much steeper than are the curves for the other solvents. In solvents other than water, the ammonium and the tetramethylammonium ions have a relatively high resistance and the resistance change in going from the ammonium to the tetraethylammonium ion is relatively small. In water the resistances of the smaller ions is low and the increase in resistance on the addition of four carbon atoms is much the same all the way from the ammonium to the tetra-*n*-amylammonium ion. Compared to other solvents, in water, small ions have much too low a resistance, large ions have too high a resistance. The exceptionally low resistance of small ions in water has not been accounted for up to now.

It may be pointed out that Walden's rule is only an approximation. In water, the resistance of the tetraethylammonium ion is approximately the same as that of this ion in ethylene chloride and nitrobenzene. In pyridine, however, the resistance is much less than in water. The tetrabutylammonium ion has much the same resistance in pyridine, nitrobenzene and ethylene chloride, but it has a much higher resistance in water.

V. Summary

1. A new technique is described for measuring the conductance of aqueous salt solutions to low concentrations.

2. The conductance of five symmetrical quaternary ammonium salts, from tetramethyl to tetra-*n*-amylammonium, has been measured.

3. The conductance of potassium chloride has been remeasured as has also that of potassium bromate.

4. All salts conform to Onsager's equation within the limit of experimental error.

5. It is suggested that, in evaluating Λ_0, measured values of Λ and C between 1×10^{-4} and 1×10^{-3} N be substituted in Onsager's equation and the equation solved for Λ_0.

6. Ion conductances have been computed from the Λ_0 values obtained from the measured conductances.

7. Equivalent ion resistances in water are compared with those of the same ions in several non-aqueous solvents.

The resistance of small ions in water is much smaller than it is in other solvents; the resistance of large ions is greater. The resistance change per added carbon atom is much greater in water than it is in other solvents.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL, INORGANIC, AND CATALYTIC CHEMISTRY OF THE INSTITUTE "NICOLAOS CANELLOPOULOS," PIRAEUS (GREECE)]

Kinetics of the Kjeldahl Reaction

BY GEORGE-MARIA SCHWAB[1] AND ELLY SCHWAB-AGALLIDIS[1a]

Introduction

The oxidation of organic compounds by concentrated sulfuric acid with the transformation of organic nitrogen to ammonium sulfate in the Kjeldahl analysis is well known. The kinetics of this reaction were first studied by Bredig and Brown,[2] who found the oxidation of aniline and naphthalene to be of the first order. They investigated the dependence of the reaction velocity on the concentration of copper and mercury present as catalysts, and determined the temperature coefficient of the reaction. Numerous papers are available on the Kjeldahl reaction, which have been ably reviewed by Lindner.[3] Kinetic studies, however, are largely lacking, and it is the intention of this paper to re-examine the catalysis and kinetics of this reaction on modern grounds.

The oxidation of aniline by sulfuric acid may be written

$$(C_6H_5NH_3)_2SO_4 + 28H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 28SO_2 + 12CO_2 + 32H_2O \quad (1)$$

although it is improbable that so complicated a reaction will proceed in one step. As is seen from the equation, large quantities of gas are evolved, approaching 5.4 l. of dry gas per gram of aniline. Bredig and Brown followed the reaction by observing the volume of the dried reaction gases at successive time intervals. In the present paper the actual reaction velocity was observed by measurement of the rate of gas evolution with a suitable flowmeter. This method is extremely simple and allows the making of a large number of observations in a short period of time.

Experimental

The apparatus used is represented by Fig. 1. The reaction vessel consisted of a test-tube B, suspended in a flask A containing anhydrous sulfuric acid which acted as a temperature control bath. The reaction tube was closed with a rubber stopper bearing a thermometer and delivery tube. The reaction gases were dried in the sulfuric acid bubbler C, and freed from acid droplets by means of glass wool in the tube D. Rate of gas evolution was measured by the flowmeter E. This was of a dead space free design, having the retarding capillary at (a) protected by glass wool at (b). The measuring liquid was sulfuric acid. The wide capillary at (c) had the purpose of damping the unavoidable fluctuations of flow. Calibration gave 2.2 cc./min. of air per cm. of H_2SO_4 or 2.95 cc./min. of reaction gas per cm. of H_2SO_4. The apparatus was heated by a hand regulated bunsen burner or electric hot-plate, and the temperature kept constant to ±1°.

