

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Kinetics of the Reduction of Aromatic Nitro Compounds with Tin and Hydrochloric Acid¹

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Recent work in this Laboratory has shown that by use of an inert atmosphere and low acid concentration the reaction³ could be successfully

$$3\text{Sn} + \text{ArNO}_2 + 6\text{HCl} \longrightarrow 3\text{SnCl}_2 + \text{ArNH}_2 + 2\text{H}_2\text{O}$$

isolated from side reactions, and thus could be used as the basis of an improved method for the quantitative determination of aromatic nitro groups.⁴ Since the reaction was quantitative and could be thus isolated from side reactions, kinetic studies of the reaction were feasible, especially since the reaction can be readily followed analytically. This paper presents the results of such studies in which cylinders of metallic tin were rotated at constant speed in acid solution of aromatic nitro compound and the course of the reaction followed by withdrawing samples and determining the concentration of tin compounds volumetrically with standard iodine and thiosulfate.

Prins⁵ and King⁶ showed that the rate of solution of zinc^{5,6} and lead⁶ in acid was proportional to the amount of nitrobenzene⁵ or *p*-nitrophenol⁶ present as oxidant or depolarizer. Their studies measured initial rates and were primarily concerned with solution of the metal in acid rather than the fate of the depolarizer; consequently no information was obtained concerning the mechanism of the reduction of the aromatic nitro compounds.

Our studies sought first to determine whether the reaction is diffusion controlled, as appears to be the case in the work cited^{5,6}; second, to establish a mechanism and rate law covering the entire course of the reaction; and third, to determine from the kinetic data whether the reduction of the nitro group is a single step process or proceeds through intermediates.

The reaction we have chosen is peculiarly suited to study of this last point, since the stannous chloride produced in the reaction will react relatively slowly with the nitro compounds, yet will reduce any intermediate reduction products very rapidly. Thus it was hoped that the amount of stannic compounds found would be descriptive of the intermediate reduction products.

(1) Presented before the 116th meeting of the American Chemical Society from a dissertation submitted by Cecil E. Vanderzee in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate College of the State University of Iowa, June, 1949.

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(3) Throughout this paper the abbreviation Ar will be used to designate the aromatic nucleus plus its substituents other than the nitro group.

(4) Vanderzee and Edgell, *Anal. Chem.*, **22**, 572 (1950).

(5) Prins, *Rec. trav. chim.*, **42**, 473, 942 (1923).

(6) King and Schack, *This Journal*, **57**, 1212 (1935).

Experimental

Apparatus and Materials.—Reagent grade tin sticks were thoroughly cleaned, then melted in 1 by 8 in. test-tubes and the molten metal cooled slowly to promote grain growth and to prevent a "pipe" from forming in the center of the specimen. After machining, the cylinders were about 2 cm. in diameter and 10 cm. long. A hole about 1.5 in. deep was drilled in one end and threaded to accommodate a 0.25 in. steel rod used as a stirring shaft. A flange about 1.5 cm. in diameter welded on the shaft above the threaded portion served to seat the cylinder. The lower portion of the shaft, including the flange, was covered with a piece of 0.25 in. gum rubber tubing, which in turn was covered with a heavy coating of "tygon" paint. Before assembling the shaft and tin cylinder, the ends of the cylinder were covered with "tygon" paint, so that in operation only the cylindrical face of the cylinder came in contact with the reaction mixture.

The stirring shaft was rotated at constant speed by a motor with a variable speed cone drive. A worm driven gear with a reduction ratio of 1:100 was mounted in line with the stirring shaft and afforded a convenient means of determining the stirring speed with a stopwatch.

The reaction vessel was a 1250-ml. wide mouth reagent bottle, whose useful capacity was 1200 ml. A slot cut in the screw cover afforded a means of removing and replacing the cover during a run, and furnished an opening for the sampling pipet as well as for the entrance of a gas delivery tube carrying carbon dioxide. Temperature within the vessel was maintained constant within 0.02°.

Conductivity water was used in all solutions and reaction mixtures. The hydrochloric acid used was the constant boiling material obtained by distilling C. p. hydrochloric acid, properly diluted, through an all glass system containing a Vigreux column. The *p*-nitrophenol was a Merck product which had been recrystallized from thiophene-free benzene with slow cooling. The long needles, almost colorless and transparent, were washed with pure solvent and dried for an hour at 50°, then broken up and dried for twenty-four hours in a vacuum desiccator. Other nitro compounds used were purified in a similar manner from methanol-water mixtures.

Procedure.—Before making any runs with a cylinder, the amorphous metal produced by machining was removed by rotating the cylinder in a weak hydrochloric acid solution containing a small amount of oxidant (nitric acid or nitrophenol).

In order to secure reproducible results a standard cleaning procedure was used in preparing the cylinder before each run. This consisted of first washing the cylinder with water and wiping with wet filter paper. Then the cylinder was rotated for three to five minutes in methanol to remove any traces of oil or grease. It was then rotated for two to three minutes in 6 *N* hydrochloric acid to ensure removal of any oxide film. On removal from the acid solution the cylinder was washed quickly with water and the run started within five minutes. After completion of a run the cylinder was wiped with wet filter paper and washed with water. At the end of each run a very thin black deposit was observed on the cylinder when it was removed from the reaction mixture. This deposit was easily removed by wiping the cylinder with wet filter paper. To test the effect of this deposit, runs were made in which the cylinder was removed and cleaned by the standard cleaning procedure at frequent intervals during the run. These runs were no different from runs which were not interrupted for cleaning.

