

CXLI.—*The Rate of Decomposition of Diazo-compounds.*
Part I. Diazo-compounds of the Benzene Series.

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IN view of the extended use, on the large scale, of aqueous solutions of diazo-salts, it is surprising how little has been published on the subject of their stability.

In the manufacture of azo-colours, the diazo-salt is usually "coupled" very shortly after its preparation, but in the production of the so-called "ice colours" on the cotton fibre, the solution often has to stand for a considerable length of time.

It is therefore of much importance to know the proper conditions under which the solution will remain undecomposed, of which the most important is the temperature.

The chief point of interest, however, lies in the study of the rate of

decomposition of diazo-salts, and the investigation of this for a number of compounds has been the subject of our work during the past year.

The decomposition of an aqueous solution of a diazo-salt is, in most cases, a simple one, and belongs to the class of unimolecular processes for which we have the well-known expression

$$\frac{1}{t} \log \frac{A}{A-x} = C \text{ (a constant).}$$

Measurements of the rate of decomposition of these compounds were first made by Hausser and Muller (*Bull. Soc. Chim.*, 1892, [iii], 7, 721; 1893, 9, 353; also *Compt. rend.*, 1892, 114, 549, 669, 760, 1438), who determined the value of $\frac{1}{t} \log \frac{A}{A-x}$ for the diazo-salts from

Aniline (sulphate and hydrochloride).

o-, *m*-, and *p*-Toluidine (sulphate),

o-, *m*-, and *p*-Aminobenzoic acid (sulphate),

m- and *p*-Sulphanilic acid,

p-Toluidine-2-sulphonic acid,

at a temperature of from 40° to 64°.

The results obtained showed that only the diazo-salts from *p*-sulphanilic acid and *p*-toluidinesulphonic acid gave a constant value for $\frac{1}{t} \log \frac{A}{A-x}$, all the others giving gradually diminishing values.

Hausser and Muller explain this unexpected result, in the case of diazobenzene only, by adducing experiments in evidence of a specific "retarding action" of the phenol formed during the decomposition.

Hantzsch (*Ber.*, 1900, 33, 2517) measured the rate of decomposition of the diazo-salts from the hydrochlorides of

Aniline,

p-Anisidine,

p-Toluidine,

ψ -Cumidine,

p-Bromoaniline,

and showed that at 25° all these substances gave a constant value for

$$\frac{1}{t} \log \frac{A}{A-x}.$$

Hantzsch suggests that the non-agreement of his results with those of Hausser and Muller may be due to the existence of secondary reactions set up at the high temperature of the experiments (40° to 64°).

We have therefore measured the rate of decomposition of diazobenzene chloride at temperatures from 20° to 60° in order to determine, if possible, the temperature at which such secondary reactions might set in, this point being shown by the diminishing values for *C*.

We shall show that, under the conditions of our experiments, the

figures for diazobenzene chloride give a constant value for the above expression at all temperatures between 20° and 60°.

Similar results were obtained with the diazotoluene chlorides.

The full list of amines and diamines, from which we have prepared and examined the corresponding diazo-salts, is as follows :

| | |
|--|-------------------------------|
| Aniline. | Benzidine. |
| <i>o</i> -, <i>m</i> -, and <i>p</i> -Toluidine. | <i>oo</i> -Dichlorobenzidine. |
| <i>p</i> -Sulphanilic acid. | Tolidine. |
| <i>o</i> -, <i>m</i> -, and <i>p</i> -Nitraniline. | Dianisidine. |
| <i>p</i> -Aminoacetanilide. | |

Most of the experiments of Hausser and Muller, and all those of Hantzsch, were made with solutions obtained by dissolving the pure, dry diazo-salt in water. The former chemists prepared the diazo-solutions from *o*- and *m*-toluidine sulphate by adding a solution of sodium nitrite to an acid solution of the amine ; they state, specially, that addition of sodium sulphate to a solution of dry diazo-*p*-toluene sulphate in pure water has no effect on the rate of decomposition, and conclude that it is immaterial whether the solution is prepared one way or the other.

Hantzsch (*loc. cit.*) states (and we have also found) that the presence of free mineral acid has no effect on the reaction. All our solutions have been prepared directly, as on the large scale ; and as our results for diazobenzene chloride agree fairly well with those of Hantzsch, we feel justified in criticising those of Hausser and Muller from the point of view of our own.

The method we used for determining the rate of decomposition was, in principle, the same as that used by the chemists to whom we have referred, namely, measurement of the volume of nitrogen evolved from time to time. The arrangement used for doing this was nearly the same as that of Hantzsch, who connected a flask containing the diazo-solution by means of a capillary tube with a nitrometer ; we have used a water-jacketed Hempel's burette, and an ordinary burette also water-jacketed. In the determinations above 30°, we interposed a very small, spiral condenser, so as to avoid any error due to the incomplete cooling of the hot nitrogen.

The question as to the measurement of time is the next consideration. It being, of course, impossible to bring the flask containing the diazo-solution to the required temperature instantaneously, it is necessary to fix on some point from which to reckon the time of reaction, so as to make the error as small as possible.

Hausser and Muller, indeed, attempted to determine the theoretical starting point from the volume of gas evolved in successive periods of time after the right temperature was reached. By extrapolation, they

found the length of time which would have been required for the evolution of the gas produced during the heating of the solution. But there are certain objections to this method, for, in the first place, the "curve of the rate" (taking volumes as ordinates and times as abscissæ) seems to have been produced backwards by freehand drawing, as by using Laplace's interpolation formula we obtain a slightly different result, and, secondly, the first few numbers obtained in these experiments (as Hantzsch proves) are much too low, owing to some of the nitrogen (at first a large proportion) remaining dissolved in the solution.

From a large number of preliminary observations, we believe that the method of Hantzsch, which we have adopted for reckoning the starting point, gives us a point which can only differ from the theoretical point by a very few seconds.

The flask then, having been nearly filled with the diazo-solution and connected by a two-holed caoutchouc stopper carrying a thermometer and a capillary tube with the measuring burette, was quickly heated to the temperature of the experiment by a Bunsen flame. The flask usually contained pieces of broken glass for purposes of adjustment and was well shaken during this operation to avoid overheating. The time was reckoned from this point, and the flask plunged into a water-bath which was kept at the right temperature by a gas regulator.

The gas evolved was now measured from time to time, and in many experiments the flask was heated to a higher temperature until, on cooling to the temperature of the bath, no increase in volume of the nitrogen was observed. This total volume of nitrogen determined experimentally always agreed well with the volume calculated from the amount of diazo-salt taken.

The correction for the expansion of the liquid and the small volume of air in the flask was always determined experimentally and subtracted from the readings of the burette.

In the following tables, A is the total volume of nitrogen at the temperature and pressure of the experiment calculated from the weight of diazo-salt contained in the solution; x is the corrected volume of nitrogen at the same temperature and pressure evolved during the time t (in minutes), C is the constant calculated according to the equation $C = \frac{1}{t} \log \frac{A}{A-x}$.

1. *Diazobenzene Chloride.*

9.3 Grams of aniline (1/10 mol.) dissolved in 30 c.c. of hydrochloric acid of sp. gr. 1.16 (3/10 mol.) cooled with ice and 6.9 grams of sodium nitrite added (100 c.c. of a solution containing 69 grams NaNO_2 per

litre). The solution thus obtained was made up to 1400 c.c., and therefore contained 10 grams of diazobenzene chloride in a litre.

Thirty-five c.c. were taken in each experiment. A fresh solution made in the above proportions was used for each experiment:

Temperature 20°.

| 1. <i>A</i> = 60 c.c. (13°, 750 mm.). | | | 2. <i>A</i> = 61 c.c. (14°, 741 mm.). | | |
|--|-----------|-----------|--|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 116 | 9.7 c.c. | 0.00066 | 451 | 31.4 c.c. | 0.00069 |
| 131 | 11.1 " | 0.00068 | 474 | 32.6 " | 0.00070 |
| 159 | 13.6 " | 0.00070 | 486 | 33.2 " | 0.00070 |
| 180 | 15.3 " | 0.00070 | 506 | 34.4 " | 0.00071 |
| 192 | 16.2 " | 0.00071 | 532 | 36.4 " | 0.00074 |
| 355 | 26.3 " | 0.00070 | 545 | 37.4 " | 0.00075 |
| 393 | 29.8 " | 0.00076 | 578 | 39.2 " | 0.00077 |
| 422 | 30.5 " | 0.00073 | 596 | 40.1 " | 0.00078 |
| 439 | 31.5 " | 0.00073 | 607 | 40.5 " | 0.00078 |
| 458 | 32.6 " | 0.00074 | 1382 | 55.3 " | 0.00074 |
| 481 | 33.7 " | 0.00074 | | | |
| 1282 | 51.4 " | 0.00066 | | | |
| 1329 | 52.8 " | 0.00069 | | | |
| 1354 | 53.9 " | 0.00073 | | | |
| 1424 | 54.5 " | 0.00073 | | | |
| Range 16 to 91%. Mean 0.00071 | | | Range 52 to 92%. Mean 0.000736 | | |

Mean of the two experiments, 0.00072.