For each determination the bath A was heated to the desired reaction temperature and tube B with the cold

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[1] In the development of the experimental method and part of the measurements we were most effectively supported by Mr. C. Parisis, and we wish to express our gratitude and acknowledgment here, as equally to Mr. W. C. Oelke (Iowa) for rewriting and editing the manuscript.

[2] G. Bredig and J. W. Brown, *Z. physik. Chem.*, **46**, 502 (1903).

[3] J. Lindner, in G.-M. Schwab's "Handbook of Catalysis, Vol. VII, Catalysis in Organic Chemistry," R. Criegee, Springer, Vienna, 1943, II, 605.

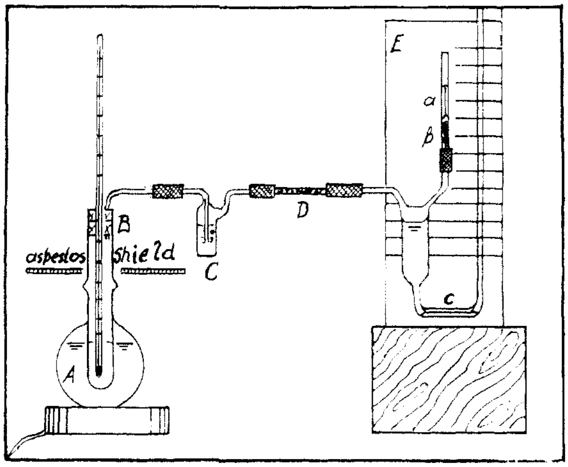

Fig. 1.

reaction mixture was immersed. After a few minutes, when constant temperature had been reached, the remainder of the apparatus was connected. The reaction velocity was determined from readings of the flowmeter as a function of time.

Bumping, troublesome in preliminary experiments, was almost entirely eliminated by the use of 0.15 g. of purified, powdered pumice in each run. That this material did not act as a catalyst was proven by varying the amounts of pumice, using 0.1, 0.15 and 0.2 g. of pumice per 3 cc. of reacting mixture without affecting the velocity. Quartz powder, glass capillaries and pumice gave identical velocities in no case greater than the observed velocity in the absence of solid additions.

Materials

The sulfuric acid was Kahlbaum concentrated, z. a., which had been previously heated in bulk to 320° to prevent boiling during the experiment. The aniline was freshly distilled and dissolved in a ratio of 10 cc. to 82 cc. sulfuric acid giving a 1.2 *N* solution of aniline sulfate in sulfuric acid. Different preparations of this solution gave identical results. Of the various catalysts, mercury was added as mercuric oxide, copper as cupric oxide and selenium as the element. In each case the catalyst was dissolved in the sulfuric acid by slight heating before the aniline solution was added.

Discussion

Part I. The Spontaneous Reaction.—A typical experiment carried out at 293° with 1 cc. of aniline sulfate solution diluted by 2 cc. of sulfuric acid, without catalyst is shown in Fig. 2. The reaction velocity in flowmeter units (cm. H_2SO_4) is plotted on a logarithmic scale against time.

From the first order reaction law

$$\mathrm{d}x/\mathrm{d}t = k'(a - x) \qquad (2)$$

by integration and substitution, we arrive at the relation

$$\log \mathrm{d}x/\mathrm{d}t = \log ak' - kt = A - kt \qquad (3)$$

where $k = k'/2.3$ and log $\mathrm{d}x/\mathrm{d}t$ is a linear function of time.

We may introduce a factor ϵ, converting millimoles of aniline reacting into flowmeter units of gaseous products.

$$\epsilon = \frac{24.5 \text{ cc./millimole of gas} \times 20 \text{ millimoles gas/millimole aniline}}{2.95 \text{ cc. gas/min./cm. } H_2SO_4 \text{ on manometer}} \qquad (4)$$

$$\epsilon = 166 \text{ cm. } H_2SO_4\text{/millimole aniline reacting/minute.}$$

Then, expressing the rate of the reaction, $\mathrm{d}x/\mathrm{d}t$, in flowmeter units

$$A = \log a\epsilon k' \qquad (5)$$

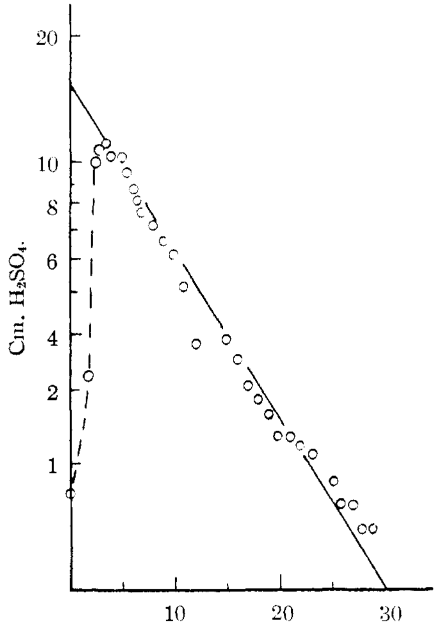

Fig. 2.

