THE STUDY OF THE BROMINATION OF BENZENE

A Thesis
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Historical

In the bromination of benzene it has long been known that the reaction proceeds slowly even in sunlight, but that when a halogen carrier is present, the reaction is more rapid.

Numerous qualitative studies made by Aronheum[1], A. Page[2], Schenfelen[3], Gustavson[4], and Willgerodt[5], proved that of the Elements Molybdenum, Iron and Aluminium were the more energetic halogen carriers. It was supposed that an intermediate unstable addition product was formed between the hydrocarbon and the halogen carrier which was easily broken up by the addition of halogens into the halogen acids and a substituted hydrocarbon.

Bruner[6] was the first to make a quantitative study of the bromination of benzene. A soluble halogen carrier iodine bromide was used, although series were run with ferric chloride, aluminium chloride and ferrous bromide. The concentration of halogen and halogen carriers were extremely small.

With iodine bromide as halogen carrier, Bruner pointed out that the reaction in regard to bromine was probably of the fourth order, and expressed the possible reaction by the following equation:

$$C_6H_6 + 2\ Br_2 = C_6H_5Br + HBr_3 = C_6H_6Br + HBr + Br_2.$$

Considering the reaction as belonging to the first order, his constants varied greatly, but as a second order reaction the results obtained were constant.

Bruner maintains that nucleus substitution is effected by halogen atoms or ions which result from the dissociation of the halogen molecules. The velocity measurements of Bruner and Dluska favor this hypothesis, since nucleus substitution processes apparently take place according to the requirements of the equation for a unimolecular change, if the concentration of the bromine is small. For higher concentrations of bromine the values obtained for the unimolecular constant decrease as the reaction proceeds. This is attributed to the removal of the active bromine from the solution by the formation of a perbromide (HBr_3).

Bruner's idea that nucleus substitution is due to ionic bromine is also maintained by Bancroft[7], who further assumes that nuclear substitution occurs when negative bromine ions are present in excess of the positive bromine ions.

Holleman[8], assumes that nucleus substitution is brought about by a perbromide HBr_n. The formation of these polyhalogen compounds is actually favored by low temperature and increasing concentration of solution, and these are the conditions which also favor nucleus substitution.

Slator[9], has the following criticism of Bruner's results in the experiments where iodine bromide was used as halogen carrier. "There was an abrupt change in the velocity of the reaction, which was entirely disregarded when the final calculations were made. Hydrobromic acid was liberated in the course of the reaction and Bruner in consequence had a mixture of bromine and hydrobromic acid as the brominating agent. Besides that, he did not consider the amount of bromine combined with iodine, although he afterwards pointed out that iodine bromide reacts but slowly. Probably Bruner measured a delayed reaction of the first order,and because of the many complications not considered, secured results that agreed very well with a second order reaction. It is evident that reactions carried out in this way are much too complicated to determine accurately their proper order. The simplest way to eliminate these complications would be to follow the reaction only until 10 to 15% of the bromine had reacted."

Victor Meyer and Mueller[10] found that when aliphatic hydrocarbons were brominated in presence of iron wire, the reaction proceeded slowly if kept at ordinary temperatures; if the reaction mixture was heated to the temperature of the water bath, the reaction took place rapidly with a quantitative yield of the bromide.

H. S. Fry found that when benzene was brominated in presence of iron wire, even at ordinary temperatures, the reaction was completed in an hour. The progress of the reaction can be followed by carefully reading temperature changes.

It was to follow this reaction quantitatively that this study was undertaken.

Preparation of Materials

The chief materials used in this study were pure bromine, benzene, brombenzene and hydrobromic acid.

Bromine

The bromine used was purified by Baxter's [11] method. The bromine was first dissolved in calcium bromide solution which had been made from about one third of the original material by means of lime and ammonia, the bromine was then distilled from this solution. The product was covered with several times its volume of water and converted into hydrobromic acid by means of hydrogen sulphide generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtering from precipitated sulphur and sulphur bromide, the filtrate was distilled and the fraction boiling at 120° C, consisting of 48 per cent hydrobromic acid, was caught. The acid was boiled for some time with the occasional addition of small quantities of potassium permanganate to eliminate the last traces of iodine. Finally the residual hydrobromic acid was heated with the theoretical quantity of pure potassium permanganate, the bromine condensed in a flask cooled with ice. The bromine was finally distilled over concentrated sulphuric acid to remove the last traces of moisture.

Benzene

Kahlbaum's pure benzene was dried over fused calcium chloride, then carefully fractionated, only the portion distilling at 80° C. was used. The distillate was preserved in glass stoppered bottles over metallic sodium. The benzene was thiophene free.

Brombenzene

Brombenzene was prepared from dry benzene and pure bromine using iron wire as halogen carrier. The crude brombenzene was carefully freed from free bromine and ferric bromide by a thorough washing with dilute sodium hydroxide solution, dried over fused calcium chloride, fractionated, the portion boiling at 156 to 157° C. was used.

Hydrobromic Acid

Hydrobromic acid was prepared by brominating a solution of naphthalene in xylene. The hydrobromic acid gas evolved was passed through two U tubes filled with red phosphorus to remove traces of free bromine, the gas was then passed through a U tube filled with phosphorus pentoxide to remove last traces of moisture, finally bubbling through benzene or brombenzene until the latter became saturated.

Iron Wire

The iron wire used was a select piano wire, Brown and Sharp gage Number 18.