Taking the first experiment, it will be seen that no value for *C* is recorded until 116 minutes have elapsed. The numbers obtained before this time are much lower and gradually increase until they become constant.

This apparent departure from the law is due to the fact that the solution must become saturated with nitrogen before the correct volume is measured in the burette. That this is the correct explanation was very clearly proved by Hantzsch, and we have therefore left out these irregular figures from our tables.

That there are considerable sources of error both at the beginning and towards the end of the reaction is obvious, and we shall therefore usually note the range of the reaction through which our observations extended (thus, for example, "range = 20 to 60 per cent." means that our numbers extend from the point at which 20 per cent. of the diazo-salt has been decomposed until 60 per cent. has been decomposed). The range

of our observations is usually considerably wider than that of Hausser and Muller or Hantzsch.

The above numbers agree fairly well with those obtained by Hantzsch at a temperature of 25°, whose results for *C* varied in four experiments from 0·00064 to 0·00072, the range covered by three experiments being 12 to 62 per cent. (The fourth experiment was made according to an admittedly more inexact titration method.)

There is not much difference in the constants at these temperatures, but, as will be seen, the constants increase enormously at higher temperatures.

| Series. | No. of observations. | Extreme values of <i>t</i> . | Extreme values of <i>x</i> . | <i>C</i> . | | |
|--|----------------------|------------------------------|--|------------|----------|----------|
| | | | | Lowest. | Highest. | Mean. |
| <i>Temperature 30°.*</i> | | | | | | |
| I. <i>A</i> = 60·45 c.c. (16°, 756 mm.) | 16 | 45 to 382 | 15·4 c.c. to 56·1 c.c. (range 25 to 92 %) | 0·00278 | 0·00305 | 0·002947 |
| II. <i>A</i> = 59·8 c.c. (15°, 761 mm.) | 12 | 53 to 314 | 17·2 c.c. to 53·0 c.c. (range 30 to 90 %) | 0·00278 | 0·00305 | 0·002956 |
| | | | | | Mean... | 0·00295 |
| <i>Temperature 40°.</i> | | | | | | |
| I. <i>A</i> = 59·7 c.c. (16°, 765 mm.) | 12 | 25 to 75 | 23·5 c.c. to 46·5 c.c. (range 40 to 78 %) | 0·00864 | 0·00888 | 0·00876 |
| II. <i>A</i> = 59·7 c.c. (13·5°, 756·5 mm.) | 8 | 31·5 to 78·5 | 27·8 c.c. to 47·2 c.c. (range 46 to 80 %) | 0·00864 | 0·00902 | 0·00879 |
| | | | | | Mean... | 0·00877 |

* The figures obtained in this and the following experiments are of the same character as those in the experiments at 20°. We have therefore arranged our results in an abbreviated form, giving, however, one set of figures in full for each substance.

We made our next experiments at a temperature of 50°, the same as that at which Hausser and Muller worked.

We have already mentioned that our experiments were not made under the same conditions as those of the above chemists, but apart from this there is much that is open to criticism in the figures which Hausser and Muller give.

A serious error occurs in the numbers for diazobenzene chloride (*Bull. Soc. Chim.*, 1892, [iii], 7, 721) which we quote here. We have added a new column showing the values for *C*, which we obtain on calculating out Hausser and Muller's results.

Experiment 1.—Solution contained 6.25 grams of diazobenzene chloride per litre. $A = 660$ c.c.

| t . | x . | C . (Hausser and Muller) | C . Recalculated, C. and N. |
|-------|----------|-------------------------------|----------------------------------|
| 16.5 | 207 c.c. | 0.0303 | 0.0099 |
| 26.5 | 300 „ | 0.0285 | 0.0099 |
| 36.5 | 343 „ | 0.0262 | 0.0087 |
| 46.5 | 361 „ | 0.0232 | 0.0074 |
| 56.5 | 370 „ | 0.0205 | 0.0063 |

Range 31 to 56 per cent.

Experiment 2.—Solution contained 9.47 grams of diazobenzene chloride per litre (the solution used in our experiments contained 10 grams per litre). $A = 453$ c.c.

| t . | x . | C . (Hausser and Muller) | C . Recalculated, C. and N. |
|-------|----------|-------------------------------|----------------------------------|
| 12.6 | 206 c.c. | 0.0360 | 0.0209 |
| 17.6 | 255 „ | 0.0348 | 0.0204 |
| 22.6 | 285 „ | 0.0332 | 0.0190 |
| 27.6 | 305 „ | 0.0317 | 0.0176 |
| 32.6 | 317.5 „ | 0.0299 | 0.0160 |
| 42.6 | 332.5 „ | 0.0267 | 0.0135 |

Range 45 to 73 per cent.

There is thus a very great discrepancy which we are quite unable to account for. We were led to check these results after drawing a curve showing the course of the decomposition. It was obvious that the curve could not represent the reaction. We may add that we have recalculated all the numbers given in the various experiments by Hausser and Muller and find them to be correct.

Turning now to the figures given in the same paper for diazobenzene sulphate, we find that four experiments were made with three different solutions, containing respectively 3.38, 6.7, and 10.8 grams of diazo-salt per litre.

The corresponding values for C did not differ very much from each other; hence Hausser and Muller conclude that the decomposition is not influenced by the concentration.

The numbers for C , however, in each experiment are not constant, they gradually diminish as the decomposition goes on; thus in

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| | | |
|--------|--------------------------------------|--------------------------|
| Exp. 1 | they diminish from 0.0298 to 0.0210. | Range 49 to 80 per cent. |
| " 2 | " " 0.0289 " 0.0177. | " 44 " 82 " |
| " 3 | " " 0.0325 " 0.0191. | " 45 " 84 " |
| " 4 | " " 0.0334 " 0.0206. | " 50 " 86 " |

From these numbers, Hausser and Muller conclude that the phenol formed in the reaction has a specific retarding action, and to prove this made a fifth experiment, to which phenol was added.

From the result of this, they claim to have shown that their explanation was a true one, but on comparing the figures obtained, we do not think the conclusion is justified. The solution contained 22.5 grams of diazo-salt per litre, with 10.5 grams of phenol per litre, and the values for C diminished from 0.0259 to 0.0216 (range 48 to 89 per cent.).

We have compared the values of C in the above experiments at points representing equal amounts of decomposition. Thus, when 56 per cent. had decomposed, the value of C in two experiments was 0.0284 and 0.0318, and in the phenol experiment 0.0259. When 66 per cent. had decomposed, we find $C = 0.0267$, 0.0297, and in the phenol experiment 0.0255.

Here the value for C in the phenol experiment is less than that in the two ordinary experiments, although these differ from each other more than one of them differs from the phenol experiment. But at a later stage we find:

At 75 per cent. decomposition the value of C was 0.0230 and 0.0221, and in the phenol experiment 0.0248.

At 80 per cent. decomposition the value of C was 0.0210 and 0.0222, and in the phenol experiment 0.0242.

Here the value for C in the phenol experiment is greater than that in the other experiments.

Experiments were made (Hausser and Muller, *loc. cit.*) adding, instead of phenol, phenylsulphuric acid, sugar, and oxalic acid, and from equally unconvincing data the authors conclude that substances containing the benzene nucleus retard the reaction, whilst those belonging to the fatty series have no action.

We think, however, that the results of Hausser and Muller do not lead to this conclusion, and in order to test this point further we have made experiments also at 50° to see if, under the conditions of working, the addition of phenol has any effect on the reaction.

We think our numbers prove conclusively that there is no trace of either a retarding or accelerating action produced by this substance.

Temperature 50°.

The solution contained 10 grams of diazobenzene chloride per litre as before.

