 grams, a 92.0% recovery.

The known solution contained 0.250 ml. acetaldehyde, 0.100 ml. benzene, 0.250 ml. chlorobenzene, and 5.66 ml. phenetole, in enough ethanol to make a total of 500 ml.

These quantities correspond to our approximate expected yields of 8.9% acetaldehyde, 2.4% benzene, 4.9% chlorobenzene and 90% phenetole in 50 ml. For each determination a 10 ml. aliquot, containing 8.92×10^{-5} moles of aldehyde was used and compared to blank sample of 10 ml. absolute ethanol.

Since benzene forms an azeotrope with ethanol, it was known that in a fractionation the benzene would distill over in the first few milliliters, and to test the behavior of chlorobenzene and phenetole, a solution of 0.010 ml. chlorobenzene (equivalent to a yield of 1%) and 1.000 ml. phenetole (equivalent to an 80% yield) in 100 ml. ethanol was made. The solution was distilled through the Todd column and four 5 ml. portions, then two 10 ml. portions, were collected. It was found that the chlorobenzene came over entirely in the first four fractions and the phenetole in the last two. From another aliquot of the known solution four fractions were collected, then the remainder was distilled through the small distilling apparatus with ethylene glycol added as a chaser. All the phenetole was recovered here also.

Procedure for runs 1-4. The apparatus was set up and brought to the required temperature in a water bath at least two hours before it was to be used. The temperature variation was noted by a Beckmann thermometer, and recorded. The leveling bulb was adjusted so the alcohol in the buret

read zero when open to the atmosphere, and then closed off.

The diazonium salt was allowed to come to room temperature, then the desired sample removed and weighed in a glass stoppered weighing bottle. The tube containing the diazonium salt was placed in Dry Ice, evacuated with a vacuum pump for a few minutes, then alternately flushed with nitrogen and evacuated 10-15 times, and finally stored under an atmosphere of nitrogen at Dry Ice temperature until the next time it was to be used.

The 0.7028 g. (0.005 moles) samples of the diazonium salt were weighed on a magnetically damped chainomatic balance in order to minimize the time in which the compound was exposed to the air.

The salt in the weighing bottle was transferred to the reaction vessel by means of a special long-stemmed powder funnel. From the ethanol previously brought to the temperature of the water bath, 50 ml was pipetted into the reaction mixture. Mixing was accomplished by a magnetic stirrer while the alcohol was being added. The apparatus was open to the atmosphere for approximately one minute during this operation. The stopcock was then closed to the atmosphere and connected with the gas buret. The time when the stopcock was closed was taken as the zero time of the reaction. The time was followed by an electric clock with a sweep second hand. Readings were made with the

leveling bulb at the same level as the liquid in the buret and were taken at five minute intervals. The barometer was read at the zero time of the reaction and then approximately every hour afterwards. The readings on the gas buret of the nitrogen evolved were taken every 5 minutes until at least twice the half-time of the reaction was over. After this it was only necessary to take scattered readings until the amount of nitrogen evolved remained constant, showing the reaction to be complete.

In all the reactions run, the amount of nitrogen evolved would exceed the 100 ml. limit of the gas buret, so it was necessary to refill the buret. The volume of gas was allowed to reach the 100 ml. mark exactly. At this point the stopcock was turned to open the buret to the atmosphere, and at the same time close off the reaction vessel. Very quickly the level in the buret was adjusted to zero by manipulating the leveling bulb, at which time the stopcock was turned back to close off the atmosphere, and reopen the reaction vessel.

When the reaction was over the stirring was stopped and the reaction flask removed from the bath. The contents of the flask were emptied into a 50 ml. volumetric flask. It was necessary to add less than 1 ml. of 95% ethanol to the flask to bring it to a total of 50 ml.

Calculations; conversion to S.T.P. The total volume of the

reaction vessel was 210 ml. Since 50 ml. of ethanol was used in the reaction, the gas volume was only 160 ml. During the time of the reaction when the atmospheric pressure has remained constant, the volume at standard conditions is calculated from

$$\text{Vol. STP} = \text{Vol. obs.} \times F_0$$

$$\text{where } F_0 = \frac{AP_0 - VP_{\text{EtOH}}}{760} \times \frac{273.18}{T}$$

and AP_0 is the atmospheric pressure at zero time, VP_{EtOH} is the vapor pressure of ethanol at the temperature of the apparatus, and T is the temperature in degrees absolute.

After the atmospheric pressure changed to AP_1 , then

$$\text{Vol. STP} = (\text{Vol. obs.} + 160) F_1 - (160 \times F_0)$$

$$\text{where } F_1 = \frac{AP_1 - VP_{\text{EtOH}}}{760} \times \frac{273.18}{T}$$

When the volume of gas in the buret reached 100 ml. and was then emptied, at an atmospheric pressure of AP_e , any change in atmospheric pressure after this time requires the calculation

$$\text{Vol. STP} = (\text{Vol. obs.} + 160) F_1 + (100 \times F_e) - (160 \times F_0)$$

where F_e = the correction factor at any particular subsequent atmospheric pressure.

