[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD COLLEGE]

RELATIVE RATES OF REDUCTION OF AROMATIC NITRO COMPOUNDS[1]

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The method recently developed[2] for a study of the valence forces influencing the carbon–halogen bond in halogen phenols and halogen naphthols has been applied, in a slightly modified form, to the determination of the relative rates of reduction of a number of aromatic nitro compounds. The work was undertaken to obtain quantitative data upon the effect of various groups upon the rate of reduction of the nitro group to the amino group by an acid stannous chloride solution. The work was extended to show that, in addition to the nature and position of the various groups introduced into the benzene nucleus, the speed of the reduction is influenced markedly by factors which control the hydrogen-ion concentration of the solution.

Method of Reduction.—The method of reduction was briefly as follows: exactly 50.00 cc. of an alcoholic hydrochloric acid solution was pipetted into a 300-cc. Erlenmeyer flask, the air was displaced by a stream of nitrogen, just enough weighed $SnCl_2 \cdot 2H_2O$ was introduced to make the solution equivalent to exactly 50.00 cc. of a tenth normal iodine solution, the flask was placed in a thermostat heated to 75°, and when the contents of the flask had reached this temperature, a weighed sample of the nitro compound was introduced. At the end of a definite period of time the flask was removed, cooled and the excess stannous chloride titrated with a standard tenth normal iodine solution.

The addition of a weighed sample of the solid $SnCl_2 \cdot 2H_2O$ for each reduction is more tedious than the former method of using a standard solution of this reducing agent, but this method has an advantage in that it permits of a more exact control of the concentration of the reducing agent; in the former procedure some oxidation inevitably took place during the preparation of the standard solution and we were never able to prepare two solutions of exactly the same reducing strength. The weight of the $SnCl_2 \cdot 2H_2O$ required to reduce 50.00 cc. of the $N/10$ iodine solution had to be determined by actual titration, for it was found that different samples of the salt of C. P. grade varied slightly in composition. The weight used in each of the reductions reported in this paper was 0.6000 g.

The alcoholic hydrochloric acid solution used in Table I was prepared by making up 20.00 cc. of 37% hydrochloric acid to exactly one liter with 95% alcohol. This concentration of acid was more than enough to form

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[1] Presented in substance before the Organic Division of the American Chemical Society at the Detroit Meeting, September, 1927.

[2] Sampey, THIS JOURNAL, 49, 2849 (1927).

both the stannic chloride salt and the hydrochloride of the amine. The concentration of the nitro compound taken for each reduction was exactly equivalent to the concentration of the stannous chloride solution, *e. g.*, 0.0700 g. of dinitrobenzene would oxidize as much stannous chloride as 0.1025 g. of nitrobenzene. Each of the nitro compounds was carefully purified before reduction.

TABLE I

RELATIVE RATES OF REDUCTION OF AROMATIC NITRO COMPOUNDS

Compound	Wt., g.	Time, min.	0.1 *N* I_2, cc.	Amt. red., %	Wt., g.	Time, min.	0.1 *N* I_2, cc.	Amt. red., %
Nitrobenzene	0.1025	15	34.7	30.6	0.1025	15	34.9	30.2
o-Nitrochlorobenzene	.1313	15	11.0	78.0	.1313	15	11.0	78.0
m-Nitrochlorobenzene	.1313	15	15.3	69.4	.1313	15	15.4	69.2
p-Nitrochlorobenzene	.1313	15	22.5	55.0	.1313	15	22.3	55.4
o-Nitrobromobenzene	.1683	15	11.5	77.0	.1683	15	11.4	77.2
m-Nitrobromobenzene	.1683	15	15.1	69.8	.1683	15	14.9	70.2
p-Nitrobromobenzene	.1683	15	20.9	58.2	.1683	15	21.0	58.0
o-Nitro-iodobenzene	.2075	15	11.6	76.8	.2075	15	11.8	76.4
m-Nitro-iodobenzene	.2075	15	14.6	70.8	.2075	15	14.5	71.0
p-Nitro-iodobenzene[a]	.2075	15	20.6	58.8	.2075	15	20.7	58.6
o-Nitrotoluene	.1141	15	31.0	38.0	.1141	15	31.1	37.8
m-Nitrotoluene	.1141	15	36.3	27.4	.1141	15	36.5	27.0
p-Nitrotoluene	.1141	15	39.8	20.4	.1141	15	39.6	20.8
m-Nitraniline	.1150	10	18.0	64.0	.1150	10	18.2	63.6
p-Nitraniline	.1150	15	35.5	29.0	.1150	15	35.2	29.6
o-Nitrophenol	.1158	15	32.2	35.6	.1158	15	32.3	35.4
m-Nitrophenol	.1158	15	37.7	24.6	.1158	15	37.4	25.2
p-Nitrophenol	.1158	15	45.5	9.0	.1158	15	45.7	8.6
o-Nitrobenzoic acid	.1390	15	25.5	49.0	.1390	15	25.4	49.2
m-Nitrobenzoic acid	.1390	15	23.5	53.0	.1390	15	23.6	52.8
p-Nitrobenzoic acid[a]	.1390	15	17.5	65.0	.1390	15	17.3	65.4
m-Dinitrobenzene	.0700	10	16.6	66.8	.0700	10	16.8	66.4
p-Dinitrobenzene	.0700	10	26.2	47.6	.0700	10	26.3	47.4
2,4-Dinitrochlorobenzene	.0844	10	20.7	58.6	.0844	10	20.6	58.8
2,4-Dinitrobromobenzene	.1028	10	16.7	66.6	.1028	10	16.9	66.2
2,4-Dinitrotoluene	.0759	10	15.7	68.6	.0759	10	16.0	68.0
2,4,6-Trinitrotoluene	.0630	8	18.0	64.0	.0630	8	17.8	64.4
2,4,6-Trinitrobenzoic acid	.0715	8	19.3	61.4	.0715	8	19.6	60.8