In Experiment 3 (p. 1421), the solution contained 4.57 grams of phenol per litre, this being the same proportion of phenol to diazo-salt as that in the experiments of Hausser and Muller :

| 1. $A=58.3$ (7° , 753 mm.). | | | 2. $A=58.3$ (7° , 753 mm.). | | |
|--|-----------|--------|--|-----------|--------|
| $t.$ | $x.$ | $C.$ | $t.$ | $x.$ | $C.$ |
| 5.5 | 17.7 c.c. | 0.0286 | 9 | 26.0 c.c. | 0.0285 |
| 6 | 19.3 " | 0.0291 | 9.5 | 27.3 " | 0.0289 |
| 6.5 | 20.85 " | 0.0295 | 10 | 28.5 " | 0.0291 |
| 7 | 22.55 " | 0.0303 | 11 | 30.6 " | 0.0294 |
| 7.5 | 24 " | 0.0307 | 12 | 32.6 " | 0.0296 |
| 8 | 25.4 " | 0.0311 | 13 | 34.4 " | 0.0298 |
| 9 | 27.8 " | 0.0313 | 14 | 36.0 " | 0.0298 |
| 10 | 29.9 " | 0.0312 | 16 | 38.85 " | 0.0296 |
| 12 | 33.6 " | 0.0311 | 18 | 41.3 " | 0.0297 |
| 13 | 35.4 " | 0.0312 | 20 | 43.25 " | 0.0294 |
| 15.5 | 39.1 " | 0.0311 | 22 | 45.0 " | 0.0292 |
| 17 | 41.0 " | 0.0310 | 24 | 46.45 " | 0.0288 |
| 19 | 43.1 " | 0.0307 | 26 | 47.7 " | 0.0285 |
| 21 | 45.0 " | 0.0306 | | | |
| 23 | 46.5 " | 0.0301 | | | |
| 26 | 48.4 " | 0.0296 | | | |
| 30 | 50.25 " | 0.0287 | | | |
| Range 30 to 84 %. Mean 0.0303 | | | Range 44 to 80 %. Mean 0.0293 | | |

Mean of experiments 1 and 2, 0.0298.

These figures show very clearly that the addition of phenol to the diazo-solution has absolutely no influence on the course of the reaction.

A fourth experiment was made at this temperature with a solution of different concentration, namely, containing 5 grams of diazo-salt per litre :

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| 3. | | | 4. | | |
|-------------------------------------|-----------|--------|-------------------------------------|-----------|--------|
| $A=60.1$ (18.8° , 753 mm.). | | | $A=30.1$ (14.3° , 753 mm.). | | |
| $t.$ | $x.$ | $C.$ | $t.$ | $x.$ | $C.$ |
| 8 | 24.3 c.c. | 0.0281 | 11 | 15.1 c.c. | 0.0275 |
| 9 | 27.1 " | 0.0289 | 13 | 17.2 " | 0.0283 |
| 10 | 29.5 " | 0.0293 | 15 | 18.9 " | 0.0286 |
| 12 | 33.6 " | 0.0296 | 17 | 20.3 " | 0.0287 |
| 13 | 35.4 " | 0.0297 | 21 | 22.6 " | 0.0287 |
| 16 | 40.6 " | 0.0305 | 24 | 23.8 " | 0.0283 |
| 17 | 41.9 " | 0.0305 | 28 | 25.1 " | 0.0278 |
| 18 | 43.0 " | 0.0303 | | | |
| 20 | 45.3 " | 0.0304 | | | |
| 22 | 47.1 " | 0.0302 | | | |
| 24 | 48.5 " | 0.0298 | | | |
| 27 | 50.3 " | 0.0291 | | | |
| 30 | 51.8 " | 0.0286 | | | |
| Range 40 to 86 %. Mean 0.0296 | | | Range 50 to 83 %. Mean 0.0283 | | |

The very slightly less value of C in experiment 4 is sufficiently accounted for by the greater proportion of nitrogen which can be retained in the more dilute solution: thus, as Hausser and Muller and Hantzsch have shown, the concentration has no influence on the course of the reaction:

Temperature 60° .

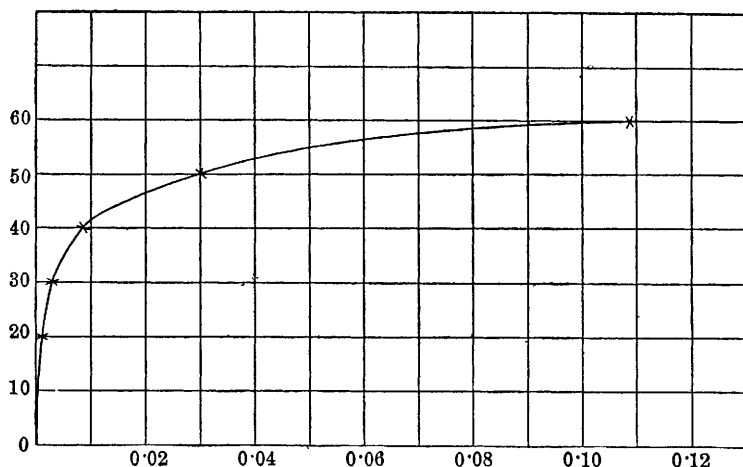
| Series. | No. of observations. | Extreme values of $t.$ | Extreme values of $x.$ | $C.$ | | |
|---|----------------------|----------------------------------|---|---------|----------|--------|
| | | | | Lowest. | Highest. | Mean. |
| I. $A=58.7$ c.c. (7° , 748 mm.) | 9 | $1\frac{1}{2}$ to $6\frac{1}{2}$ | 16.4 c.c. to 45.4 c.c. (range 28 to 77 %) | 0.102 | 0.1181 | 0.1103 |
| II. $A=58.7$ c.c. (8° 750 mm.) | 10 | 1.5 to 6 | 17.4 c.c. to 44.8 c.c. (range 30 to 76 %) | 0.102 | 0.111 | 0.1078 |
| | | | | | Mean... | 0.1090 |

An examination of the values for C at the various temperatures shows that they increase enormously as the temperature is raised.

This is seen very clearly in the curve where the following values for C are ordinates and the temperatures are abscissæ:

| Temperature. | C. |
|--------------|---------|
| 20° | 0·00072 |
| 30 | 0·00295 |
| 40 | 0·00877 |
| 50 | 0·0298 |
| 60 | 0·109 |

CURVE No. 1.

2. *Diazo-o-toluene Chloride.*

10·7 Grams of *o*-toluidine (1/10 mol.) dissolved in 30 c.c. of hydrochloric acid of sp. gr. 1·16 (3/10 mol.), cooled with ice and 6·9 grams of sodium nitrite added (100 c.c. of the normal solution). The solution of diazo-*o*-toluene chloride was made up to 1400 c.c. and therefore contained 11 grams of diazo-salt per litre. Thirty-five c.c. were taken in each experiment.

Temperature 20°.

| 1. $A=58\cdot3$ (8·5°, 758 mm.). | | | 2. $A=58\cdot3$ (8·5°, 758 mm.). | | |
|-------------------------------------|------|---------|-------------------------------------|------|---------|
| $t.$ | $x.$ | $C.$ | $t.$ | $x.$ | $C.$ |
| 147 | 26·4 | 0·00178 | 147 | 26·3 | 0·00177 |
| 166 | 29·4 | 0·00184 | 166 | 29·3 | 0·00183 |
| 188 | 32·6 | 0·00189 | 188 | 32·4 | 0·00187 |
| 199 | 33·9 | 0·00190 | 199 | 33·8 | 0·00189 |
| 222 | 36·2 | 0·00189 | 222 | 36·3 | 0·00191 |

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Temperature 20° (continued).

| 1. $A=58.3$ (8.5° , 758 mm.). | | | 2. $A=58.3$ (8.5° , 758 mm.). | | |
|--|-----------|-----------|--|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 236 | 37.6 | 0.00190 | 236 | 37.7 | 0.00191 |
| 299 | 42.7 | 0.00191 | 286 | 41.9 | 0.00193 |
| 388 | 47.5 | 0.00188 | 295 | 42.6 | 0.00193 |
| 430 | 49.2 | 0.00187 | 384 | 47.3 | 0.00189 |
| 474 | 50.4 | 0.00183 | 433 | 49.2 | 0.00186 |
| | | | 455 | 49.8 | 0.00184 |
| Range 45 to 85 %. Mean 0.00187 | | | Range 45 to 85 %. Mean 0.00187 | | |

Mean of the two experiments, 0.00187.