The diameter of the cylinder was determined before each

run and the stirring speed adjusted to give a constant peripheral velocity.

Reaction mixtures were made up to contain 0.005 to 0.01 mole of nitro compound per liter. They were freshly prepared before each run by weighing out the desired amount of nitro compound and dissolving it in the proper amount of conductivity water and constant boiling hydrochloric acid. The water had recently been boiled and transferred to tightly stoppered bottles at 85 to 90°, so that the oxygen content of the solution was estimated to be about the same as that of water at 80°. Throughout each run the reaction mixture was protected from oxygen by means of a steady stream of carbon dioxide.

Sampling was done with 10-ml. pipets, cleaned and dried before taking each sample. Each pipet was adjusted to withdraw the same amount of solution with enough excess to allow for careful adjustment of the meniscus before discharging the sample. The time of sampling was taken as the mid-point of filling the pipet.

Analytical Procedures.—Stannous tin was determined by discharging samples of reaction mixture into an excess of standard iodine (0.01 to 0.015 *N*) under an inert atmosphere and titrating the excess iodine with standard thiosulfate (0.005 to 0.01 *N*), adding starch indicator just before the end-point was reached. Because with such dilute reagents the effect of induced oxidation⁷ might be serious, the validity of the procedure was tested by comparing results of analyses made with air-free and ordinary iodine solutions. Excellent agreement was observed, provided the acidity of the sample of stannous tin did not exceed 2 *N* hydrochloric acid. Since most of the runs were made at much lower acidity (0.25 *N* hydrochloric acid), the analytical procedure was considered reliable.

Several procedures were tested for the determination of the total tin present in the reaction mixture. The method of Kolthoff,⁸ in which all of the tin is first reduced to the stannous state by powdered iron in an inert atmosphere, was found to be adaptable and reliable for use with dilute iodine solutions (0.1 to 0.15 *N*).

The iodine solutions were standardized by the usual methods against thiosulfate, using reagent grade potassium dichromate and potassium iodate, once recrystallized from conductivity water, as primary standards. The iodine solutions were also standardized against reagent grade tin by the method described above for total tin. The normalities obtained by the several methods were in excellent agreement with each other. Dilute solutions were prepared by proper dilution of standard stock solutions just before use.

Scope.—A systematic study of the reaction was made by varying independently the hydrochloric acid concentration, stirring rate and temperature; all these variables were studied using *p*-nitrophenol on account of its greater solubility. Some runs were made with other compounds to test the effect of structure⁹.

In the early exploratory runs and in those runs in which the hydrochloric acid concentration was varied, only the stannous content was determined. Both stannous and total tin were determined in the studies of stirring rate, temperature and structure. Some of these runs were carried out practically to completion and involved approximately twenty determinations of stannous tin and ten to twelve determinations of the total tin present. In the determinations at elevated temperatures, volumes were corrected for thermal expansion, using for these dilute acid solutions (0.25 *M*) the coefficient of thermal expansion of water. Since small differences appeared to exist between different cylinders, all runs made to explore a particular variable were made with the same cylinder.

The influence of the several factors investigated can be discussed best in terms of the mechanism of the reaction. For that reason we shall first develop the proposed mechanism and rate law, and then compare it with the experimental results.

The Mechanism and Rate Law

Since the reaction was expected to be diffusion controlled, the data from several exploratory runs were first tested against the equation for a first order rate law

$$-d(\text{ArNO}_2)/dt = kA(\text{ArNO}_2)/V \quad (1)$$

where *A* is the area of the cylinder and *V* is the volume of the reaction mixture. If the nitro compound were reduced cleanly to the amine at the surface, so that

$$3(\text{ArNO}_2)_0 = 3a = 3(\text{ArNO}_2) + \text{Sn}^{+2} \quad (2)$$

then

$$k = \frac{2.303 V}{A(t_2 - t_1)} \log \frac{3a - \text{Sn}_1^{+2}}{3a - \text{Sn}_2^{+2}} \quad (3)$$

The first order constants thus calculated were found to decrease during the reaction, the decrease being quite small over the first part but quite great after the reaction was 80 to 90% complete; this behavior was not dependent on the area-volume ratio.

In order to secure the advantages of graphical analysis in the examination of our experimental data, we have introduced the use of a specialized or "heterogeneous" time coordinate τ . It is defined through the relation

$$d\tau = Adt/V_1 \text{ or } \tau = A \sum_i \Delta t_i/V_1 \quad (4)$$

in which *A* is the area of the reacting surface, *t* is the time, *V*₁ is the volume of the reaction mixture during the time interval Δt_i that has elapsed between the removal of the (*i* - 1)th and the *i*th samples, and the summation is over-all time intervals from the beginning of the reaction including the elapsed time in the current interval. Thus, for a reaction from which two samples have been removed, Δt_1 is the time from the start of the reaction to the removal of the first sample, Δt_2 is the time between the removal of the first and the second samples, and Δt_3 is the time which has elapsed since the removal of the second sample.

Introducing the heterogeneous time coordinate, equations (1) and (2) yield the expression

$$-\log (3a - \text{Sn}^{+2})/3a = k\tau/2.303 \quad (5)$$

Use of equation 5 in analysis of the experimental data yielded curves of the form shown in Fig. 1, the curvature of the initial portion becoming more noticeable when the data were plotted on a large scale.⁹ If no stannic compounds were formed, the plot of equation 5 should yield a straight line.

Calculation of the amount of nitro compound reacting with the stannous chloride, using rate constants obtained by Klemenc,¹⁰ showed that the amount of nitro compound reduced in this manner was far too small to account for the observed deviation from a first order rate law.