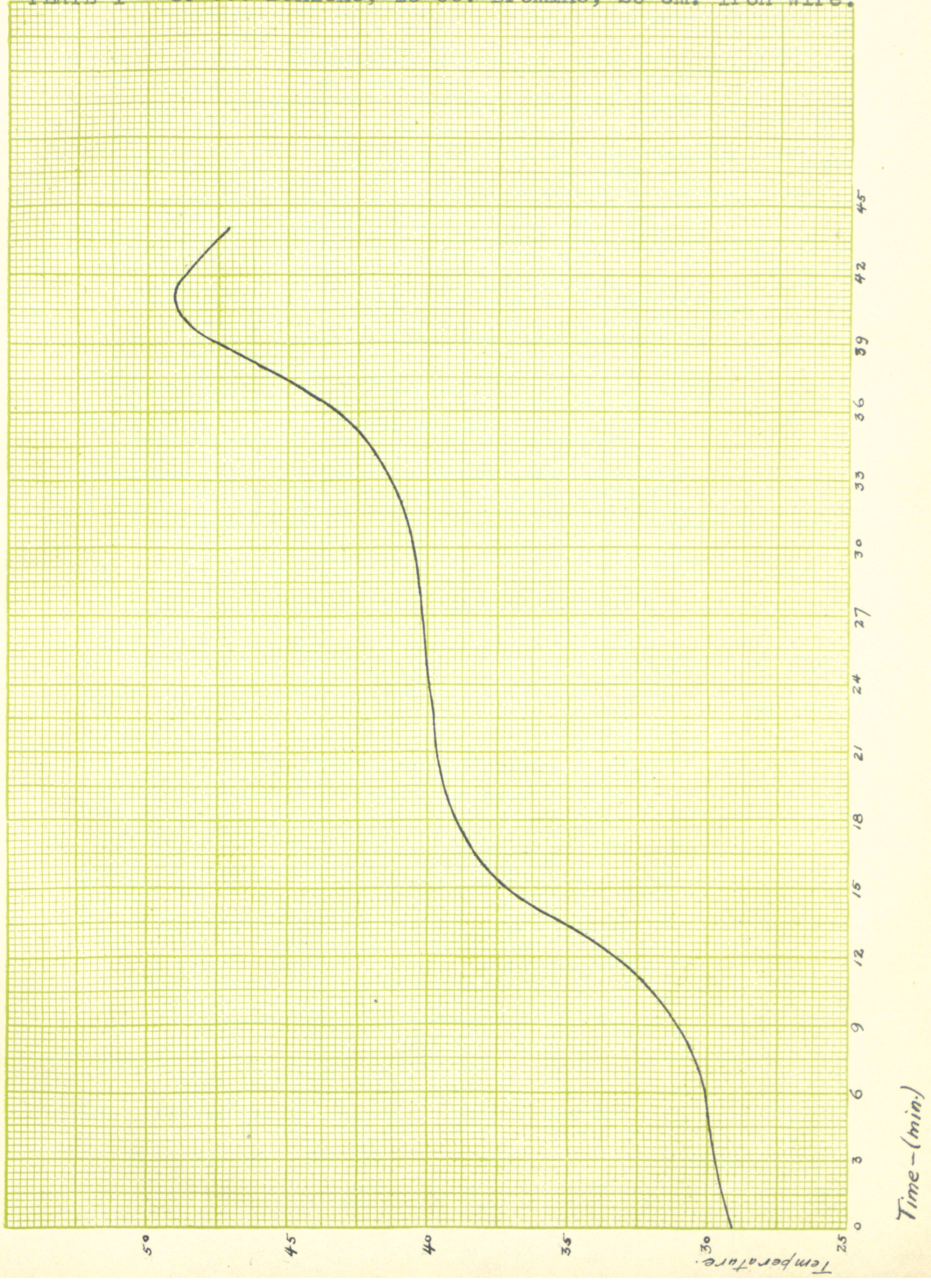
Experimental

The temperatures of reaction mixtures of benzene and bromine in presence of iron wire, as catalyzer, plotted against time is shown in the following diagram. (Plate I).

The temperature increase at first was very slow, gradually increasing and becomes a maximum at 20 minutes. The temperature increase is again slow and for a second time increases to a maximum at 41 minutes. In this curve there appears to be two maximum points. It was assumed that perhaps after the first maximum the reaction was slowed up either because one reaction had been completed and that the second reaction was just starting or that the products so far formed had acted as negative catalyzers.

Bruner showed that the hydrobromic acid formed in the reaction probably combined with free bromine to form HBr_3 and thus remove from the reaction mixture a definite quantity of bromine, which would tend to slow up the reaction. Whether the two maximum points correspond to the formation of C_5H_6Br and to $C_5H_4Br_2$ could not be determined. From the quantitative study of this reaction no such an abrupt change took place, indicating that in all probability both reactions proceed simultaneously.

PLATE I 80 cc. Benzene, I5 cc. Bromine, 20 cm. Iron Wire.



In the present study no attempts were made to determine the relative amounts of the mono and dibrom benzene, but it was particularly necessary to determine the actual percentages of bromine that remained after definite time intervals. These determinations make possible definite comparisons of time, temperature, and extent of bromination.

It was found impossible to determine the very large amounts of bromine present by using sodium thiosulphate because the bromine oxidized the sodium thiosulphate thus vitiating the results. A solution of phenol although giving quantitative results was found too slow for practical purposes. Aniline hydrochloride gave concordant results and a determination was completed rapidly. Solution of aniline hydrochloride used was approximately three times normal.

A determination of bromine was carried out as follows: A known amount of aniline hydrochloride solution was run into a 250 cubic centimeter glass stoppered bottle from a burette, then the bromine solution was added from another burette until the solution in the bottle acquired a faint brown tint. More aniline hydrochloride solution was added until a test portion no longer showed the presence of free bromine, when added to starch potassium iodide paste. Reaction of bromine upon aniline hydrochloride takes place according to the following equation:

$C_5H_6NH_2 + 3\ Br_2 = C_6H_2Br_3NH_2 + 3\ HBr.$

In running a series a blank consisting of 80 cubic centimeters of benzene and 15 cubic centimeters of bromine was titrated with aniline hydrochloride. The ratio of the number of cubic centimeters of bromine solution to 1 cubic centimeter of aniline hydrochloride solution was taken to represent 100 per cent bromine. To run a determination, 20 centimeters of iron wire was bent into such shape that it would present the greatest amount of its surface to the solvents and the least amount (only 2 or 3 points, so as to speak) in contact with the surface of the vessel. The wire thus bent was introduced into a four ounce thermos bottle together with 80 cubic centimeters of benzene. The temperature was carefully recorded and immediately 15 cubic centimeters of bromine were introduced. Simultaneously with the introduction of the bromine a stop watch was started. Thus an accurate account of the time and temperature were recorded. The flask was shaken so as to prevent a separation of the reaction mixture into two separate layers, and a reading of the temperature was made every minute. In running a series the reaction was stopped after four minutes or some multiple of 4 minutes, and titrating to determine the amount of unchanged bromine, that is the quantity of bromine which was not substituted.

From the results obtained an effort was made to determine if possible the order of the reaction. A modification of the equation for a first order reaction was found to yield concordant results. The formula was developed as follows:

Let y = amount of catalyst ($FeBr_3$) formed from solution of Fe in Br_2 in time, t. By experiment we find (from loss in weight of Fe) that the rate is constant.

$$\frac{dy}{dt} = Ko \,, \quad y = Kot + K_1 \,. \qquad \text{When } t = o,\ y = o$$

$$\therefore \quad y = Kot \qquad \therefore K_1 = o.$$

Let x = amount of Br_2 reacting in time t.

By law of mass action, the rate of reaction is proportional to the concentration of the reacting substances.

$$\therefore \quad \frac{dx}{dt} = K(A - x)$$

Where K = constant proportional to the concentration of the catalyst at time t.

A = initial concentration of Bromine.

$K = K'y = K'Kot = ct$ Where c = constant = $K'Ko$

$$\frac{dx}{dt} = ct\,(A - x)$$

$$\int\frac{dx}{A - x} = \int ctdt + \text{constant}$$

$$-\log(A - x) = \frac{ct^2}{2} + \text{constant}$$

When t = o x = o

$$\therefore -\log A = \text{constant}$$

$$\therefore \log A - \log(A - x) = \frac{ct^2}{2}$$

$$\log\frac{A}{A - x} = \frac{c}{2}t^2$$

For purposes of calculation and plotting, the following forms are more suitable:

$$\frac{c}{2} = \frac{1}{t^2} \log \frac{A}{A - x}$$

$$\log \frac{c}{2} = \log \left(\log \frac{A}{A - x}\right) - 2 \log t.$$

In the development of the above equation it was assumed that the rate of solution of the iron wire was a constant. This assumption was shown to be correct by the following data. Note that in the last column the amount of iron used up in one minute is, with the exception of the first two readings, continuously constant.

Iron consumed	
In 4 minutes	In 1 minute
0.0041	0.0010
0.0032	0.0008
0.0026	0.0006
0.0021	0.0005
0.0021	0.0005
0.0022	0.0005
0.0024	0.0006
0.0021	0.0005
0.0020	0.0005

On the other hand, the assumption that the velocity of the reaction was proportional to the amount of catalyzer present could not be shown to hold. Ferric bromide was assumed to be the active catalyzer, but since ferric bromide is insoluble in benzene, an experiment was carried out in which the ferric bromide was dissolved in a portion of the total bromine. The remainder of the bromine was added to the benzene and then the benzene bromine solution was added to the solution of ferric bromide in bromine. On the addition of the first drop of the benzene solution the reaction was exceedingly violent, but when all of the benzene bromine solution was added the reaction ceased. As the result of this experiment all attempts to use ferric bromide as a separately added catalyzer were discontinued.