[a] Because of the insolubility of the nitro compound, it was added before the stannous chloride; the reduction was timed from the addition of the stannous chloride, after the solution reached the temperature of the thermostat.

One of the interesting observations to be made from Table I is found in the relative rates of reduction of the ortho, meta and para isomers of the same compounds: the meta isomer lies intermediate, instead of in contrast to the ortho and para; the ortho is reduced the most rapidly, the para most slowly in every case except with the three nitrobenzoic acids. It is also worth noting that the corresponding chloro-, bromo- and iodo-nitrobenzenes are reduced at nearly the same rate; this is in sharp contrast to the effects produced on the speed of reduction by the introduction of certain of the other groups. Table I is not as complete as desired, because a number of the nitro compounds prepared and purified were too colored after reduction to permit the detection of the end-point in the iodine titration.

From the previous work[3] on the removal of halogens by acids when ortho or para to amino groups, there was the possibility that the rate reported for the reduction of *o*- and *p*-nitro-iodobenzene and of 2,4-dibromonitrobenzene might also be due to the removal of the positive halogen. When samples of these halogen nitro compounds were heated for more than an hour in the presence of more than enough stannous chloride to reduce all the nitro groups, there was no removal of the halogen atoms. Only when the acidity of the solution was increased several fold did we note the removal of the halogen along with the reduction of the nitro group.

Effect of Hydrogen-Ion Concentration.—An increase in the hydrogen-ion concentration of the solution had a marked effect upon the rate of reduction of the nitro compounds. The alcoholic hydrochloric acid solutions used in Table II were prepared as follows:

Solution A	37% HCl, 10.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution B	37% HCl, 30.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution C	37% HCl, 50.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution D	37% HCl, 100.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.

The accuracy with which these solutions were made may be judged by the two check analyses, for a fresh solution was prepared for each reduction. The 100.00 cc. of water included in each of these solutions was added for reasons set forth in Table III. Exactly 50.00 cc. of each of these solutions was introduced into the Erlenmeyer flask for the reduction; the quantities of the *o*-nitrotoluene and stannous chloride were the same as in Table I.

TABLE II

EFFECT OF ACIDITY UPON THE RATE OF REDUCTION OF *o*-NITROTOLUENE

	Soln. A		Soln. B		Soln. C		Soln. D	
Reduction time, min.	15	15	15	15	15	15	15	15
0.1 *N* iodine, cc.	37.5	37.4	32.5	32.7	28.8	28.9	18.1	17.9
Amt. reduced, %	25.0	25.2	35.0	34.6	42.4	42.2	63.8	64.2

The pronounced increase in the rate of reduction with an increase in the acidity of the solution becomes more interesting when compared with the results of Adams, Cohen and Rees[4] on the reduction of aromatic nitro compounds to amines with hydrogen and platinum-oxide platinum black as a catalyst; they found that appreciable quantities of hydrochloric acid lowered the rate of reduction.

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[3] Nicolet and Sampey, THIS JOURNAL, **49**, 1796 (1927).