(9) In practice it was convenient to calculate τ by the expression $0.4343 A \sum \Delta t_i/V_1$ and the values of τ given in the tables and graphs were so calculated.

(10) Klemenc, *Ann.*, **433**, 351-357 (1923); **435**, 321 (1924).

(7) Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., 1928, Vol. I, pp. 134-151.

(8) Kolthoff and Furman, *ibid.*, Vol. 2, p. 411.

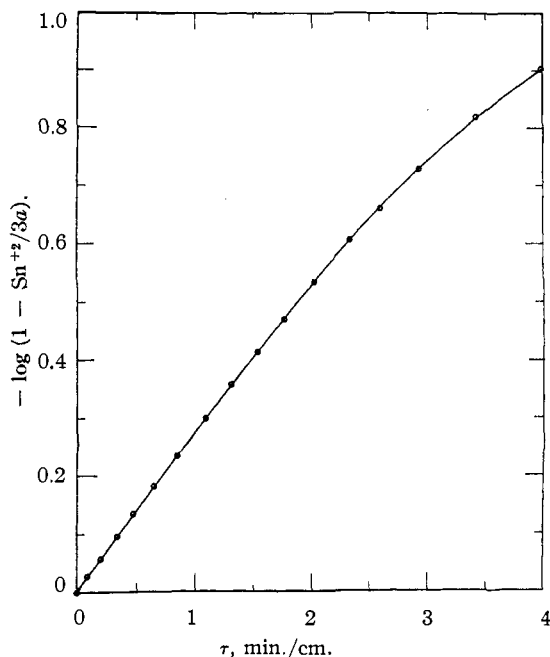


Fig. 1.—Curve for a typical run (29a).

It was observed that when the quantity “ $3a$ ” in equation 5 was reduced by a small fraction α , between 7 and 10%, the resulting equation

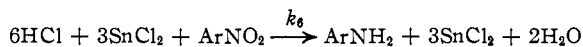
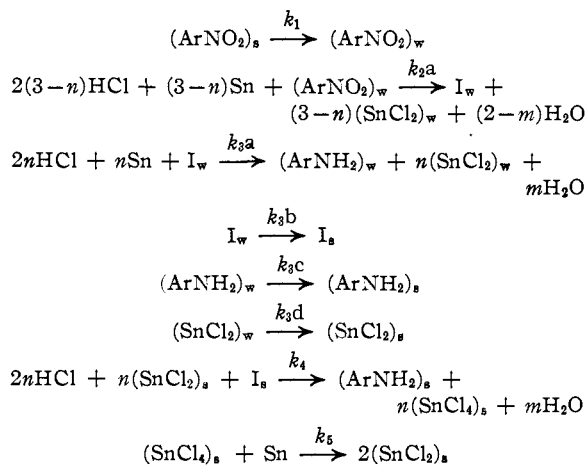
$$-\log \frac{(1 - \alpha)3a - \text{Sn}^{+2}}{(1 - \alpha)3a} = k\tau/2.303 \quad (6)$$

would represent the experimental data quite well; thus modified, the points fell on a straight line within the limits of analytical accuracy over 80 to 90% of the reaction, and values of α and k were quite reproducible from one run to another. This behavior strongly indicated that an almost constant fraction of the tin was in solution in the stannic state, and that reduction of the nitro group was nearly complete before significant amounts of stannic tin were reduced. Such was found to be the case and in most of the runs both stannous and total tin were determined.

As a result of preliminary analysis of the data, it appears that the reduction may be represented by the processes: (1) the diffusion of the nitro compound to the surface as a primary process, followed by (2) reduction of the nitro compound on the surface to some intermediate state at a rate greater than the diffusion of the nitro compound to the surface, followed by (3) (a) reduction of a constant fraction of the intermediate to the final product (amine) before the intermediate has time to diffuse away into solution, and (b) diffusion of the remaining fraction of the intermediate into the solution before it can react with the surface, followed by (4) reaction of the intermediate in solution with the stannous compounds to form the amine and stannic compounds, which (5) diffuse to the surface to react slowly with the metallic tin and form more stannous compounds;

(6) paralleling the above processes, a slow reaction between the remaining nitro compound and the stannous compounds in solution.

Denoting the intermediate I and letting s and w refer to the solution and the wall of the cylinder, respectively, we can represent the reaction in detail.



Except for reaction systems with a very small ratio of area to volume, step 6 is very slow in comparison to the other steps and may be disregarded. According to the work of Bekier and Basinski,¹¹ step 5 is described by a first order rate law. We shall describe step 4 by a second order expression; since this term can be eliminated in solving the system of rate equations, its exact order is not essential. We can represent the other heterogeneous steps as first order, since k_1 , k_{3b} , k_{3c} and k_{3d} refer to diffusion processes, and in 2a and 3a the hydrochloric acid is present in large excess.