Series 1. This series was designed to show relationship between temperature obtained, the time and quantity of bromine used up during bromination of benzene. Bromination of 80 cubic centimeters of benzene, with 15 cubic centimeters of bromine in presence of 20 centimeters of iron wire.

Blank. 1.9560 Aniline 17.80 c.c. Bromine 9.1 c.c.

Time.	Aniline	Bromine.	Ratio	% consumed	Velocity Constant.
4	11.4 c.c.	6.8	1.9159	2.19	0.0006063
8	11.9	6.25	1.9040	2.80	0.0001922
12	13.55	7.65	1.7712	9.53	0.0002695
16	12.3	7.30	1.6849	13.93	0.0002542
20	12.7	7.95	1.5975	18.51	0.0002222
24	14.	9.1	1.5385	21.46	0.0001822
28	14.55	10.15	1.4335	26.71	0.0001722
32	11.20	8.80	1.2716	35.09	0.0001832
36	0.55	49.2	0.0111	99.43	0.0001884
				Average	0.0001816

PLATE II 80 cc. Benzene, I5cc. Bromine, 20 cm. Iron Wire.

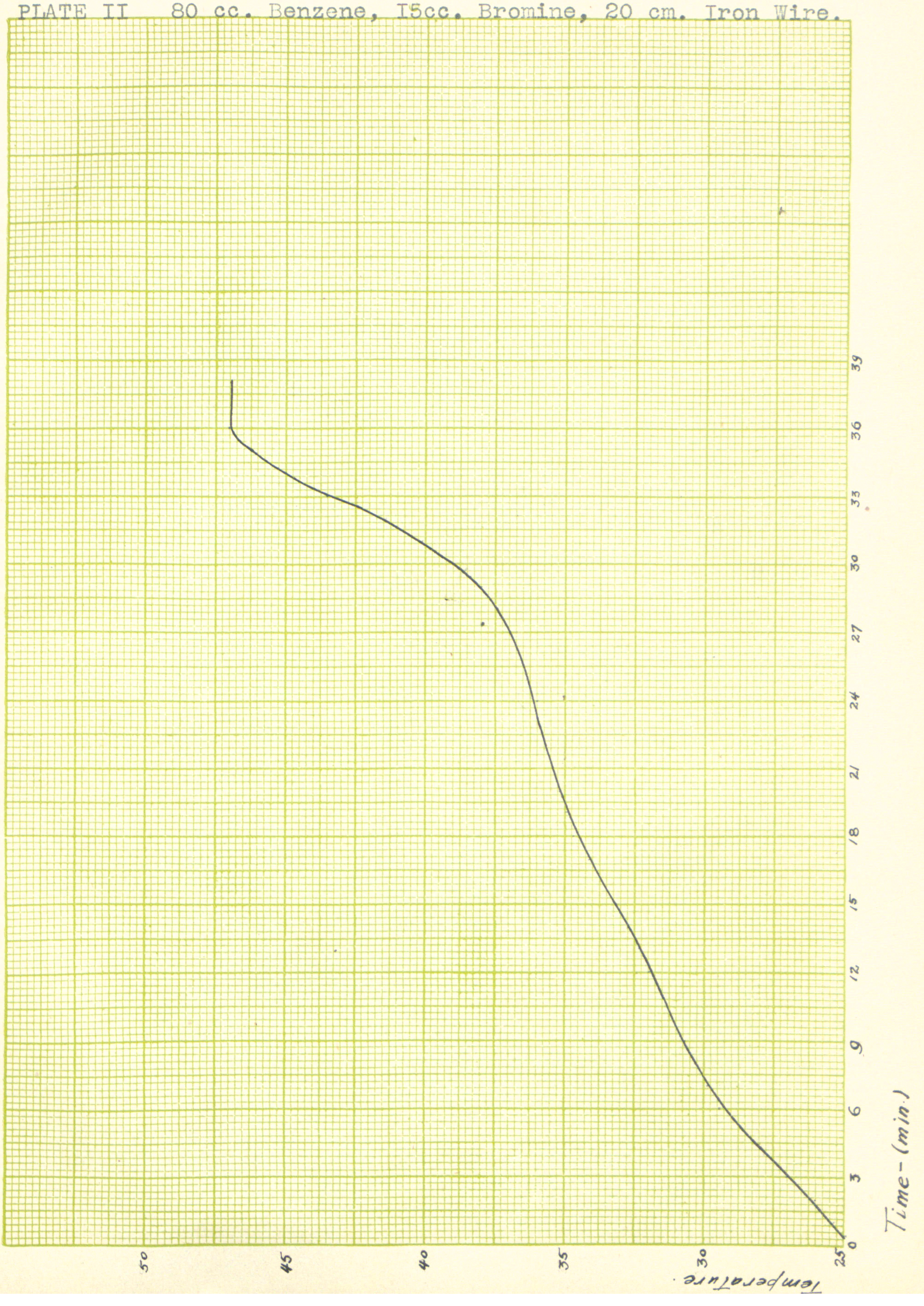


PLATE III 80 cc. Benzene, I5 cc. Bromine, 20 cm. Iron Wire. Shows per cent of Bromine consumed in equal time intervals.

Time.	Iron Consumed
4	0.0020
8	0.0024
12	0.0030
16	0.0035
20	0.0040
24	0.0045
28	0.0065
32	0.0070
36	0.0085

It is at once apparent from the data obtained in above series that (1) all of the bromine was consumed in 36 minutes (2) the close agreement between constants obtained employing the equation; $K = \frac{1}{t^2} \log \frac{A}{A - x}$ indicate that reaction is one of the first order (3) these results contradict the conclusions of Bruner.

<u>Series 2</u>. In this series of experiments the object was to determine the effect if any of the presence of hydrobromic acid upon the velocity of the reaction. Of course whenever a hydrocarbon is brominated, hydrobromic acid is produced and as the reaction proceeds the concentration of the hydrobromic acid increases from 0 to the saturation point. Hence in this series, before bromine was added to the benzene, the benzene was completely saturated with hydrobromic acid at 20° C. which was

generally the initial temperature of the reaction mixture.

The results of the bromination of 80 cubic centimeters of benzene saturated with hydrobromic acid when treated with 15 cubic centimeters of bromine and 20 centimeters of iron wire as catalyzer are embodied in the following table.

Blank. 1.9455 Aniline 14.3 c.c. Bromine 7.35 c.c.
1.9444 15.75 8.1

Time.	Aniline	Bromine	Ratio	% Consumed
4	15.70 c.c.	8.10 c.c.	1.9382	0.34
8	16.	8.3	1.9277	0.83
12	18.60	9.75	1.9076	1.92
16	17.11	9.1	1.8791	3.43
20	16.35	8.9	1.8258	6.12
24	18.6	10.4	1.8038	7.25
28	17.9	10.5	1.7047	12.35
32	17.5	10.4	1.6827	13.49
36	17.4	10.1	1.6237	16.51
40	17.5	10.4	1.5865	18.42
44	17.	10.8	1.5749	19.07
48	0.3	48.	0.0062	99.68

PLATE IV 80 cc. Benzene sat. with HBr, I5 cc. Bromine, 20 cm. Iron Wire.