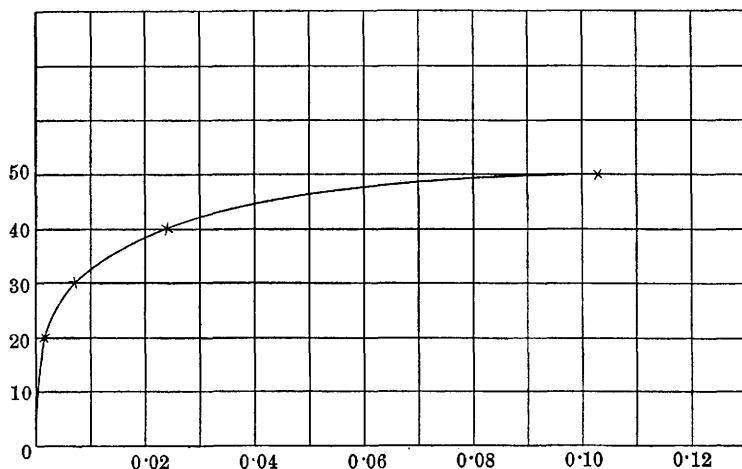
| Series. | No. of observations. | Extreme values of <i>t.</i> | Extreme values of <i>x.</i> | <i>C.</i> | | |
|---|----------------------|-----------------------------|--|-----------|----------|---------|
| | | | | Lowest. | Highest. | Mean. |
| <i>Temperature 30°.</i> | | | | | | |
| I. <i>A</i> = 60.6 c.c. (8.5°, 730 mm.) | 9 | 24 to 74 | 19.2 c.c. to 41.9 c.c. (range 31 to 70 %) | 0.0069 | 0.0073 | 0.00708 |
| II. <i>A</i> = 60.6 c.c. (8.5°, 730 mm.) | 8 | 27 to 60 | 21.1 c.c. to 37.7 c.c. (range 35 to 62 %) | 0.00688 | 0.00713 | 0.00704 |
| | | | | | Mean... | 0.00706 |
| <i>Temperature 40°.</i> | | | | | | |
| I. <i>A</i> = 58.8 c.c. (8°, 750 mm.) | 10 | 13 to 30 | 29.2 c.c. to 46.8 c.c. (range 50 to 80 %) | 0.0229 | 0.0247 | 0.0240 |
| II. <i>A</i> = 58.8 c.c. (8°, 750 mm.) | 8 | 10 to 24 | 23.8 c.c. to 42.5 c.c. (range 40 to 70 %) | 0.0225 | 0.0244 | 0.0236 |
| | | | | | Mean... | 0.0238 |
| <i>Temperature 50°.</i> | | | | | | |
| I. <i>A</i> = 58.8 c.c. (8°, 750 mm.) | 11 | 1.5 to 6.5 | 16.6 c.c. to 44.7 c.c. (range 28 to 75 %) | 0.0954 | 0.103 | 0.0997 |
| II. <i>A</i> = 58.8 c.c. (8°, 750 mm.) | 11 | 1.5 to 7 | 16.7 c.c. to 46.3 c.c. (range 28 to 79 %) | 0.0961 | 0.113 | 0.1057 |
| | | | | | Mean... | 0.1027 |

The collected values for C are therefore :

| Temperature. | C . |
|--------------|---------|
| 20° | 0.00187 |
| 30 | 0.00706 |
| 40 | 0.0238 |
| 50 | 0.1027 |

graphically represented by the following curve :

CURVE NO. 2.



Our results again differ from those of Hausser and Muller, who measured the rate of decomposition of diazo-*o*-toluene sulphate (*Bull. Soc. Chim.*, 1893, [iii], 9, 353). The diazo-salt was prepared in exactly the same way as was ours, except that we used hydrochloric instead of sulphuric acid.

The concentration of our solution was very near that employed in Hausser and Muller's first experiment, their second solution being twice as strong. Their experiments were made at 40° and the results were: 1, value for C gradually diminished from 0.026 to 0.020; 2, value for C gradually diminished from 0.0251 to 0.020.

As is seen above, we obtain a *constant* value for $C = 0.0238$. Hausser and Muller do not offer any explanation of their results.

3. *Diazo-m-toluene Chloride.*

The diazo-salt was prepared from *m*-toluidine exactly as in the case of *o*-toluidine.

DECOMPOSITION OF DIAZO-COMPOUNDS. PART I. 1425

Temperature 20°.

| 1. $A=60.9$ (12.5°, 739 mm.). | | | 2. $A=60.9$ (12.5°, 739 mm.). | | |
|----------------------------------|-----------|-----------|----------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 135 | 28.3 | 0.00201 | 97 | 22.4 | 0.00205 |
| 143 | 29.7 | 0.00203 | 109 | 24.8 | 0.00208 |
| 160 | 32.5 | 0.00207 | 122 | 27.0 | 0.00208 |
| 176 | 34.7 | 0.00208 | 135 | 29.0 | 0.00208 |
| 192 | 37.1 | 0.00213 | 143 | 30.2 | 0.00208 |
| 206 | 38.7 | 0.00213 | 160 | 33.1 | 0.00213 |
| 226 | 40.8 | 0.00213 | 176 | 35.3 | 0.00214 |
| 282 | 45.2 | 0.00209 | 206 | 38.6 | 0.00212 |
| 313 | 47.2 | 0.00207 | 226 | 40.5 | 0.00210 |
| 324 | 48.0 | 0.00208 | 243 | 42.1 | 0.00210 |
| 347 | 49.1 | 0.00205 | 282 | 45.1 | 0.00208 |
| | | | 324 | 47.9 | 0.00207 |
| | | | 350 | 49.7 | 0.00210 |
| Range 47 to 81 %. Mean 0.00208 | | | Range 37 to 82 %. Mean 0.00209 | | |

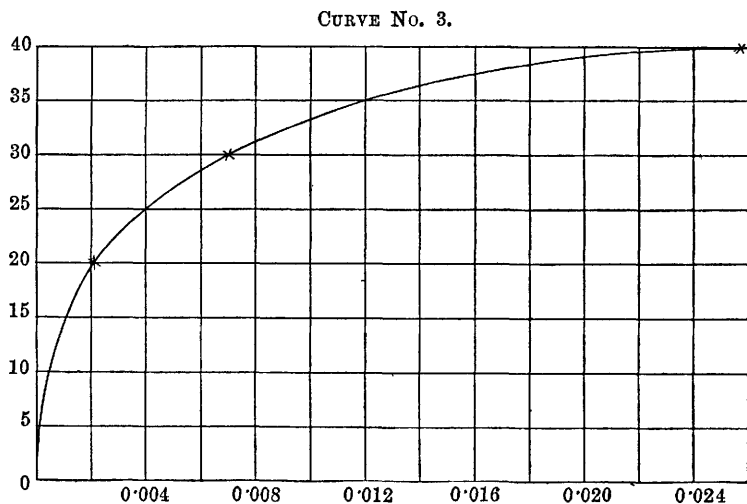
Mean of the two experiments, 0.002085.

| Series. | No. of observations. | Extreme values of <i>t</i> . | Extreme values of <i>x</i> . | <i>C</i> . | | |
|--|----------------------|------------------------------|--|------------|----------|---------|
| | | | | Lowest. | Highest. | Mean. |
| <i>Temperature 30°.</i> | | | | | | |
| I. <i>A</i> = 60·8 c.c. (12·5°, 740 mm.) | 11 | 40 to 122 | 28·6 c.c. to 52·2 c.c. (range 47 to 86 %) | 0·0069 | 0·00712 | 0·00702 |
| II. <i>A</i> = 60·9 c.c. (12·5°, 739 mm.) | 11 | 38 to 113 | 26·9 c.c. to 50·7 c.c. (range 44 to 84 %) | 0·00665 | 0·00720 | 0·0069 |
| | | | | | Mean... | 0·00696 |
| <i>Temperature 40°.</i> | | | | | | |
| I. <i>A</i> = 60·2 c.c. (12°, 745 mm.) | 8 | 8½ to 24 | 22·6 c.c. to 44·7 c.c. (range 37 to 74 %) | 0·0245 | 0·0256 | 0·0252 |
| II. <i>A</i> = 60·0 c.c. (12°, 747 mm.) | 8 | 8½ to 22 | 23·4 c.c. to 43·6 c.c. (range 40 to 72 %) | 0·0253 | 0·0268 | 0·0262 |
| | | | | | Mean... | 0·0257 |

We have for the values of C ,

| Temperature. | C . |
|--------------|----------|
| 20° | 0.002085 |
| 30 | 0.00696 |
| 40 | 0.0257 |

graphically represented by the following curve :



Hausser and Muller's results (*loc. cit.*), for diazo-*m*-toluene sulphate prepared in solution (that is, as above) diminished from 0.0305 to 0.0219 at 40°. The concentration in this experiment was the same as ours. Two other experiments with solutions of different concentration gave different, although still diminishing, values for C .

4. Diazo-*p*-toluene Chloride.

The diazo-salt was prepared from *p*-toluidine exactly as in the case of *o*-toluidine.