Then for “steady state” conditions at the surface of the cylinder, we obtain the set of rate equations

$$\frac{-d(\text{ArNO}_2)}{dt} = \frac{k_1A}{V} (\text{ArNO}_2) \quad (7)$$

$$\frac{d(\text{I}_s)}{dt} = \frac{k_3A}{V} (\text{ArNO}_2) - k_4(\text{I}_s)(\text{SnCl}_2) \quad (8)$$

$$\frac{d(\text{ArNH}_2)}{dt} = \frac{k_2A}{V} (\text{ArNO}_2) + k_4(\text{I}_s)(\text{SnCl}_2) \quad (9)$$

$$\frac{d(\text{SnCl}_4)}{dt} = nk_4(\text{I}_s)(\text{SnCl}_2) - \frac{k_5A}{V} (\text{SnCl}_4) \quad (10)$$

$$\begin{aligned} \frac{d(\text{SnCl}_2)}{dt} &= (3k_1 - nk_3) \frac{A}{V} (\text{ArNO}_2) - nk_4(\text{I}_s)(\text{SnCl}_2) + \frac{2k_5A}{V} (\text{SnCl}_4) \quad (11) \end{aligned}$$

$$\frac{d(\text{Sn}_T)}{dt} = \frac{(3k_1 - nk_3)A}{V} (\text{ArNO}_2) + \frac{k_5A}{V} (\text{SnCl}_4) \quad (12)$$

in which Sn_T = total tin in solution, $k_3 = \beta k_1$, $k_2 = (1 - \beta)k_1$, and $\beta = k_{3b}/(k_{3a} + k_{3b})$, where β is the fraction of intermediate escaping back into

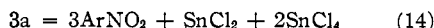
(11) Bekier and Basinski, *J. chim. phys.*, **27**, 256 (1930).

solution. All concentration terms in equations 7-12 refer to concentrations in solution.

The work of Goldschmidt and co-workers¹² indicated that stannous chloride reduces nitroso and hydroxylamino compounds very rapidly. Therefore we shall assume that, except for the very first part of the reaction while stannous chloride is very small, the intermediate I_s will be reduced as rapidly as it is formed so that the following conditions will hold

$$I_s \approx 0 \text{ and } dI_s/dt \approx 0 \quad (13)$$

Making use of the relation



and the "heterogeneous" time coordinate τ defined in equation 4, we can arrive at the following solutions for the equations 7, 10, 11 and 12

$$3ArNO_2/3a = (3a - SnCl_2 - 2SnCl_4)/3a = \theta_1 \quad (15)$$

$$2SnCl_4/3a = \alpha(\theta_s - \theta_1) \quad (16)$$

$$(3a - SnCl_2)/3a = \theta_1 + \alpha(\theta_s - \theta_1) \quad (17)$$

$$(3a - SnCl_2)/3a = \theta_1 + \frac{\alpha}{2}(\theta_s - \theta_1) \quad (18)$$

in which

$$\alpha = (2/3)(nk_3)/(k_1 - k_5); \theta_1 = e^{-k_1\tau}; \theta_s = e^{-k_5\tau} \quad (19)$$

Direct determinations of k_5 with our apparatus were consistent with values obtained by Bekier,¹¹ and showed that k_5 was usually less than 1 or 2% of k_1 . Thus the reduction of the stannic compounds is unimportant except for the last few per cent. of the over-all reaction. Since k_5 is very small compared with k_1 , $\theta_s \approx 1$ over most of the reaction, and equation 17 will reduce to equation 6, which was found to fit the experimental data over a considerable portion of the reaction.

One method of determining the rate constants k_1 and nk_3 from the data consisted of successive approximations of α until equation 6 gave what was judged to be the best straight line. A second method of evaluating constants from the data involved plotting the logarithm of $(3a - SnCl_2)/3a$ against τ . The slope of this curve, measured with a tangentiometer, was plotted against $(3a - SnCl_2)/3a$. Extrapolation of this curve to $(3a - SnCl_2)/3a = 1$ gave $k_1 - (2/3)nk_3$ for the intercept; the slope of this curve, measured and extrapolated in the same way, had the intercept $(2/3)nk_3$ when k_5 was small. An example of this method is given in Fig. 2.

When analyses for both stannous and total tin were available, equation 15 was used for determining k_1 , logarithmic plots yielding satisfactory straight lines. The relationship

$$(SnCl_4)/(SnCl_2 + 2SnCl_4) = nk_3/3k_1 \quad (20)$$

was used to determine nk_3 , since k_5 was small compared to k_1 .

Table I presents the results of four consecutive runs, showing the reproducibility of the rate constants.

(12) Goldschmidt and Ingebretsen, *Z. physik. Chem.*, **48**, 435 (1904); Goldschmidt and Sunde, *ibid.*, **66**, 1 (1906).

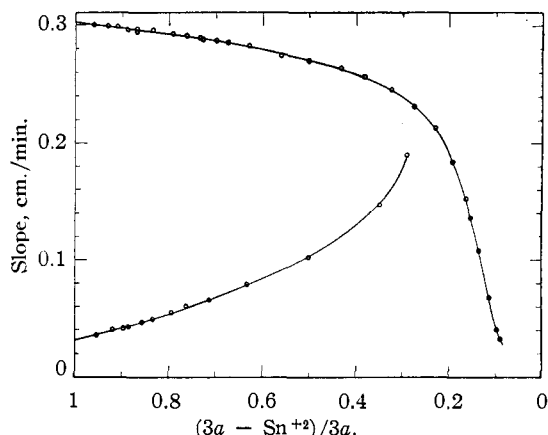


Fig. 2.—Extrapolation curves for calculation of rate constants: upper curve, slope of curve obtained by plotting the logarithm of $(3a - Sn^{+2})/3a$ against τ ; lower curve, slope of upper curve. Values obtained in this example for run 35 were $k_1 - (2/3)nk_3 = 0.302$ cm./min.; $(2/3)nk_3 = 0.032$ cm./min.

TABLE I

EXAMPLES OF THE GENERAL REPRODUCIBILITY OF RESULTS

All runs were made with *p*-nitrophenol in 0.45 *M* hydrochloric acid at 25°, and stirring rate 105.5 cm./sec. with cylinder number 2.