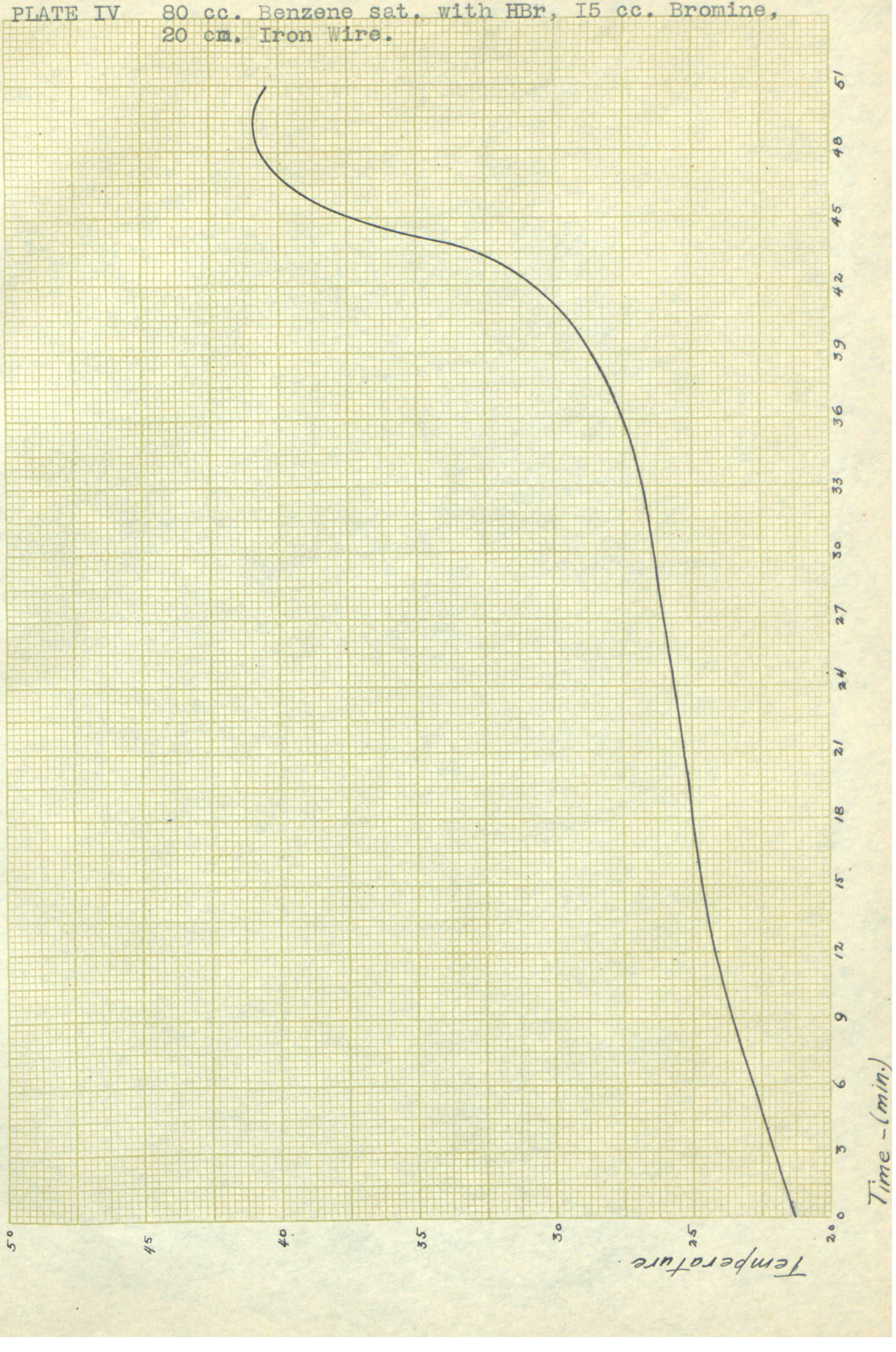


PLATE V 80 cc. Benzene sat. with HBr, I5 cc. Bromine, 20 cm. Iron Wire.

Time.	Velocity Constant	Iron Consumed
4	0.00007347	0.0019
8	5672	0.0022
12	5819	0.0032
16	6098	0.0035
20	6857	0.0044
24	5675	0.0049
28	5808	0.0062
32	6150	0.0066
36	6047	0.0085
40	5526	0.0096
44	5975	0.0101
48	2148	0.0110

Average 0.00005963

The data in this table reveals the following facts; (1) all of the bromine was consumed in 48 minutes while in the preceding series the time was only 36 minutes, further a comparison of series 1 with series 2 shows that the speed of reaction in the second series is much less than series 1 with very few exceptions occasioned undoubtedly by unavoidable errors in experimental manipulations, indicate that here also from the standpoint of the equation $K = \frac{1}{t^2} \log \frac{A}{A - x}$ the reaction was one of the first order. This is further confirmed by results of applying other equations for constants to the above data, uniform results were only obtained with equation of the first order. These results do not agree with Holleman, who maintains that nucleus bromination depended upon the formation of a perbromide. If a perbromide were formed the reaction would necessarily belong to a higher order. (2) The fact that in the above series the speed of reaction was retarded even though the reaction was begun in a solution of C_6H_6 saturated with hydrobromic acid, indicates that the claims made by Holleman for the accelerating effect of hydrobromic acid are seriously questioned. (3) This decrease in the speed of reaction can not be explained by a limitation of the action of the iron wire for this is evident when one compares the amounts of iron consumed in equal time intervals in series 1 and series 2, the quantities of iron used are practically identical. (4) It may be assumed that the slower speed of reaction indicated in series 2 may be due to the linking up of the centric valencies of the benzene nucleus with the hydrobromic acid molecules and thus inhibit their functioning in the mechanism of substitution. It is generally conceded by theoretical chemists that the centric valencies of benzene do play some part in substitution reactions through the formation of intermediate addition compounds. (5) It has been customary to assume that the benzene molecule forms molecular complexes with the halogen carrier. If the halogen carrier is iron or bromide of iron, the complete insolubility of either of these in benzene would not warrant this customary explanation.

Series 3. Bromination of brombenzene in presence of iron wire.

In order to throw more light upon the bromination of benzene, it is necessary to take into account the action of bromine upon brombenzene. This follows from the fact that brombenzene is a primary product of the interaction of bromine upon benzene, and since para dibrom benzene is also formed, it is evident that bromine undoubtedly reacts with brombenzene to form para dibrom benzene. Some may assume that the formation of para dibrom benzene does not necessarily involve the formation of brombenzene, but since both products are invariably formed in varying quantities when bromine acts upon benzene, one must study in this thesis the action of bromine upon brombenzene. This will throw some light perhaps upon the relative quantities of bromine consumed on the one hand by benzene and on the other by brombenzene. Further more, the possibility of brombenzene acting as catalyzer in the ultimate consumption of the bromine has not been considered by previous investigators.