If the reaction is of the first order, log $\mathrm{d}x/\mathrm{d}t$ in flowmeter units, plotted against time should give a straight line. This is true of the experimental data plotted in Fig. 2, if allowance is made for the decrease in *a* during the initial heating period of a few minutes. The intercept at $t = 0$ is $A_{\text{obsd.}} = 1.18$, which agrees well with $A_{\text{calcd.}}$. Using the value $k' = 2.3 \times 0.04$ min.$^{-1}$ and $a = 1.2$ millimoles aniline per 3 cc. solution, we obtain

$$A_{\text{calcd.}} = \log a\epsilon k' = 1.2 \times 166 \times 2.3 \times 0.04 = 1.26 \qquad (6)$$

Thus the reaction may be considered essentially of the first order.

Experiments of this kind were carried out at different temperatures between 284° and 307°. Figure 3 shows the velocity constant *k* (for time in minutes) plotted on a log scale against the reciprocal of the absolute temperature. From the Arrhenius equation the slope of this line leads to the activation energy, in this case 38.2 kcal. This may be compared to Bredig and Brown's value of 34 kcal. based upon times of equal consumption of reactant.

Our data, converted from *k* to *k'* and from min.$^{-1}$ to sec.$^{-1}$ and substituted in the integrated Arrhenius equation gives an integration constant of 11.91. This temperature independent factor $10^{11.9}$ sec.$^{-1}$ is considerably lower than that for a unimolecular change, which is usually 10^{13} to 10^{14}. Hence the rate determining factor is not the unimolecular decay of a primary product such as sulfanilic acid, but rather a pseudo unimolecular change in which the oxidizable species reacts on collision with sulfuric acid molecules of constant concentration.

For the number of collisions per second between a solute molecule and molecules of the solvent, Moelwyn-Hughes[4] gives the equation

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(4) E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932).

$$Z = 3\pi\eta\sigma/2m_1 \quad (7)$$

where σ is the diameter and m_1 the mass of a single solute molecule and η is the viscosity of the solvent.

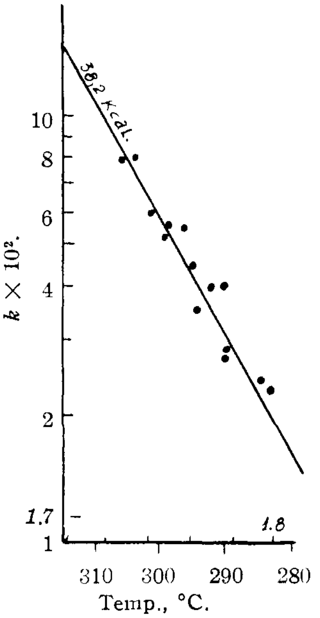

Fig. 3.

For concentrated sulfuric acid, the literature data for the viscosity between 0 and 90° can be represented by the Andrade formula

$$\log_{10}\eta = \bar{5}.46 + 1.17 \times 10^3\, T^{-1}$$

or

$$\eta = 2.89 \times 10^{-5} e^{5350/RT} = Be^{5350/RT} \quad (7a)$$

Moelwyn-Hughes gives for the unimolecular velocity constant

$$k' = Ze^{-E'/RT} \quad (8)$$

The terms constituting Z are all independent of temperature except the viscosity. This varies with temperature as shown above. Removing all temperature dependent factors we can calculate a temperature independent factor

$$Z_0 = k_0' = (3\pi\sigma/2m_1)B \quad (8a)$$

$$\sigma = 1.55\sqrt[3]{M/d} = 5 \times 10^{-8}\text{ cm.} \quad m_1 = 93/N_0 \quad (8b)$$

$$Z_0 = k_0' = \frac{(3)(3.14)(5 \times 10^{-8}\text{ cm.})(6.02 \times 10^{23})(2.89 \times 10^{-5})}{(2)(93)} \quad (8c)$$

$$= 10^{10.72}\text{ sec.}^{-1}$$

The agreement with the experimental value of $k_0' = 10^{11.9}$ is seen to be better. The assumption of 2 internal degrees of freedom participating in the activation would make it complete. Nevertheless, this cannot be considered as proof for direct action of sulfuric acid molecules on aniline, or a primary derivative, as a rate determining step for the following experimental reasons.