[4] Adams, Cohen and Rees, *ibid.*, **49**, 1093 (1927).

Inhibitory Effect of Water.—In the runs reported in Table II, 100.00 cc. of water was added to each alcoholic solution in order to lessen any effects which might have been produced by a change in the moisture content as the acidity of the solution was increased. In Table III evidence is presented of just how pronounced is the inhibitory effect of water on the rate of reduction. The solutions used in Table III were made up as follows:

Solution A	37% HCl, 10.00 cc.	....	Abs. alcohol to 500.00 cc.
Solution B	37% HCl, 10.00 cc.	Water, 30.00 cc.	Abs. alcohol to 500.00 cc.
Solution C	37% HCl, 10.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution D	37% HCl, 10.00 cc.	Water, 190.00 cc.	Abs. alcohol to 500.00 cc.

No effort was made to prepare a more anhydrous solution than Solution A, because of the insoluble nature of $SnCl_2 \cdot 2H_2O$ in such a solution. The concentrations of *o*-nitrotoluene and stannous chloride were the same as in the previous reductions.

TABLE III

EFFECT OF MOISTURE UPON THE RATE OF REDUCTION OF *o*-NITROTOLUENE

	Soln. A		Soln. B		Soln. C		Soln. D	
Reduction time, min.	15	15	15	15	15	15	15	15
0.1 *N* iodine, cc.	29.5	29.6	31.3	31.0	37.5	37.4	40.8	41.0
Amt. reduced, %	41.0	40.8	37.4	38.0	25.0	25.2	18.4	18.0

Effect of Stannous Chloride Concentration.—In Table IV the concentration of the stannous chloride was varied over a wide range. If we assume from the equation

$$\underset{a}{3SnCl_2} + \underset{b}{RNO_2} + 7HCl = 3SnCl_4 + RNH_2 \cdot HCl + 2H_2O$$

that each molecule of RNO_2 which is reduced is done so rapidly and completely, then at the time t when we measure $a-x$, we must consider that the concentration of the nitro compound, b, has become $b-x/3$; *i. e.*, three moles of stannous chloride have been used for each mole of RNO_2 disappearing. Then from the integration of the equation

$$\frac{dx}{dt} = K(a - x)\left(b - \frac{x}{3}\right)$$

we obtain

$$K = \frac{-3}{t(3b - a)} \ln \frac{a(3b - x)}{3b(a - x)}$$

This equation can be used except where $a = 3b$; in Run III below, where $a = 3b$, the integration of the equation

$$\frac{dx}{dt} = \frac{K}{3}(a - x)^2$$

becomes

$$K = \frac{3x}{at(a - x)}$$

In Table IV are set forth the results of substituting the data in the above equations when the concentration of the stannous chloride was increased ten-fold. In order to reduce the effects of any change in hydrogen-ion concentration, acetic acid was used as the solvent: 50.00 cc. of water and 10.00 cc. of 37% hydrochloric acid were added to 500.00 cc. of glacial acetic acid; 50.00 cc. of this solution and 0.1313 g. (0.0167 moles) of *m*-nitrochlorobenzene were introduced into an Erlenmeyer flask for each reduction. The amounts of stannous chloride ranged from 0.1500 g. to 1.5000 g., which gave a concentration in terms of moles, estimated from titrations against a standard iodine solution, of 0.0125 to 0.1250.

TABLE IV

EFFECT OF STANNOUS CHLORIDE CONCENTRATION ON THE REDUCTION OF *m*-NITROCHLOROBENZENE

Run	t, min.	a	x	$a - x$	$3b - x$	K
I	15	0.0125	0.0072	0.0053	0.0428	−3.75
II	15	.0250	.0133	.0117	.0368	3.59
III	15	.0500	.0247	.0253	.0253	3.90
IV	15	.0625	.0286	.0339	.0215	3.76
V	15	.0750	.0315	.0435	.0186	3.59
VI	15	.1125	.0384	.0741	.0117	3.31
VII	15	.1250	.0401	.0849	.0100	3.28

Summary

1. A table is given of the relative rates of reduction to amines of twenty-eight aromatic nitro compounds by an acid stannous chloride solution.
2. An increase in the hydrogen-ion concentration of the stannous chloride solution increases the speed of the reduction.
3. Water has an inhibitory effect upon the speed of the reduction.
4. When the stannous chloride concentration is varied ten-fold, constants calculated for a second order reaction hold well for such a complex system.

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