Temperature 30°.

| Series. | No. of observations. | Extreme values of t . | Extreme values of x . | C . | | |
|--------------------------------|----------------------|-------------------------|---|----------|----------|----------|
| | | | | Lowest. | Highest. | Mean. |
| $A=58.9$ c.c. (8°, 749 mm.) | 9 | 300 to 4310 | 7.8 c.c. to 54.6 c.c. (range 13 to 92 %) | 0.000202 | 0.000219 | 0.000209 |

DECOMPOSITION OF DIAZO-COMPOUNDS. PART I. 1427

Temperature 40°.

| 1. | | | 2. | | |
|----------------------------------|-----------|-----------|----------------------------------|-----------|-----------|
| <i>A</i> = 59.1 (8.5°, 748 mm.). | | | <i>A</i> = 59.1 (8.5°, 748 mm.). | | |
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 180 | 19.7 | 0.000978 | 210 | 22.3 | 0.000980 |
| 200 | 21.6 | 0.000988 | 230 | 23.9 | 0.000979 |
| 230 | 24.1 | 0.000989 | 260 | 26.4 | 0.000989 |
| 260 | 26.5 | 0.000994 | 301 | 29.4 | 0.000993 |
| 301 | 29.6 | 0.00100 | 368 | 34.0 | 0.001011 |
| 372 | 33.9 | 0.000995 | 454 | 39.0 | 0.001032 |
| 457 | 38.8 | 0.001011 | 491 | 40.7 | 0.001032 |
| 491 | 40.7 | 0.001032 | 580 | 43.5 | 0.000997 |
| 580 | 43.3 | 0.000988 | 630 | 45.4 | 0.001007 |
| 634 | 45.0 | 0.000981 | | | |
| Range 33 to 75 %. Mean 0.000995 | | | Range 37 to 76 %. Mean 0.001002 | | |

Mean of the two experiments, 0.000999.

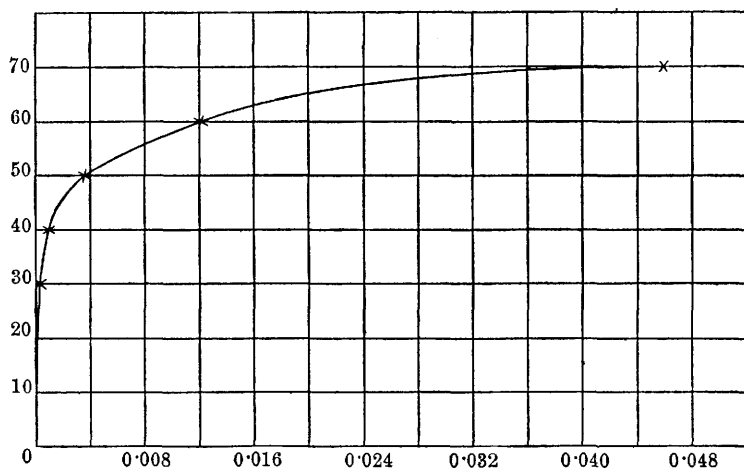
| Series. | No. of observations. | Extreme values of <i>t.</i> | Extreme values of <i>x.</i> | <i>C.</i> | | |
|---|----------------------|-----------------------------|--|-----------|----------|---------|
| | | | | Lowest. | Highest. | Mean. |
| <i>Temperature 50°.</i> | | | | | | |
| I. <i>A</i> = 59.1 c.c. (8°, 747 mm.) | 9 | 66 to 208 | 24.5 c.c. to 48.3 c.c. (range 41 to 81 %) | 0.00352 | 0.00368 | 0.00361 |
| II. <i>A</i> = 59.1 c.c. (8°, 747 mm.) | 6 | 80 to 144 | 28.2 c.c. to 41.2 c.c. (range 47 to 70 %) | 0.00352 | 0.00360 | 0.00356 |
| III. <i>A</i> = 59.1 c.c. (8°, 747 mm.) | 5 | 80 to 181 | 28.2 c.c. to 45.7 c.c. (range 47 to 78 %) | 0.00352 | 0.00358 | 0.00356 |
| | | | | | Mean... | 0.00358 |
| <i>Temperature 60°.</i> | | | | | | |
| I. <i>A</i> = 59.5 c.c. (8°, 742 mm.) | 8 | 20 to 46 | 24.5 c.c. to 42.4 c.c. (range 41 to 71 %) | 0.0115 | 0.0119 | 0.0118 |
| II. <i>A</i> = 59.6 c.c. (8°, 740 mm.) | 9 | 20 to 62 | 24.7 c.c. to 48.8 c.c. (range 41 to 81 %) | 0.0116 | 0.0128 | 0.0122 |
| | | | | | Mean... | 0.0120 |
| <i>Temperature 70°.</i> | | | | | | |
| I. <i>A</i> = 59.5 c.c. (8.5°, 743 mm.) | 8 | 6 to 15 | 27.3 c.c. to 46.8 c.c. (range 46 to 78 %) | 0.0445 | 0.0463 | 0.0455 |
| II. <i>A</i> = 59.5 c.c. (8.5°, 743 mm.) | 11 | 4 to 17 | 20.2 c.c. to 49.3 c.c. (range 34 to 82 %) | 0.0450 | 0.0479 | 0.0467 |
| | | | | | Mean... | 0.0461 |

Collecting all the results for diazo-*p*-toluene chloride, we have:

| Temperature. | <i>C</i> . |
|--------------|------------|
| 30° | 0·000209 |
| 40 | 0·000999 |
| 50 | 0·00358 |
| 60 | 0·0120 |
| 70 | 0·0461 |

or graphically the following curve:

CURVE No. 4.



Hantzsch obtained the value 0·000081 at 25°, and Hausser and Muller numbers diminishing from 0·024 to 0·018 for the sulphate at 64°.

The above experiments on diazobenzene and the diazotoluenes extend over a wide range of temperature, and show that at all these temperatures the rate of decomposition is in accordance with the law, thus confirming Hantzsch's results at a low temperature and being opposed to those of Hausser and Muller at higher temperatures. Of the substances still to be described, only one (diazo-*p*-sulphanilic acid) was examined by Hausser and Muller, who found a constant value for *C*. We have therefore only measured the rates of decomposition of the following diazo-salts at one or two temperatures.

5. *Diazo-p-sulphanilic Acid.*

17.3 Grams of sulphanilic acid were dissolved in water and caustic soda. Forty c.c. of hydrochloric acid of sp. gr. 1.16 (4/10 mol.) were added and then 6.9 grams of sodium nitrite in solution. The solution of diazo-salt was made up to 1400 c.c. and then contained 15.7 grams of diazo-salt per litre. Thirty-five c.c. were taken in each experiment.

Temperature 60°.

| 1. $A = 58.7$ (8°, 752 mm.). | | | 2. $A = 58.7$ (8°, 752 mm.). | | |
|---------------------------------|-----------|-----------|---------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 25 | 18.1 | 0.00640 | 11 | 8.6 | 0.00625 |
| 30 | 21.3 | 0.00652 | 15 | 11.8 | 0.00649 |
| 35 | 23.9 | 0.00648 | 20 | 15.5 | 0.00665 |
| 45 | 28.3 | 0.00635 | 32 | 22.3 | 0.00648 |
| 51 | 31.6 | 0.00658 | 35 | 23.7 | 0.00641 |
| 59 | 33.4 | 0.00619 | 43 | 27.1 | 0.00625 |
| 66 | 35.7 | 0.00616 | 51 | 29.9 | 0.00606 |
| 76 | 38.9 | 0.00621 | 76 | 38.2 | 0.00601 |
| 90 | 42.9 | 0.00633 | 90 | 42.5 | 0.00621 |
| Range 30 to 72 %. Mean 0.00636 | | | Range 15 to 72 %. Mean 0.00631 | | |

Mean of the two experiments, 0.00633.

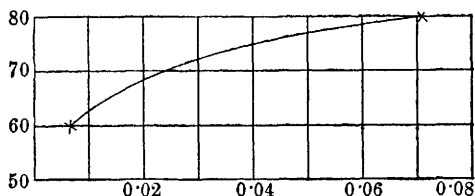
Temperature 80°.

| Series. | No. of observations. | Extreme values of <i>t.</i> | Extreme values of <i>x.</i> | <i>C.</i> | | |
|--------------------------------------|----------------------|-----------------------------|--|-----------|----------|--------|
| | | | | Lowest. | Highest. | Mean. |
| I. $A = 58.7$ c.c. (9°, 752 mm.) | 9 | 2 to 9 | 16.4 c.c. to 44.7 c.c. (range 28 to 75 %) | 0.0681 | 0.0711 | 0.0696 |
| II. $A = 58.7$ c.c. (9°, 752 mm.) | 8 | 2.5 to 8 | 20.2 c.c. to 42.9 c.c. (range 34 to 72 %) | 0.0712 | 0.0744 | 0.0723 |
| | | | | | Mean... | 0.0709 |

We have drawn a curve through the two points given by the above determination, and it is interesting to observe that from this curve the value for *C* at 64°, the temperature at which Hausser and Muller

made their experiments on this substance, corresponds almost exactly with the value they found, namely, 0.0106, as the mean of four experiments.