Series 3

Blank

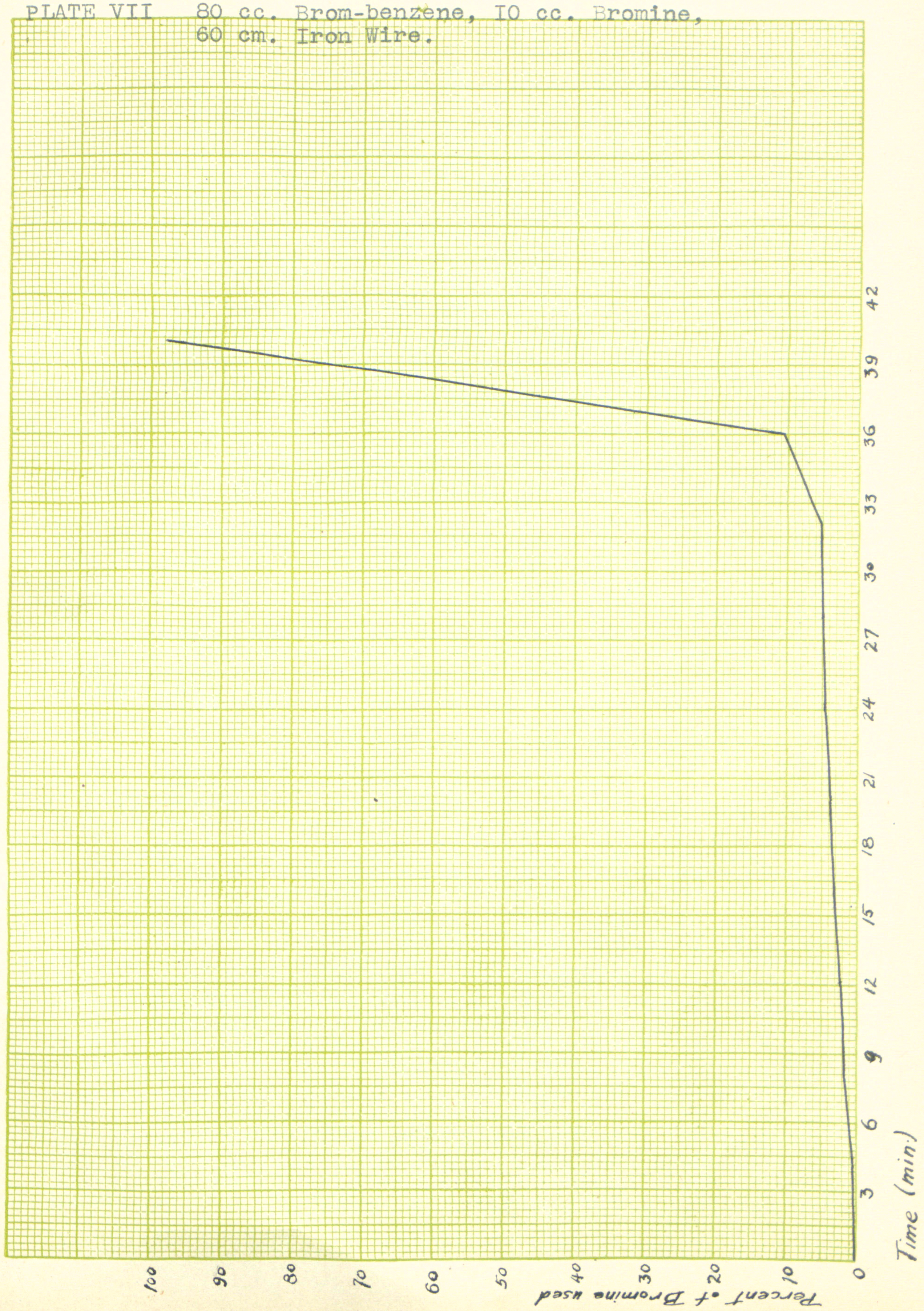
A-	Br-		
13.75	9.85	1.3959	Average 1.4002
18.40	13.10	1.4045	

Time.	Aniline	Bromine	Ratio	% Consumed	Velocity Constant
4	16.45	11.80	1.3940	0.44	0.0001225
8	17.60	12.80	1.3750	1.79	0.0001225
12	12.80	9.35	1.3689	2.23	0.00006798
16	15.75	11.60	1.3577	3.03	0.00005219
20	13.60	10.10	1.3455	3.90	0.00004320
24	15.05	11.25	1.3377	4.46	0.00005175
28	13.55	10.40	1.3301	5.00	0.00002842
32	14.80	11.15	1.3273	5.12	0.00002229
36	14.95	11.95	1.2518	10.59	0.00002980
40	1.00	30.35	0.0329	97.66	0.0003943

Time.	Iron Consumed
4	0.0080
8	0.0095
12	0.0124
16	0.0247
20	0.0264
24	0.0270
28	0.0285
32	0.0565
36	0.0581
40	0.0630

PLATE VI 80 cc. Brom-benzene, IO cc. Bromine,
60 cm. Iron Wire.

PLATE VII 80 cc. Brom-benzene, I0 cc. Bromine,
60 cm. Iron Wire.



In this series 80 c.c. brom benzene, 10 c.c. bromine and 60 cms. iron wire were used. If 80 c.c. brom benzene, 15 c.c. bromine are used, the reaction mixture at the end of the series becomes solid, due to the separation of para-di-brombenzene and this would interfere with the proper estimation of unchanged bromine.

After repeated trials 10 c.c. of bromine was found to be the proper quantity to use in order to prevent super saturation of para-di-brom-benzene.

The reaction was found to be too slow when 20 or 40 cms. of iron wire was used and in order to speed up the reaction, 60 cms. of iron wire was found sufficient.

The data in this table reveals the following facts: (1) All the bromine used was consumed in 40 minutes; (2) the fact that we have really two distinct series of reaction velocity constants due in all probability to the fact that para-di-brombenzene acts as a negative catalyzer thus tending to slow up the reaction; (3) the slowing down of the reaction as indicated by the smaller reaction velocity constants can not be attributed to the fact that the amounts of iron present varied since the amount of iron consumed per unit of time is constant as seen from the table; (4) as seen from the table, the reaction velocity constants are much slower than when benzene itself was brominated. No comparison however can be made since the quantity of bromine used in this series was less than was used for benzene, and the amount of iron used was much greater.

Series 4. This series of experiments was carried out to determine the effect if any of the presence of hydrobromic acid upon the velocity of the reaction. Brombenzene was saturated with dry hydrobromic acid at 20° C. In this series as in series #3, 80 c.c. of brombenzene, 10 c.c. of bromine and 60 cms. of iron wire was used.

Series 4

Blank 1.4327 Aniline 15.76 c.c. Bromine 11 c.c.

Time.	Aniline	Bromine	Ratio	% Consumed	Velocity Constant
4	15.10	11.05	1.3665	4.60	0.0012780
8	9.75	13.15	1.3489	5.83	0.0004076
12	10.60	13.90	1.3113	8.46	0.0002666
16	11.35	14.50	1.2775	10.82	0.0001948
20	10.15	12.50	1.2315	11.90	0.0001375
24	13.15	16.50	1.2547	12.41	0.00009991
28	12.60	15.90	1.2619	14.03	0.00008184
32	13.90	16.40	1.1799	17.63	0.00008175
36	12.90	14.70	1.1403	20.39	0.00007641
40	15.40	16.90	1.0975	23.39	0.00007231
44	17.40	17.90	1.0281	28.23	0.00006250
48	18.75	19.10	1.0187	28.88	0.00005473
52	17.90	17.40	0.9720	32.14	0.00005370
56	40.00	10.40	0.2660	81.85	0.00002663

PLATE VIII 80 cc. Brom-benzene, I0 cc. Bromine, 60 cm. Iron Wire.