Run no.	Initial $ArNO_2$ mole/liter	k_1 , cm./min.	nk_3 , cm./min.
21a	0.009119	0.340	0.032
21b	.009133	.341	.034
22a	.004746	.339	.030
22b	.004390	.338	.029

In order to test more closely the agreement between the proposed rate law and the data, the rate constants were inserted into the appropriate

TABLE II

COMPARISON OF RATE LAW WITH EXPERIMENT

Run no. 29a, cylinder no. 3, *p*-nitrophenol, 25°, stirring rate 105.5 cm./sec.; results calculated by equation 17; total time 2.5 hours.

$k_1 = 0.307$ cm./min.; $k_5 = 0.005$ cm./min.; $HCl = 0.5 N$; $nk_3 = 0.033$ cm./min.; $3a = 0.02848 M$; $A = 69.55$ sq. cm.

τ , min./cm.	Sn^{+2} , exp., <i>M</i>	Sn^{+2} , calcd., <i>M</i>	Sn^{+2} (calcd.-exp.) <i>M</i>
0.087	0.00167	0.00158	-0.00009
.197	.00352	.00344	-
.337	.00565	.00561	-
.478	.00759	.00757	-
.651	.00975	.00976	1
.845	.01188	.01189	1
1.100	.01420	.01430	10
1.306	.01597	.01597	0
1.536	.01753	.01754	1
1.765	.01883	.01886	3
2.020	.02018	.02013	-
2.325	.02136	.02136	0
2.595	.02222	.02225	3
2.920	.02314	.02314	0
3.420	.02415	.02414	- .00001

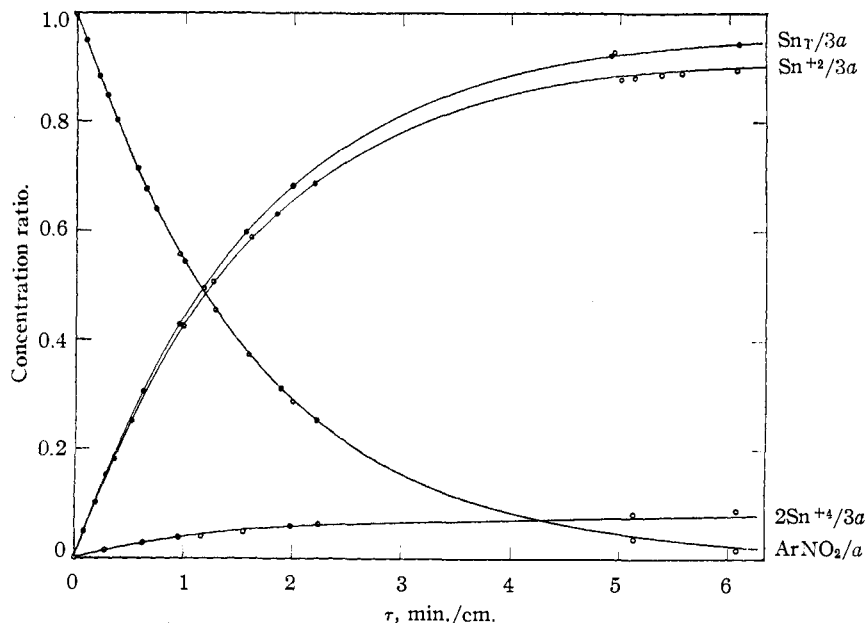


Fig. 3.—Comparison of rate law with experimental data for run 41: cylinder no. 2a in 0.01 *M* *p*-nitrophenol and 0.25 *M* hydrochloric acid at 25°; stirring rate 75.4 cm./sec. Curves are calculated by rate equations using $k_1 = 0.271$ cm./min., $nk_3 = 0.032$ cm./min., and $k_5 = 0.002$ cm./min.

equation and the concentration of stannous and total tin actually calculated for comparison with the analytical values for a number of runs. Table II shows the result of such a comparison for one of the early runs in which only stannous tin was determined. The agreement between experimental and calculated results is excellent. The high values observed for the first two analyses may well mean that the "steady state" condition for the intermediate has not yet been reached (equation 13).

For runs in which both the stannous and total tin were determined, an example is given in Table III and in Fig. 3, in which the experimental points are compared with the calculated curves. The excellent agreement between experimental and calculated values for all three components, stannous tin, total tin and remaining nitro compound, is clearly shown. The amount of stannous tin reacting with the nitro compound by the homogeneous reaction (step 6 in the mechanism), calculated by graphical evaluation of $k_6 \int_0^t (\text{SnCl}_2) (\text{ArNO}_2) dt$, using Klemenc's¹⁰ value for k_6 , 1×10^{-4} liter mole⁻¹ sec.⁻¹, is 0.00020 mole per liter at the termination of the reaction. This accounts for practically all of the difference between experimental and calculated values for stannous tin.