CURVE No. 5.



We are here, for the only time, in agreement with Hausser and Muller's results, and it is important to note that their experiments were made (1) with the solid diazo-compound, (2) in three different concentrations.

6. *Diazo-o-nitrobenzene Chloride.*

3.45 Grams of *o*-nitraniline (1/40 mol.) were dissolved in 11 c.c. of hydrochloric acid of sp. gr. 1.16 (4.5/40 mol.) and diazotised by the addition of a solution of 1.73 grams of sodium nitrite. The diazo-solution was made up to 700 c.c. Seventy c.c. of this solution were taken in each experiment.

This solution differs from the corresponding ones from aniline and the toluidines in being more dilute; instead of a diazo-solution containing 1/10 mol. in 1400 c.c., we have 1/20 mol. in the same volume, and, as is well known, it is necessary to use a fairly large excess of acid in order to diazotise the nitranilines successfully, so that we have here $4\frac{1}{2}$ mols. of acid to 1 mol. of base. We do not think that these changes are sufficiently great to prevent us from comparing the constants for the diazo-salts from the nitranilines with those from the other amines examined.

This diazo-salt is exceedingly stable: at 70°, only about 50 per cent. was decomposed after $17\frac{1}{2}$ hours, so that we have determined the rate of decomposition at 100°.

DECOMPOSITION OF DIAZO-COMPOUNDS. PART I. 1431

Temperature 100°.

| 1. $A=59.1$ (8.5°, 748 mm.). | | | 2. $A=59.1$ (8.5°, 748 mm.). | | |
|---------------------------------|-----------|-----------|---------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 7 | 5.1 | 0.00560 | 5.5 | 4.0 | 0.00553 |
| 17 | 11.5 | 0.00553 | 10 | 7.1 | 0.00556 |
| 20 | 13.2 | 0.00549 | 17 | 11.2 | 0.00537 |
| 31 | 19.5 | 0.00561 | 25 | 15.6 | 0.00532 |
| 35 | 21.5 | 0.00561 | 35 | 20.8 | 0.00538 |
| 45 | 26.1 | 0.00562 | 45 | 25.3 | 0.00539 |
| 50 | 28.3 | 0.00566 | 55 | 29.4 | 0.00543 |
| 70 | 35.5 | 0.00569 | 65 | 32.6 | 0.00536 |
| 80 | 38.6 | 0.00575 | 79 | 37.4 | 0.00551 |
| 90 | 41.2 | 0.00576 | 115 | 45.7 | 0.00560 |
| 100 | 43.5 | 0.00578 | 135 | 48.9 | 0.00565 |
| Range 9 to 73 %. Mean 0.00564 | | | Range 7 to 82 %. Mean 0.00546 | | |

Mean of the two experiments, 0.00555.

7. Diazo-*m*-nitrobenzene Chloride.

The diazo-salt was prepared from *m*-nitraniline exactly as in the case of *o*-nitraniline.

Temperature 80°.

| 1. $A=59.9$ (13°, 753 mm.). | | | 2. $A=59.9$ (13°, 753 mm.). | | |
|--------------------------------|-----------|-----------|--------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 74 | 24.1 | 0.00302 | 60 | 20.5 | 0.00303 |
| 81 | 26.1 | 0.00307 | 70 | 23.4 | 0.00307 |
| 93 | 29.1 | 0.00310 | 85 | 26.9 | 0.00305 |
| 99 | 30.6 | 0.00314 | 100 | 30.4 | 0.00308 |
| 148 | 39.5 | 0.00316 | 120 | 34.6 | 0.00312 |
| 164 | 41.7 | 0.00315 | 157 | 41.0 | 0.00319 |
| 181 | 44.5 | 0.00326 | 168 | 42.7 | 0.00323 |
| 212 | 47.7 | 0.00326 | 206 | 46.3 | 0.00313 |
| 230 | 49.5 | 0.00330 | 219 | 47.9 | 0.00319 |
| 254 | 50.3 | 0.00313 | | | |
| 277 | 52.6 | 0.00330 | | | |
| Range 40 to 88 %. Mean 0.00317 | | | Range 34 to 80 %. Mean 0.00312 | | |

Mean of the two experiments, 0.003145.

Temperature 100°.

| Series. | No. of observations. | Extreme values of <i>t</i> . | Extreme values of <i>x</i> . | <i>C</i> . | | |
|---|----------------------|------------------------------|--|------------|----------|--------|
| | | | | Lowest. | Highest. | Mean. |
| I. <i>A</i> = 58.2 c.c. (8°, 758 mm.) | 14 | 4 to 25 | 14.8 c.c. to 49.6 c.c. (range 25 to 83 %) | 0.0315 | 0.0332 | 0.0322 |
| II. <i>A</i> = 58.2 c.c. (8°, 758 mm.) | 14 | 2 to 23 | 8.3 c.c. to 48.2 c.c. (range 14 to 81 %) | 0.0324 | 0.0334 | 0.0329 |
| | | | | | Mean... | 0.0325 |

8. *Diazo-p-nitrobenzene Chloride.*

This diazo-salt was prepared from *p*-nitraniline exactly as in the case of *o*-nitraniline.

Temperature 80°.

| 1. | | | 2. | | |
|----------------------------------|------------|------------|----------------------------------|------------|------------|
| <i>A</i> = 58.3 (8.5°, 758 mm.). | | | <i>A</i> = 58.3 (8.5°, 758 mm.). | | |
| <i>t</i> . | <i>x</i> . | <i>C</i> . | <i>t</i> . | <i>x</i> . | <i>C</i> . |
| 22 | 18.1 | 0.00734 | 25 | 19.9 | 0.00726 |
| 25 | 20.4 | 0.00748 | 28 | 22.0 | 0.00735 |
| 28 | 22.3 | 0.00748 | 32 | 24.6 | 0.00744 |
| 32 | 24.9 | 0.00756 | 36 | 26.9 | 0.00747 |
| 36 | 27.0 | 0.00750 | 41 | 29.6 | 0.00751 |
| 41 | 29.6 | 0.00751 | 46 | 31.5 | 0.00734 |
| 46 | 31.4 | 0.00730 | 53 | 34.7 | 0.00741 |
| 53 | 34.5 | 0.00734 | 58 | 36.6 | 0.00740 |
| 66 | 38.6 | 0.00714 | 66 | 39.0 | 0.00727 |
| 76 | 42.0 | 0.00728 | 71 | 40.4 | 0.00722 |
| 82 | 43.8 | 0.00737 | 89 | 45.1 | 0.00725 |
| 96 | 47.0 | 0.00742 | 96 | 46.5 | 0.00723 |
| Range 31 to 80 %. Mean 0.00739 | | | Range 34 to 80 %. Mean 0.00734 | | |

Mean of the two experiments, 0.00736.

The foregoing figures show that, in each case, the reaction is a unimolecular one, and before describing our experiments on the remaining substances, namely, aminoacetanilide and the diamines of the benzene series, we shall now discuss the results up to this point, as the decomposition of the diazo-salts of the latter substances is not quite so simple. In most of the above series of experiments, the value

of C seems to rise to a maximum at about the point of 50 per cent. decomposition. This is no doubt due to the slight increase of temperature in the flask (sometimes 0.5° to 1°) produced by the heat evolved in the reaction.

Before proceeding to compare these constants more closely, we must here remark that the solutions of the diazo-salts from aniline, the toluidines, and sulphanilic acid were all equivalent, that is, contained the same number of molecules. The amount of free hydrochloric acid was the same, but there was an extra mol. of sodium chloride present in the diazo-solution of sulphanilic acid, as we started from the sodium salt.

In the case of the diazo-salts from the nitranilines, although their diazo-solutions were all exactly equivalent among themselves, yet it was necessary to use a larger amount of hydrochloric acid, and it was found more convenient to make up the solutions to half the concentration of the previous ones.

We think that we are quite justified in comparing the constants of the diazonitrobenzene salts with those of the other substances, as Hantzsch has shown very clearly (*loc. cit.*) that difference in concentration has no effect on the rate of the reaction in the substances which he examined, and this is, of course, applicable to all unimolecular reactions. Hantzsch has also shown that the presence of hydrochloric acid has no influence on the rate of decomposition.