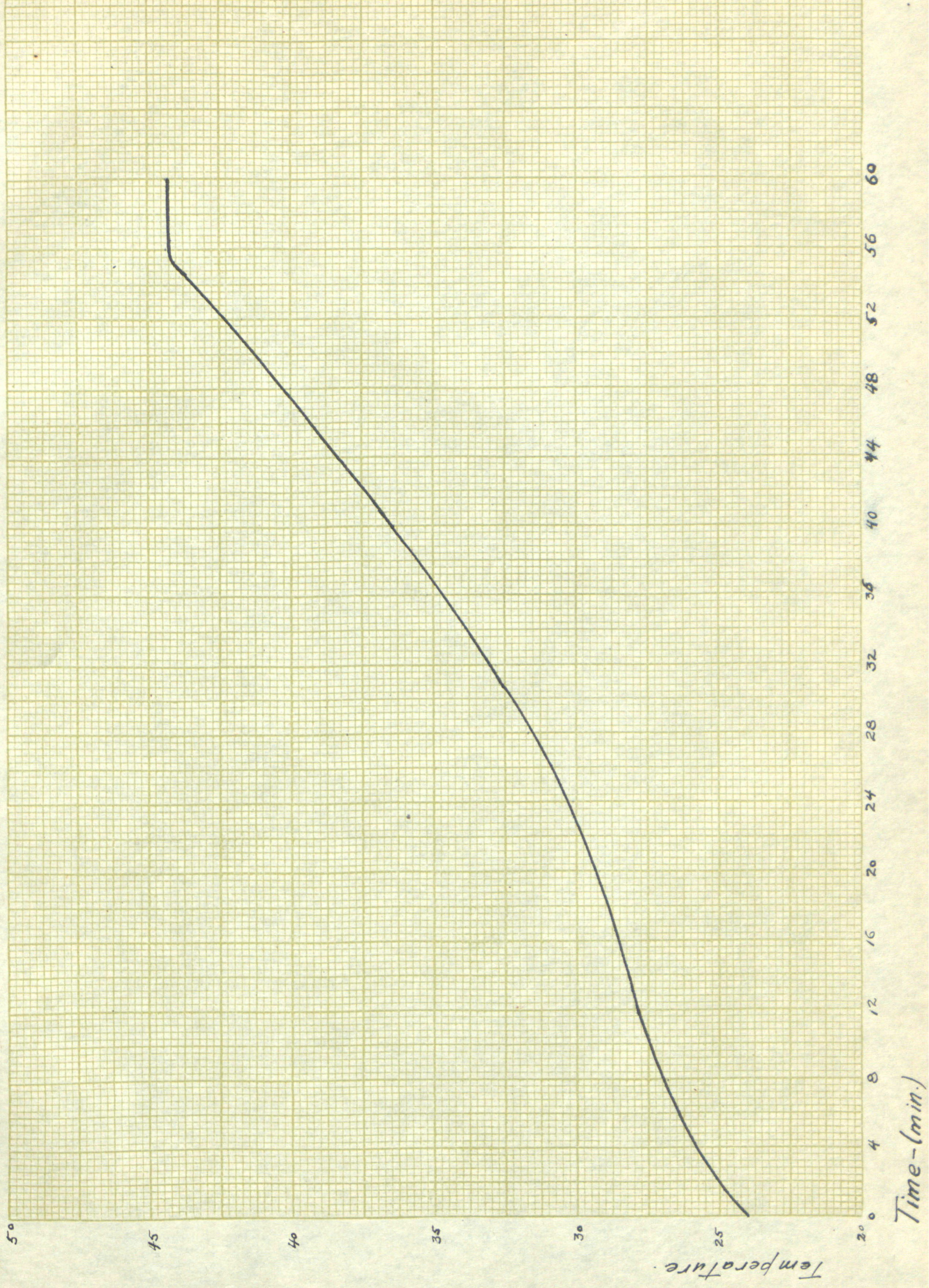


PLATE IX 80 cc. Brom-benzene, IO cc. Bromine,
60 cm. Iron Wire.

Time.	Iron Consumed
4	0.0104
8	0.0130
12	0.0206
16	0.0272
20	0.0359
24	0.0575
28	0.0914
32	0.0915
36	0.1180
40	0.1315
44	0.1337
48	0.1458
52	0.2953
56	0.3133

It is apparent from the data in the above tables (1) that the reaction velocity of series #4 is slower than in series #3. This slowing up is probably due to the presence of large quantities of hydrobromic acid and the formation of para-di-brom-benzene. In series #2 the slowing down of the reaction was explained by the fact that hydrobromic acid probably linked up with the centric valencies of benzene, thus inhibiting them functioning in the mechanism of substitution. A second reason may be found in the presence of para-di-brom-benzene which from data secured in series #3 seems to be responsible for the slowing down of the bromination of brombenzene. Equilibrium was reached at 56 minutes with 81.85% of bromine consumed.

During the development of the problem of the bromination of benzene and brombenzene, it was deemed necessary to determine the rate of reaction between benzene, brombenzene and bromine both in the light and in the dark without a catalyzer.

Series 5. A solution of benzene and bromine was prepared in the proportion of 80 c.c. of benzene and 15 c.c. of bromine. The exact quantity of bromine present in this solution was determined by titrating a known quantity against a standard solution of aniline hydrochloride.

Half of the above solution was placed in a clear glass bottle, the other half in an amber glass bottle, both placed in a light place, and where the temperature was nearly constant. At frequent intervals each solution was titrated and the amount of bromine consumed was represented in per cent. The following table will show results for both solutions. The time being expressed in days, A represents aniline hydrochloride and Br for the benzene bromine solution.

SERIES 5

BLANK RATIO 2.0194

A - 15.55 c.c. Br. 7.7 c.c.

Time	Light Glass Bottle				Ratio	% Consumed
1	A	13.65	- Br.	6.8	2.0073	0.6070
2	A	12.35	- Br.	6.4	1.9297	4.4470
3	A	10.65	- Br.	5.55	1.9189	4.9770
4	A	11.6	- Br.	6.1	1.9016	5.83
5	A	11.1	- Br.	6.	1.8500	8.38
6	A	12.4	- Br.	6.85	1.8102	10.36
7	A	14.	- Br.	7.8	1.7948	11.12
8	A	14.	- Br.	7.85	1.7834	11.68
9	A	12.05	- Br.	7.	1.7214	14.75
10	A	14.4	- Br.	8.4	1.7142	15.11
11	A	10.95	- Br.	6.45	1.6914	16.24
12	A	13.	- Br.	7.7	1.6883	16.39
13	A	17.	- Br.	10.25	1.6585	17.87
14	A	12.3	- Br.	7.7	1.5974	20.89
16	A	15.7	- Br.	10.	1.5700	22.25
19	A	16.3	- Br.	10.55	1.5450	23.49
26	A	10.2	- Br.	7.15	1.4265	28.86
35	A	14.45	- Br.	11.2	1.2901	36.11
45	A	10.15	- Br.	9.15	1.1093	45.06
61	A	10.0	- Br.	6.6	0.6600	67.31