Calculations of kinetics. Knowing the reaction to be first order, the Guggenheim (13) method was used. The time interval was always taken as at least twice the half-time of the

reaction. A plot of $\log (V_t - V_{t-\Delta})$ vs. time in minutes gives a straight line with a slope equal to $-\frac{K}{2.303}$

Analysis of the products. Of the 50 ml. of the reaction mixture, 20 ml. were pipetted out and diluted to 50 ml. with 95% ethanol. This 50 ml. was distilled through the Todd column. Four 5 ml. portions were obtained and then two 10 ml. portions. The column was shut off and allowed to cool and drain for 1-2 hours. The pot residue was then transferred to a 50 ml. flask, 20 ml. ethylene glycol was added, and upon distillation through the small distillation apparatus, 10 ml. fractions were collected. The various fractions were diluted, if necessary, and run on the spectrophotometer.

All the benzene and chlorobenzene were found in the first four 5 ml. fractions; however small amounts of phenetole appeared in these fractions also. Phenetole absorbs at 278 and 271 millimicrons, chlorobenzene at 271, 264 and 257 millimicrons, and benzene at 260.5, 254.3 and 248.5 millimicrons. At 278, where phenetole has a peak, there is no absorbance due to benzene or chlorobenzene. At 271 both phenetole and chlorobenzene have peaks, but there is no absorbance due to benzene. At 248.5, where benzene has a high peak, there is no interference from phenetole and a very small absorbance from chlorobenzene.

In a determination, readings on the spectrophoto-

meter were taken starting at 300 millimicrons to determine background, down to about 230, where ethanol starts to absorb. Any background, if present, was then subtracted from the reading observed at 278, the difference being representative of the concentration of phenetole. The absorbance at 271 by this amount of phenetole was found and subtracted from the reading at 271, the resulting difference being due to chlorobenzene. The absorbance of this amount of chlorobenzene was found at 248.5, and subtracted from the reading at 248.5, the difference being due to benzene.

Fractions 5, 6, and 7 contained only phenetole, and the concentration was found from the absorbance at 271, its highest peak.

The readings on all samples were plotted to be certain there were no extraneous unexpected materials present.

Each acetaldehyde determination was run in duplicate together with a blank. In a 50 ml. ground glass stoppered erlenmeyer flask was placed 10 ml. of the reaction mixture, and in a third, 10 ml. of absolute ethanol. To each of the flasks was added 50 ml. of the reagent. The flasks were allowed to stand for 24 hours with occasional scratching to induce precipitation. At the end of this time the flasks were placed in an ice-salt bath for one hour. No precipitate was ever found to form in the blanks. The solutions were then filtered under suction into sintered

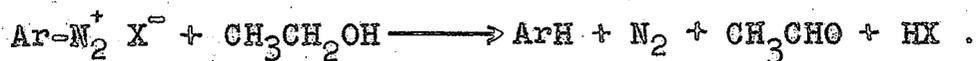
glass crucibles, and the precipitates washed with water. The crucibles were then dried overnight in an oven at 105° , and then for 2 hour intervals until they reached constant weight.

Introduction of Oxygen. The ethanol used in reaction 4 was the purified ethanol into which oxygen (dry) had been passed through a gas dispersion disk for 30 minutes. In all other respects the procedure was the same.

Reaction 5. The apparatus has already been described. The 50 ml. purified ethanol at 70° was added to 0.005 mole diazonium salt and the resulting solution was maintained at a temperature of 70° . There was no reason for stirring as the reaction proceeded quite well by itself. After 20 minutes the reaction had stopped, and the flask was allowed to cool to room temperature. The same determinations were carried out as in all the other reactions.

SUMMARY

By running kinetics and analyzing both the acetaldehyde and benzene formed in the reaction between benzenediazonium chloride and ethanol, the results obtained indicate that not all the earlier workers were correct. These results confirmed the 3% yield of benzene at 25° as reported by Kelley, and showed by the yield of acetaldehyde being no greater than that of benzene in each case that the two are formed in equivalent amounts. The possibility of oxygen increasing the yield of acetaldehyde and not benzene was shown to be improbable when the ethanol saturated with oxygen had no effect on the kinetics, and no increase in the amount of acetaldehyde found. The effect of higher temperatures on the amount of aldehyde was tried, but there were only minor differences. Thus the experimental results seem to indicate that the oxidation-reduction portion of the reaction proceeds stoichiometrically according to the equation



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