Comparing first of all the values for C for the three diazotoluene chlorides and diazobenzene chloride, we find that the introduction of the methyl group in the ortho- or meta-position in the latter makes the compound less stable, but in the para-position renders it much more stable.

Of the diazo-*o*- and diazo-*m*-toluene chlorides, the *m*-compound is the less stable. This conclusion is the same as that at which Hausser and Muller arrived (*Bull. Soc. Chim.*, 1893, [iii], 9, 353).

The introduction of the acid groups SO_3H and NO_2 has the effect of enormously increasing the stability. Diazosulphanilic acid is much more stable than diazo-*p*-toluene chloride, and all three diazonitrobenzene chlorides are much more stable than diazosulphanilic acid.

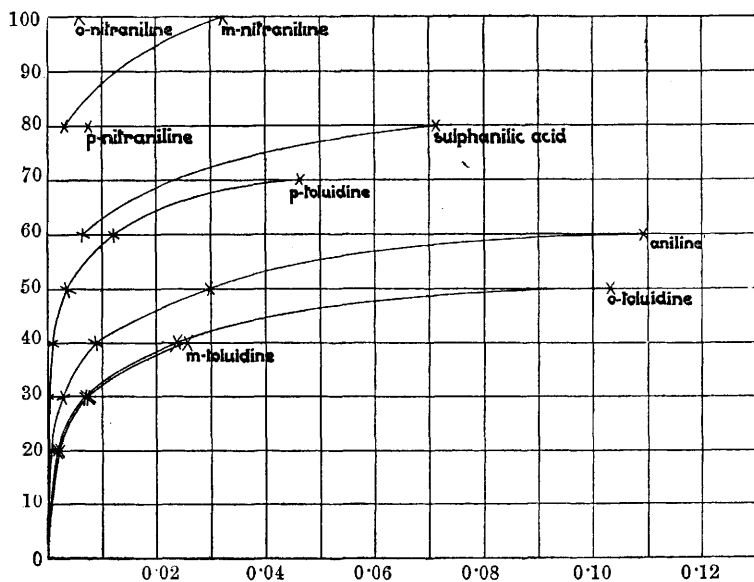
In the case of the diazonitrobenzene salts, the most stable is the ortho-, then comes the meta-, and lastly, the para-compound. The influence of the position of the nitro-group on the stability of the diazo-compound is thus quite different from that of the methyl group.

We have collected the values for C in the following table and curve (p. 1434):

| Temp- erature. | Diazo-salts from | | | | | | | |
|-------------------|------------------|------------|----------|----------|---------------------------|--------------|---------|---------|
| | Aniline. | Toluidine. | | | Sulph- anilic acid. | Nitraniline. | | |
| | | Ortho. | Meta. | Para. | | Ortho. | Meta. | Para. |
| 20° | 0·00072 | 0·00187 | 0·00208 | — | — | — | — | — |
| 30 | 0·00295 | 0·00706 | 0·00696* | 0·000209 | — | — | — | — |
| 40 | 0·00877 | 0·0238 | 0·0257 | 0·000999 | — | — | — | — |
| 50 | 0·0298 | 0·1027 | — | 0·00358 | — | — | — | — |
| 60 | 0·109 | — | — | 0·012 | 0·00633 | — | — | — |
| 70 | — | — | — | 0·0461 | — | — | — | — |
| 80 | — | — | — | — | 0·0709 | — | 0·00314 | 0·00736 |
| 90 | — | — | — | — | — | — | — | — |
| 100 | — | — | — | — | — | 0·00555 | 0·0325 | — |

* This figure appears to be slightly too low.

CURVE NO. 6.



Before we can compare the stability of, for instance, diazo-*p*-nitrobenzene chloride with the diazo-chlorides from aniline and the toluidines, it is necessary to know whether the ratio of the constants at different temperatures is the same.

By putting the value of C for diazobenzene chloride at each temperature equal to unity, and calculating the corresponding values of C for the three diazotoluene chlorides, we obtain the following :

| Temperature. | Diazobenzene chloride. | Diazo- <i>o</i> -toluene chloride. | Diazo- <i>m</i> -toluene chloride. | Diazo- <i>p</i> -toluene chloride. |
|--------------|------------------------|------------------------------------|------------------------------------|------------------------------------|
| 20° | 1 | 2·6 | 2·9 | — |
| 30 | 1 | 2·4 | 2·36 * | 0·07 |
| 40 | 1 | 2·7 | 2·9 | 0·11 |
| 50 | 1 | 3·4 | — | 0·12 |
| 60 | 1 | — | — | 0·11 |

* See note on previous page.

We shall, therefore, not be far from the truth if we compare diazo-*p*-nitrobenzene chloride (at 80°) with diazosulphanilic acid (at 80°), diazosulphanilic acid (at 60°) with diazobenzene chloride or diazo-*p*-toluene chloride (at 60°), and hence obtain a comparison between the stabilities of these diazo-salts.

Carrying this out, and putting the value of C equal to unity for each substance successively, we obtain the following numbers, which show the relative rate of decomposition of each diazo-salt for any given temperature. (For comparing diazobenzene chloride and the diazo-toluene chlorides, the constants at 40° have been used.)

Diazo-salts from

| Aniline. | Toluidine. | | | Sulph-anilic acid. | Nitriline. | | |
|----------|------------|-------|-------|--------------------|------------|-------|-------|
| | Ortho. | Meta. | Para. | | Ortho. | Meta. | Para. |
| — | 1 | 1·08 | — | — | — | — | — |
| 1 | 2·7 | 2·9 | — | — | — | — | — |
| 8·7 | 23·8 | 25·7 | 1 | — | — | — | — |
| 16·6 | 45·1 | 48·7 | 1·9 | 1 | — | — | — |
| 160 | 435 | 470 | 18·3 | 9·6 | — | — | 1 |
| 378 | 1028 | 1110 | 43·1 | 22·8 | — | 1 | 2·36 |
| 2195 | 5962 | 6436 | 250 | 132 | 1 | 5·8 | 13·7 |

The very great stability of diazo-*o*-nitrobenzene chloride is thus seen at a glance; it is more than 6000 times as stable as diazo-*m*-toluene chloride, the rate of decomposition of the latter being 6436 times greater than that of the former. We may here remark that Hantzsch

found diazo-*p*-toluene chloride to be about 8 times more stable than diazobenzene chloride; this agrees with our result (8.7).

By using this table and the table of constants, it is easy to find what percentage of any of the above diazo-salts would be decomposed in a given time. For instance, if a solution of diazo-*p*-nitrobenzene chloride is prepared and kept at 20° for 1 week, the amount of decomposition may be calculated as follows.

The constant at 20° would be the constant for diazobenzene chloride (0.00072) divided by 160 = 0.0000045; $t = 1$ week = 10080 minutes, so we have:

$$C = \frac{1}{t} \log \frac{A}{A-x};$$

$$0.0000045 = \frac{1}{10080} \log \frac{100}{100-x}, \text{ whence}$$

$$x = 9.9;$$

thus, 9.9 per cent. of the diazo-solution at 20° would be decomposed in one week.

*9-Diazo-*p*-acetaminobenzene Chloride.*

Fifteen grams of *p*-aminoacetanilide (1/10 mol.) were dissolved in 30 c.c. of hydrochloric acid of sp. gr. 1.16 (3/10 mol.), the solution cooled, and 6.9 grams of sodium nitrite added. The solution thus obtained was made up to 1400 c.c. and contained 19.75 grams of diazo-salt per litre.

We have measured the rate of decomposition of the diazoacetanilide at 80° and 100°, and at each temperature find that the value of C diminishes very rapidly.

Temperature 80°.

| 1. $A = 58.6$ (8.8°, 756 mm.). | | | 2. $A = 58.6$ (8.8°, 756 mm.). | | |
|-----------------------------------|------|---------|-----------------------------------|------|---------|
| $t.$ | $x.$ | $C.$ | $t.$ | $x.$ | $C.$ |
| 20 | 7.6 | 0.00301 | 35 | 10.5 | 0.00245 |
| 56 | 15.1 | 0.00231 | 69 | 17.0 | 0.00215 |
| 95 | 19.4 | 0.00184 | 94 | 19.3 | 0.00184 |
| 392 | 25.8 | 0.00064 | 334 | 25.5 | 0.00074 |
| 1238 | 36.7 | 0.00034 | 1119 | 37.1 | 0.00039 |

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Temperature 100°. $A = 58.6$ (8°, 751 mm.).

| <i>t.</i> | <i>x.</i> | <i>C.</i> |
|-----------|-----------|-----------|
| 3 | 8.9 | 0.0238 |
| 10 | 18.1 | 0.016 |
| 47 | 27.7 | 0.0059 |
| 173 | 39.4 | 0.0028 |
| 282 | 45.3 | 0.0023 |
| 472 | 51.6 | 0.0019 |

The reaction is thus not a unimolecular one, being obviously complicated by the simultaneous decomposition of the diazo-salt and elimination of the acetyl group by the free mineral acid.