These are typical examples of the excellent agreement between the experimental results and the rate law based on the proposed mechanism. For any run, a set of constants could be found for equations 15–19 which enabled one to calculate values for both stannous and total tin

TABLE III

COMPARISON OF RATE LAW WITH EXPERIMENT

Run no. 41; stirring rate 75.4 cm./sec.; *p*-nitrophenol, cylinder no. 2a; temperature 25°; results calculated by eq. 17 and 18. Total elapsed time 4.75 hours. k_1 0.271 cm./min.; nk_3 0.032 cm./min.; HCl 0.25 *M*; k_5 0.002 cm./min.; $3a$ 0.03039 *M*; area 51.31 cm.²

τ min./ cm.	Stannous tin, <i>M</i>			Δ	Total tin, <i>M</i>			Δ
	Exp.	Calcd.	Δ		Exp.	Calcd.	Δ	
0.000	0.00000	0.00000	0.00000	—	0.00000	0.00000	0.00000	—
.0798	.00148	.00136	—	13	—	—	—	—
.1955	.00328	.00322	—	6	—	—	—	—
.2695	—	—	—	—	.00448	.00452	—	4
.3482	.00552	.00547	—	5	—	—	—	—
.5153	.00767	.00770	—	3	—	—	—	—
.6119	—	—	—	—	.00926	.00927	—	1
.7244	.01031	.01018	—	13	—	—	—	—
.947	—	—	—	—	.01297	.01303	—	6
.993	.01288	.01293	—	5	—	—	—	—
1.153	—	—	—	—	.01491	.01498	—	7
1.258	.01540	.01523	—	17	—	—	—	—
1.546	—	—	—	—	.01825	.01807	—	18
1.602	.01798	.01770	—	28	—	—	—	—
1.838	.01909	.01911	—	2	—	—	—	—
1.991	—	—	—	—	.02079	.02077	—	2
2.195	.02082	.02090	—	8	—	—	—	—
2.275	—	—	—	—	.02219	.02214	—	5
4.915	—	—	—	—	.02784	.02785	—	1
4.938	—	—	—	—	.02814	.02787	—	27
5.008	.02659	.02681	—	22	—	—	—	—
5.139	.02674	.02690	—	16	—	—	—	—
5.392	.02691	.02707	—	16	—	—	—	—
5.558	.02698	.02717	—	19	—	—	—	—
6.073	.02713	.02741	—	28	.02859	.02856	—	3
	.02717	.02741	.00024	—	.02863	.02856	—	.00007

which agreed with the experimental values within limits of experimental accuracy over the entire course of the reaction. Such agreement constitutes an extremely critical test of the proposed rate law.

Discussion

The rate constant for a heterogeneous diffusion controlled process as derived from Fick's law by the Nernst diffusion theory^{13,14} is

$$k = D/\delta \quad (21)$$

where D is the diffusion coefficient of the reagent and δ is the thickness of the "diffusion layer." Introducing the Stokes-Einstein diffusion equation, we get

$$k\eta/T = R/(6\pi r N\delta) = \text{constant} \quad (22)$$

where r is the radius of the reactant molecule and η is the viscosity of the solution.

The decrease in velocity with fifteen-fold increase in acidity, as shown by Table IV and Fig. 4, is completely accounted for by the increasing viscosity of the solution, since the product $k_1\eta$ is essentially constant as required by equation 22.

TABLE IV

VARIATION OF RATE CONSTANTS WITH ACIDITY AND WITH VISCOSITY

All runs with *p*-nitrophenol, cylinder no. 3, temperature 25°, stirring rate 105.5 cm./sec.

Concn. HCl, <i>N</i>	Viscosity, ^a cgs. × 10 ³	k_1 , cm./min.	$k_1\eta$ × 10 ³	nk_3 , cm./min.	$\eta\beta/3$
0.25	9.10	0.313	2.85	0.031	0.033
		.310	2.82	.033	.036
.50	9.26	.307	2.84	.033	.036
		.305	2.82	.031	.034
.82	9.44	.293	2.76	.030	.034
.93	9.50	.276	2.62	.022	.027
2.03	10.16	.281	2.85	.027	.032
		.282	2.86	.030	.035
3.81	11.10	.240	2.66	.010	.014

^a Taken from "International Critical Tables" from data pertaining to hydrochloric acid solutions.

Rates were studied over a wide range of temperature with the results shown in Fig. 5, in which the rate constants are plotted on a logarithmic scale against the reciprocal of the absolute temperature. As calculated from the slope of the straight line, the activation energy corresponding to k_1 is 4100 calories per mole. This value is in good agreement with the activation energy of diffusion over the same temperature range.¹⁴ Further agreement with the diffusion theory is

TABLE V

VARIATION OF RATE CONSTANTS WITH TEMPERATURE

Cylinder No. 2a, stirring rate 105.5 cm./sec., all runs with *p*-nitrophenol in 0.25 *M* HCl

<i>T</i> , °K.	k_1 , cm./min.	nk_3 , cm./min.	$\eta\beta/3$	$k_1\eta/T^a$
298	0.335	0.046	0.046	1.12×10^{-3}
	.334	.047	.047	
313	.485	.061	.042	1.14
328	.615	.075	.041	1.07
343	.845	.096	.038	1.13

^a η_r = relative viscosity = η/η_{25}° .

(13) Nernst, *Z. physik. Chem.*, **2**, 613 (1888); **47**, 52 (1904).

(14) Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd ed., Oxford University Press, New York, N. Y., 1947.