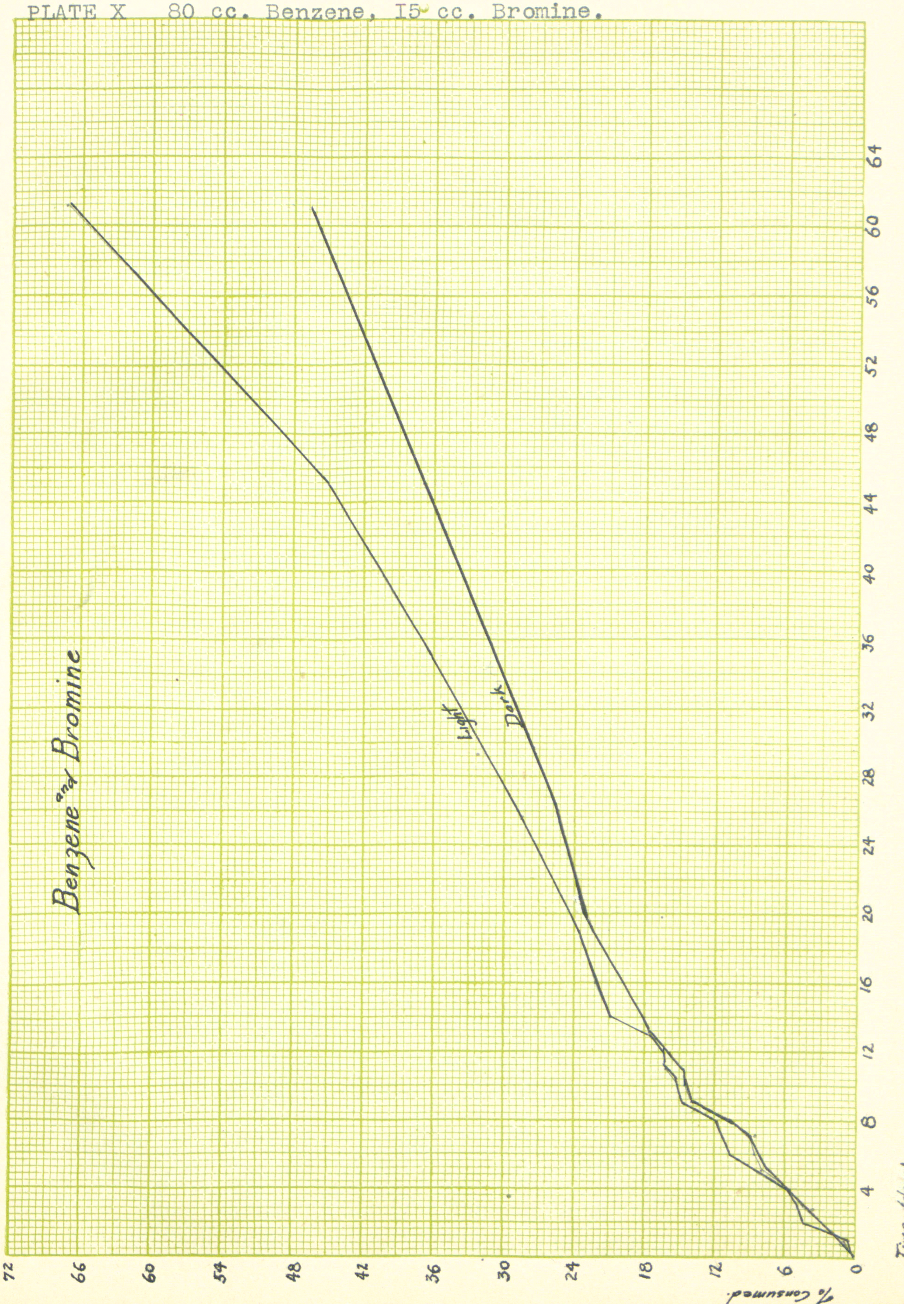
Series 5

BLANK RATIO 2.0194

A - 15.55 c.c. Br. 7.7 clc.

Time	Amber Glass Bottle	Ratio	% Consumed
1	A 12.2 - Br. 6.1	2.000	0.9670
2	A 10.7 - Br. 5.45	1.9633	2.7770
3	A 12.35 - Br. 6.4	1.9296	4.44
4	A 12.2 - Br. 6.4	1.9062	5.60
5=	A 11.6 - Br. 6.25	1.8560	8.09
6	A 10.9 - Br. 5.9	1.8476	8.50
7	A 11.85 - Br. 6.45	1.8372	9.02
8	A 12.1 - Br. 6.7	1.8059	10.57
9	A 11.90 - Br. 6.85	1.7372	13.97
10	A 14.6 - Br. 8.45	1.7278	14.43
11	A 10.6 - Br. 6.15	1.7235	14.65
12	A 7.35 - Br. 12.5	1.7007	15.78
13	A 12.7 -- Br. 7.65	1.6601	17.79
14	A 14. - Br. 8.45	1.6568	17.95
16	A 17. - Br. 10.5	1.6190	19.82
19	A 14.4 - Br. 9.25	1.5567	22.41
26	A 10.7 - Br. 7.1	1.5070	25.32
35	A 13. - Br. 9.3	1.3978	30.78
45	A 17.20 - Br. 13.5	1.2740	36.91
61	A 7.60 - Br. 7.05	1.0780	46.61

PLATE X 80 cc. Benzene, I5 cc. Bromine.



S **Series 6.** A solution of brombenzene and bromine was prepared in the proportion of 80 c.c. brombenzene and 15 c.c. bromine. The method of procedure was identical with that of Series 5.

Series 6

Blank
A - 11.3 Br - 5.6 Ratio 2.0179

Time	Light Glass Bottle		Ratio	% Consumed
1	A 14.	- Br. 6.95	2.0143	0.178
2	A 13.3	- Br. 6.65	2.0000	0.886
3	A 11.3	- Br. 5.65	2.0000	0.886
4	A 12.1	- Br. 6.05	2.0000	0.886
5	A 12.7	- Br. 6.5	1.9538	3.17
6	A 12.	- Br. 6.2	1.9354	4.08
7	A 13.0	- Br. 6.75	1.9259	4.55
8	A 15.6	- Br. 8.2	1.9024	5.72
9	A 15.1	- Br. 7.95	1.8993	5.87
10	A 13.2	- Br. 7.	1.8857	6.52
11	A 13.3	- Br. 7.2	1.8472	8.45
12	A 17.8	- Br. 9.65	1.8443	8.60
13	A 16.5	- Br. 8.95	1.8435	8.64
14	A 16.2	- Br. 8.8	1.8408	8.77
16	A 14.85	- Br. 8.2	1.8109	10.25
19	A 15.85	- Br. 8.4	1.7869	11.44
26	A 11.55	- Br. 6.6.	1.7500	12.78
35	A 13.35	- Br. 7.6	1.7500	12.78
45	A 13.8	- Br. 8.1	1.7031	15.60
61	A 12.50	- Br. 7.7	1.6234	19.55