By using acetic acid instead of hydrochloric acid, the hydrolysis does not take place, and the reaction proceeds in accordance with the law.

The *p*-aminoacetanilide was diazotised as before, but 3/10 mol. of acetic acid was used in place of the mineral acid.

Temperature 80°.

| 1. $A = 61.6$ (19°, 752 mm.). | | | 2. $A = 61.6$ (19°, 752 mm.). | | |
|----------------------------------|-----------|-----------|----------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 3 | 4.5 | 0.0110 | 6 | 8.6 | 0.0109 |
| 4 | 6.3 | 0.0117 | 8 | 11.1 | 0.0108 |
| 6 | 9.5 | 0.0121 | 10 | 13.2 | 0.0105 |
| 8½ | 12.6 | 0.0117 | 12 | 15.1 | 0.0102 |
| 10 | 14.2 | 0.0114 | 14 | 17.1 | 0.0101 |
| 12 | 16.3 | 0.0111 | 17 | 20.3 | 0.0102 |
| 14 | 18.5 | 0.0111 | 20 | 23.5 | 0.0104 |
| 17 | 21.3 | 0.0108 | 24 | 27.5 | 0.0107 |
| 20 | 24.3 | 0.0109 | 28 | 31.1 | 0.0109 |
| 23 | 27.3 | 0.0111 | 36 | 37.4 | 0.0113 |
| 28 | 31.6 | 0.0112 | 62 | 48.5 | 0.0108 |
| 33 | 35.2 | 0.0111 | | | |
| 36 | 36.8 | 0.0110 | | | |
| 40 | 38.8 | 0.0108 | | | |
| 48 | 42.2 | 0.0104 | | | |
| 60 | 46.3 | 0.0101 | | | |
| Range 7 to 75 %. Mean 0.0111. | | | Range 14 to 78 %. Mean 0.0106. | | |

Mean of the two experiments, 0.01085.

The diazoacetate is thus about 6.5 times more stable than diazo-sulphanilic acid.

In examining the tetrazo-salts prepared from the diamines, benzidine, tolidine, dianisidine, and *oo*-dichlorobenzidine, we have observed singular differences in their behaviour.

It is obvious that there might be a difference in the stability of the diazo-groups of any one substance. If this were the case, the reaction could not proceed unimolecularly, as an intermediate substance would be formed containing a single diazo-group, which would then proceed to evolve nitrogen.

The effect of this on the value of *C* (calculated as if the formula for a unimolecular reaction applied in this case) would be either to diminish or increase it.

In two cases, namely, the tetrazo-salts from benzidine and tolidine, the value of *C* gradually diminishes; in the case of the tetrazo-salt from dianisidine, the value increases, but in the case of the tetrazo-salt from *oo*-dichlorobenzidine, the value is constant, showing that the two diazo-groups in this substance are decomposed at the same rate.

10. Tetrazodiphenyl Chloride.

9.2 Grams of benzidine (1/20 mol.) were dissolved in 30 c.c. of hydrochloric acid of sp. gr. 1.16 (3/10 mol.), the solution cooled, diazotised with 6.9 grams of sodium nitrite, and made up to 1400 c.c. Thirty-five c.c. were taken for the experiments:

Temperature 50°.

| 1. <i>A</i> = 60.1 (10°, 740 mm.). | | | 2. <i>A</i> = 60.1 (10°, 740 mm.). | | |
|---------------------------------------|-----------|-----------|---------------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 100 | 22.1 | 0.00203 | 100 | 21.9 | 0.00201 |
| 140 | 28.0 | 0.00200 | 140 | 27.8 | 0.00198 |
| 189 | 33.0 | 0.00187 | 189 | 33.2 | 0.00189 |
| 232 | 36.5 | 0.00179 | 232 | 37.0 | 0.00184 |
| 420 | 45.5 | 0.00151 | 420 | 45.4 | 0.00151 |

Temperature 60°. $A = 59.0$ (10°, 754 mm.).

| <i>t.</i> | <i>x.</i> | <i>C.</i> |
|-----------|-----------|-----------|
| 33 | 23.3 | 0.0066 |
| 53 | 31.2 | 0.0062 |
| 71 | 35.7 | 0.0057 |
| 95 | 40.2 | 0.0052 |
| 248 | 50.5 | 0.0034 |

The reaction is thus not a unimolecular one, as the value of *C* is not constant. We are of opinion that the intermediate compound, diazo-*p*-hydroxydiphenyl chloride, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$, is continually being formed and decomposed.

11. *Tetrazoditolyl Chloride.*

The solution of this salt was prepared as the preceding one, substituting 10.6 grams of *o*-tolidine for the benzidine :

Temperature 50°.

| 1. $A = 58.5$ (9°, 757 mm.). | | | 2. $A = 58.5$ (9°, 757 mm.). | | |
|---------------------------------|-----------|-----------|---------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 36 | 23.6 | 0.0062 | 36 | 22.5 | 0.0058 |
| 57 | 30.9 | 0.0057 | 57 | 30.6 | 0.0056 |
| 79 | 36.6 | 0.0054 | 79 | 36.5 | 0.0054 |
| 104 | 41.2 | 0.0051 | 104 | 40.5 | 0.0049 |
| 144 | 45.1 | 0.0044 | 143 | 43.8 | 0.0042 |
| 309 | 52.3 | 0.0031 | 385 | 51.2 | 0.0023 |

Here, again, the reaction is not unimolecular, probably due to the formation and decomposition of the intermediate diazo-*p*-hydroxyditolyl chloride, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N}_2 \cdot \text{Cl}$.

12. *Tetrazo-*oo*-dichlorodiphenyl Chloride.*

The solution of this salt was prepared as No. 10, substituting 12.6 grams of *oo*-dichlorobenzidine for the benzidine :

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Temperature 100°

| $A = 59.9$ (9.5° , 741 mm.). | | |
|--------------------------------------|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 9 | 3.9 | 0.0032 |
| 20 | 7.5 | 0.0029 |
| 46 | 15.2 | 0.0028 |
| 109 | 31.1 | 0.0029 |
| 161 | 38.9 | 0.0028 |
| 185 | 43.0 | 0.0030 |
| 202 | 45.3 | 0.0030 |

Range 6.5 to 75 %. Mean 0.00294.

The decomposition in this case follows the law.*

13. *Tetrazo-oo-dimethoxydiphenyl Chloride.*

The solution of this salt was prepared as No. 10, substituting 12.2 grams of dianisidine for the benzidine :

Temperature 100°.

| 1. $A = 59.2$ (10° , 752 mm.). | | | 2. $A = 59.1$ (10° , 753 mm.). | | |
|---|-----------|-----------|---|-----------|-----------|
| <i>t.</i> | <i>x.</i> | <i>C.</i> | <i>t.</i> | <i>x.</i> | <i>C.</i> |
| 55 | 21.4 | 0.0035 | 61 | 22.6 | 0.0034 |
| 61 | 24.2 | 0.0037 | 73 | 28.0 | 0.0038 |
| 69 | 27.7 | 0.0040 | 92 | 35.6 | 0.0043 |
| 80 | 32.4 | 0.0043 | 104 | 39.8 | 0.0047 |
| 87 | 35.2 | 0.0045 | 116 | 43.4 | 0.0050 |
| 119 | 45.5 | 0.0053 | 129 | 47.0 | 0.0053 |
| 149 | 53.0 | 0.0065 | 156 | 51.9 | 0.0058 |

This reaction also is not unimolecular.

As the tetrazo-salt from dichlorobenzidine is the only salt which decomposes in accordance with the law, we can compare its constant only with those of the foregoing table. It is seen that its constant at 100° (0.00294) is less than that of *o*-nitroaniline (0.00555), so that it is 1.9 times more stable than the latter.

* The product of decomposition is not the dihydroxy-compound, as in the case of benzidine and tolidine. I am investigating this at present.—[J. C. C.]

As regards the remaining substances which do not conform to the law, we can of course only very roughly compare them among themselves.

We may say that the stability of the tetrazo-salt from dianisidine is of the same magnitude as that from dichlorobenzidine; then comes the tetrazo-salt from benzidine, about as stable as diazosulphanilic acid, and, lastly, the tetrazo-salt from tolidine is about five times as stable as diazobenzene chloride.

We are at present engaged in studying the decomposition of diazo-salts of the naphthalene series.

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