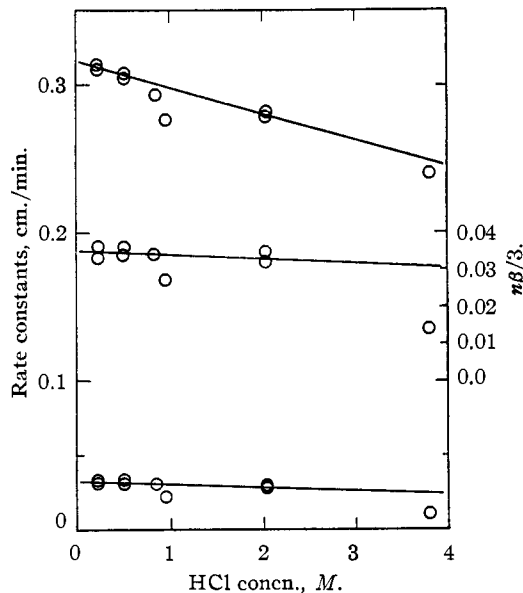


Fig. 4.—Variation of rate constants with acidity: all runs with *p*-nitrophenol; cylinder no. 3; stirring rate 105.5 cm./sec.; temperature 25°; upper curve, k_1 ; middle curve $\eta\beta/3$; lower curve, nk_3 .

afforded by the last column of Table V, the values being reasonably constant over the whole range of temperature.¹⁵

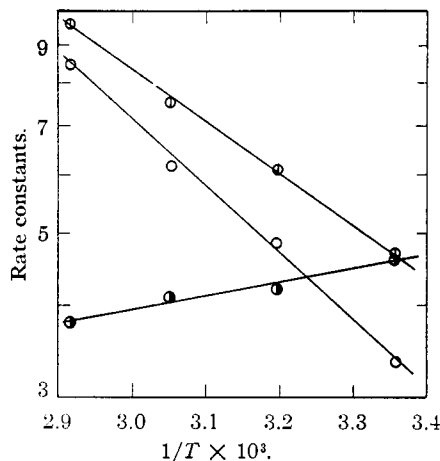


Fig. 5.—Variation of rate constants with temperature, all runs with 0.01 *M* *p*-nitrophenol in 0.25 *M* hydrochloric acid with cylinder no. 2a; stirring rate 105.5 cm./sec.; ○, $k_1 \times 10$; ⊙, $nk_3 \times 10^2$; ●, $\eta\beta \times 10^2/3$.

Calculation of the thickness of the diffusion layer δ was made by equation 22, using $r = 3 \times 10^{-8}$ cm. as an average value for *p*-nitrophenol. At a stirring rate of 105.5 cm./sec. peripheral velocity, the value found was $\delta = 2 \times 10^{-3}$ cm., which is about the average value found for diffusion controlled reactions.¹⁴

(15) For these dilute solutions the relative viscosity of water was used in the calculations.

The stirring rate was computed in terms of the peripheral velocity rather than in terms of revolutions per minute. As shown in Fig. 6, the variation of k_1 with stirring rate was found to be linear, the equation for the straight line being

$$k_1 = 0.100 + 0.00222S$$

in which the units for k_1 are cm./min. and for S are cm./sec. This variation of rate with stirring is also characteristic of diffusion controlled processes.

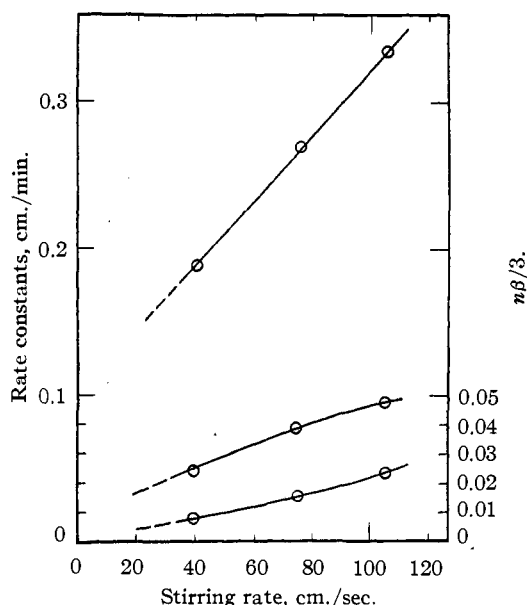


Fig. 6.—Variation of rate constants with stirring rate: all runs with 0.01 *M* *p*-nitrophenol in 0.25 *M* hydrochloric acid at 25°, with cylinder no. 2a; upper curve, k_1 ; middle curve $n\beta/3$; lower curve nk_2 .

The complete agreement between the experimental data and diffusion theory, as is evident in the comparisons above, shows that the primary process is diffusion controlled and shows the strong influence of diffusion upon step 3 in the mechanism. From the mechanism we found the relation

$$n\beta = nk_{3b} / (k_{3a} + k_{3b}) \quad (23)$$

as the fraction of nitro compound escaping into solution as an intermediate multiplied by the factor n , which depends on the oxidation state of the intermediate. Although the intermediate is most probably the hydroxylamine, in which case $n = 1$, we have no direct evidence from which we can assign a value to n . We shall therefore use the quantity $n\beta$ as an index by which we can observe the effect of stirring, temperature and acidity, and shall not attempt to state the exact fraction of intermediate formed.

The behavior of the quantity $n\beta$ is most significant. It did not change appreciably with acidity and decreased slightly with increasing temperature. These results show that k_{3a} and

k_{3b} are affected in much the same manner by these variables, with k_{3a} having a slightly higher temperature coefficient. On the other hand, $n\beta$ decreased regularly with stirring rate, becoming very small at zero stirring speed, so that the fraction of the tin appearing in the stannic state is mainly dependent on the mechanical effect of stirring. This behavior is completely in accord with step 3b being a diffusion process, and thus greatly affected by stirring, while step 3a is a surface reaction and should not be affected. Thus, the effect of stirring is strong evidence for the escape of an intermediate into solution with its subsequent reduction, since if the stannic tin were formed at the surface in any surface reaction there would be little or no variation of $n\beta$ with stirring.