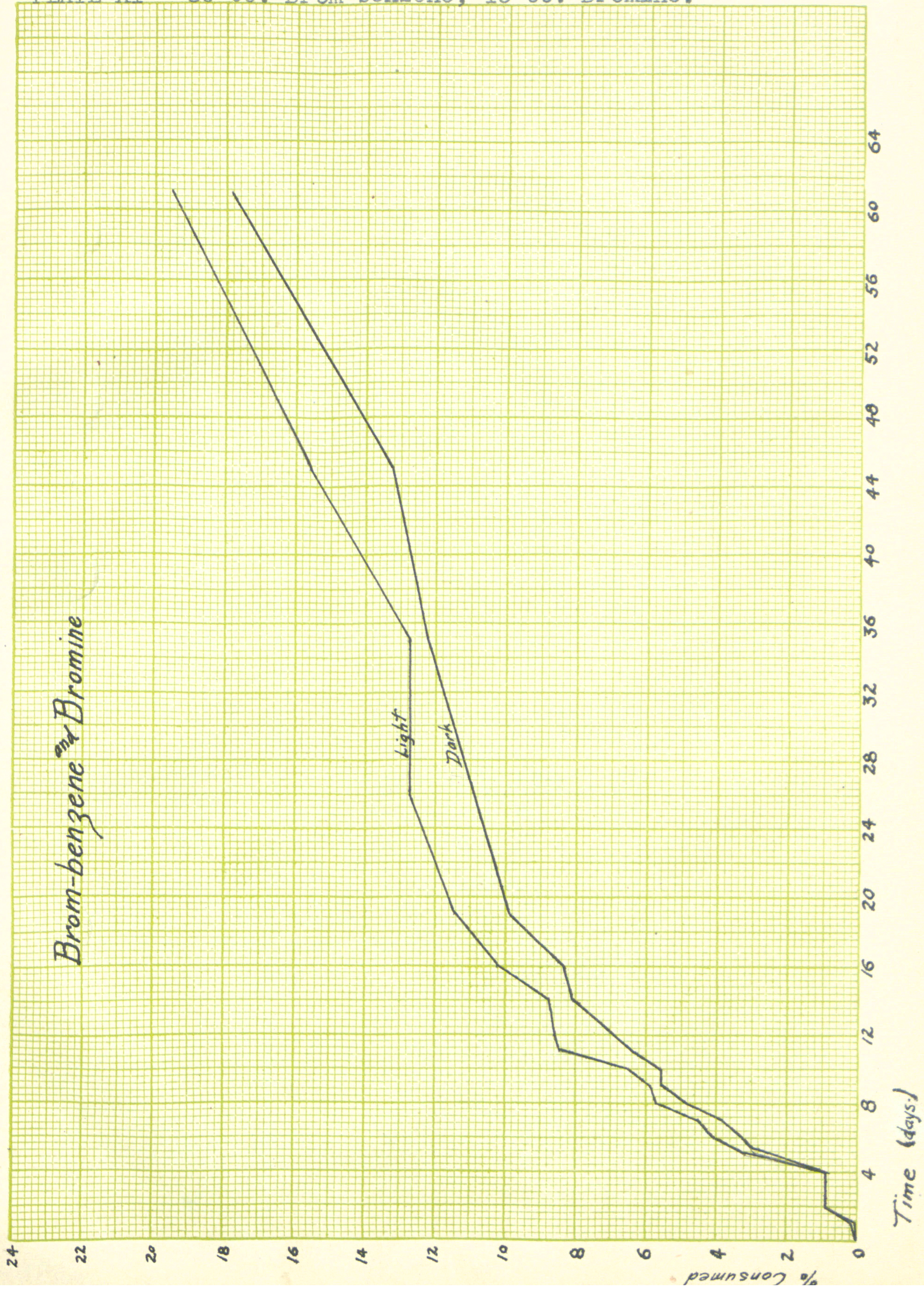
Series 6

Blank Ratio - 2.0179

A - 11.3 Br - 5.6

Time	Amber Glass Bottle	Ratio	% Consumed
1	A 12.5 - Br. 6.3	2.0161	0.089
2	A 11.5 - Br. 5.75	2.0000	0.886
3	A 12.1 - Br. 6.05	2.0000	0.886
4	A 10.6 - Br. 5.3	2.0000	0.886
5	A 11.95 - Br. 6.1	1.9590	2.91
6	A 12.9 - Br. 6.6	1.9530	3.21
7	A 13.1 - Br. 6.75	1.9407	3.82
8	A 12. - Br. 6.25	1.9200	4.85
9	A 12. - Br. 6.3	1.9047	5.60
10	A 14. - Br. 7.35	1.9047	5.60
11	A 13.6 - Br. 7.2	1.8888	6.39
12	A 11.65 - Br. 6.2	1.8790	6.88
13	A 14. - Br. 7.5	1.8666	7.49
14	A 14. - Br. 7.55	1.8543	8.10
16	A 18.5 - Br. 10.	1.8500	8.32
19	A 13.55 - Br. 7.45	1.8188	9.86
26	A 14.75 - Br. 8.2	1.7987	10.86
35	A 11.8 - Br. 6.7	1.7612	12.22
45	A 14.8 - Br. 8.5	1.7411	13.22
61	A 12.6 - Br. 7.6	1.6579	17.84

PLATE XI 80 cc. Brom-benzene, I5 cc. Bromine.



Conclusion

(1) The bromination of benzene and of mono-brom-benzene is of the first order reaction and not of the fourth as was stated by Bruner.

(2) The presence of hydrobromic acid does not change the order of the reaction, although the reaction velocities are smaller. This would indicate that perbromides if formed do not influence the order of the reaction.

(3) The bromination of benzene and of mono-brom-benzene seems to be the summation of two distinct exothermic reactions from the time, temperature diagrams. The reaction velocities would indicate that only one definite reaction had taken place.

(4) The bromination of mono-brom-benzene proceeds much slower than the bromination of benzene although in both reactions nearly 75% of the bromine is used up in the last few minutes. The rate of solution of iron is nearly a constant with time, this accumulation of ferric bromide in .solution will account for the very great reaction occurring during the last few minutes of bromination.

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11. Baxter

Data computed from given curves, for Plates # I, 2, 4, 6, 8.

TIME(min)	TEMPERATURE.				
(for all)	Plate #I	Plate #2	Plate #4	Plate #6	Plate #8
I	29.33	25.33		27.6	
2	29.66	26.00		29.0	
23	29.75	27.00		29.2	
4	29.84	27.83	22.25	29.3	25.85
5	30.00	28.50		29.5	
6	30.08	29.45		29.7	
7	30.20	29.85		30.0	
8	30.50	30.33	23.33	30.2	26.85
9	3I.05	30.70		30.4	
I0	3I.80	3I.I5		30.6	
II	32.50	3I.50		30.8	
I2	33.I6	32.00	24.05	3I.0	27.85
I3	34.35	32.33		3I.2	
I4	35.95	32.75		3I.6	
I5	37.40	33.I6		3I.8	
I6	38.08	33.70	24.85	32.0	28.50
I7	38.50	34.I6		32.I	
I8	39.00	34.70		32.3	
I9	39.25	34.95		32.6	
20	39.50	35.20	25.I6	32.8	29.20
2I	39.50	35.45		33.0	
22	39.70	35.66		33.2	
23	39.80	35.92		33.4	
24	39.84	36.00	25.50	33.6	30.I0
25	40.00	36.33		33.9	
26	40.I0	36.58		34.2	
27	40.20	37.00		34.5	
28	40.25	37.45	26.I6	34.9	3I.70
29	40.33	38.00		35.2	
30	40.50	39.00		35.9	
3I	40.70	40.08		36.5	
32	40.93	4I.45	26.70	37.5	32.85
33	4I.35	43.50		38.0	
34	4I.95	45.00		39.0	
35	42.45	46.20		40.3	
36	43.I5	47.00	27.50	4I.9	35.I6
37	44.50	46.95		43.8	
38	46.00	46.95		45.7	
39	47.50			46.7	
40	48.66		29.00	47.4	36.35
4I	49.I6			47.4	
42	48.66			47.4	
43	48II6				
44	47.66		34.00		38.35
48			40.70		40.00
5I			40.50		
52					4I.70
56					44.35
60					44.30
0	29.I7	25 at 40 sec.	2I.33	26.5	24.00