The manner by which the stirring aids in transport of material to and from the surface is mainly through reduction in the thickness of the diffusion layer, within which there is little, if any, transport of material perpendicular to the surface except by diffusion. There will exist in the layer, however, some sort of velocity gradient perpendicular to the surface. With increased stirring speeds, the shear within the layer will also be increased, and this shear presumably exerts some effect in mechanically dislodging the intermediate reduction products from the surface before reduction can be completed. Whatever the exact nature of the process, with higher stirring speeds there is a greater probability that the partially reduced nitro compound will be carried away from the surface before it can react further, while at very low stirring speeds almost all of the molecules remain at the surface long enough for complete reduction.

In Table VI we see that the value of k_1 is practically independent of the structure of the compounds listed. This was to be expected if the primary process is diffusion controlled, since the diffusion coefficients of the several compounds would be nearly the same. On the other hand, it was expected that certain structural effects might stabilize some of the intermediates more than others, so that a larger variation in $n\beta$ would be observed with certain structural arrangements in the molecule.

TABLE VI

VARIATION OF RATE CONSTANTS WITH STRUCTURE
Temperature of 25°, cylinder 3a; stirring rate 105.5 cm./sec., 0.25 *M* HCl

Compound	k_1 , cm./min.	nk_2 , cm./min.	$nk_2/3k_1$
<i>p</i> -Nitrophenol	0.323	0.041	0.042
<i>o</i> -Nitrophenol	.318	(.085)	(.089)
	.324	.050	.052
	.337	.054	.050
<i>p</i> -Nitroaniline	.314	.057	.060
	.318	.054	.056

In polarographic studies of the *o*- and *p*-nitrophenols, Astle¹⁶ interpreted his results as signi-

(16) Astle and McConnell, THIS JOURNAL, 65, 35 (1943).

ying in acid solution a single step reduction with *p*-nitrophenol at the dropping mercury electrode, but a two-step reduction with *o*-nitrophenol because of the formation of a more stable intermediate. We have not observed any large differences between the two phenols, but instead find about the same fraction of stannic tin present in both cases.

Acknowledgment.—One of us (C.V.) wishes to express his gratitude for a du Pont Fellowship during the year 1948–1949.

Summary

1. The kinetics of the reduction of aromatic nitro compounds by tin and hydrochloric acid has been studied under various conditions of acidity, temperature and stirring, the oxygen being removed from the system with carbon dioxide.

2. In the proposed mechanism, the nitro compound diffuses to the surface where it is rapidly reduced to an intermediate, a fraction of which escapes further reduction at the surface

by diffusing back into solution where its subsequent reduction results in formation of stannic compounds.

3. The rate law based on the mechanism agrees with the experimental data for both stannous and total tin concentration over the entire course of the reaction.

4. The variation of the rate constants is completely in accord with the diffusion theory of heterogeneous reactions.

5. The existence of a transitory intermediate reduction product is indicated by the formation of stannic compounds in amounts much larger than would be produced by the homogeneous reaction between stannous chloride and the nitro groups, and is supported by the results of varying the stirring rate.

6. The formation of an intermediate reduction product during the reaction indicates that the reduction of the nitro groups proceeds not by a single step but by two or more successive steps under these experimental conditions.

IOWA CITY, IOWA

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Acid-Base Studies in Gaseous Systems. VI. A Simplified Technique for Dissociation Measurements

BY HERBERT C. BROWN¹ AND MELVIN GERSTEIN²

In the first paper of this series³ there was described a technique for making precise measurements of the dissociation of addition compounds. Since that time a simplified technique has been developed for the determination of the thermodynamic constants for the dissociation reaction. Moreover, the dissociation tensimeters used in these investigations have undergone a number of improvements in design. It is the purpose of the present paper to describe these developments.

The Dissociation Tensimeter

The most recent design of the dissociation tensimeter is shown in Fig. 1. For details of operation see the first paper of this series.³

The tensimeters have been increased in size over the original models to 400–500 ml. in order to minimize the effects of surface adsorption and errors involved in bringing the mercury in the manometer, M, back to the zero point, Z.

The simple mercury seal in the original design has been replaced by a ground joint sealed by mercury, S. In practice 100–200 mm. of dry air is placed above the mercury seal. Vaporization of the mercury at elevated temperatures is minimized and a source of possible error from tempera-

ture inhomogeneity at the mercury seal is thereby eliminated. The enclosed iron rod, J, manipulated with the aid of a magnet, maintains the seal open while samples are introduced or removed.

Changes in the construction of the ground-joint, G, increase somewhat the constructional difficulties over those involved in the original design. However, the new design is more rugged than the old, reduces the quantity of mercury required in the mercury reservoir, MR, and minimizes the danger of air entering the apparatus through the ground joint, G, when the mercury level in the reservoir is low.

A more rigid, sturdier construction has been achieved by the introduction of the two bridges, B.

The Method of Matched Samples

In the method of matched samples, the volumes of two dissociation tensimeters are matched to within 1 part in 2000. The two components are individually measured out, one in each tensimeter, at a temperature and pressure (usually about 20,00 mm.) such that van der Waals deviations are negligible. The sizes of the two samples are adjusted until the pressures are equal to within 1 part in 2000. With the aid of liquid nitrogen the more volatile of the two components (usually trimethylboron) is quantitatively transferred into

(1) Department of Chemistry, Purdue University, Lafayette, Ind.

(2) National Advisory Committee on Aeronautics, Cleveland, Ohio.

(3) Brown, Taylor and Gerstein, *THIS JOURNAL*, **66**, 431 (1944).