Bredig and Brown,[2] working at concentrations of 0.016 N, *i. e.*, 1/25 of that (0.4 N) in the present experiments, give a constant of $k = 0.00031$ min.$^{-1}$ at 275°, which is 1/43 of our mean value; while at 300° and 0.008 N they find $k = 0.00051$ min.$^{-1}$ which is 1/260 of our mean value. From the first value and these authors' temperature coefficient of 34 kcal./mole, k_0' is calculated to be $10^{8.6}$ sec.$^{-1}$, and with our temperature coefficient of 38 kcal./mole, $k_0' = 10^{10.3}$ sec.$^{-1}$; in any case less than even the simple theory requires.

In order to ascertain if this discrepancy is due to different concentration conditions, the experiments shown in Fig. 4 were carried out. The solid line is that taken from Fig. 2 for 0.4 N aniline. It will be seen that with double the concentration, (empty circles) the velocity constant is doubled, but with a threefold increase in concentration, (dotted circles) there is little additional increase. Apparently, the reaction follows the first order law in a given experiment, but from experiment to experiment the first order constant increases with the initial concentration. This might be explained by assuming a catalytic influence of a magnitude not altered by the reaction, such as the total concentration of anilinium and ammonium ions. That this is *not* the case is shown by the halved circles (◐) in Fig. 4 which represent reactions in which ammonium sulfate was added up to double the initial concentration of aniline.

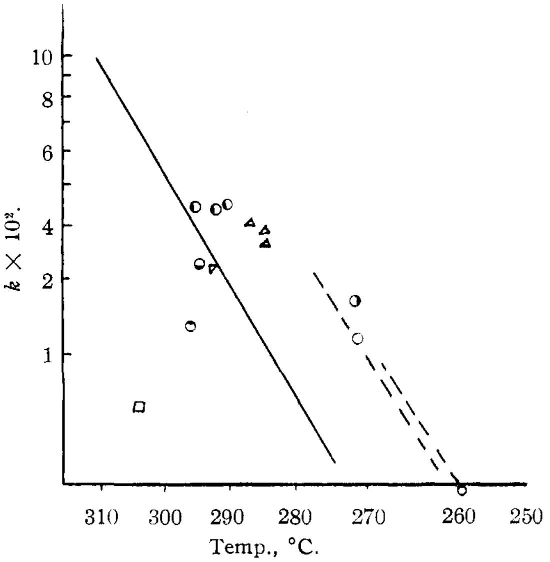

Fig. 4.—O, 2 cc. aniline; ⊙, 3 cc. aniline; ◐, 1 cc. aniline + 2 cc. $(NH_4)_2SO_4$; △, 1 cc. aniline + residue; ▽, 1 cc. aniline + boiled residue; ◑, 2 cc. aniline + boiled residue; ◒, 1 cc. aniline + residue of naphthalene; □, 1 cc. naphthalene; ◓, 1 cc. naphthalene + residue of aniline.

Thus the accelerating species is not the final product, but some intermediate species. The following facts lend credence to this view: (1) Full Kjeldahl digestion requires several hours even at the highest temperatures. (2) Addition of the brownish-black residual solution from a previous experiment to fresh 0.4 N aniline (△ points Fig. 4) gives almost the same effect as doubling the concentration. After prolonged boiling (▽ and ◑) the residue loses its accelerating action. (3) Naphthalene (□) reacts more slowly than aniline. The residue from this reaction (◒) does not accelerate the aniline reaction, whereas the residue from the aniline reaction (◓) does accelerate that of naphthalene.

These facts suggest that. except in the very first moment, the active oxidizing agent is not sulfuric acid itself, but a series of addition products of sulfuric acid and successive oxidation products of aniline, whose concentration is approximately constant during a considerable period of the reaction. Of course, the reaction is too complicated to establish a detailed mechanism of this kind with certainty, but it is reasonable to postulate that the concentration of oxidizing (sulfonic acid) groups remains constant and equal to the initial concentration of aniline, whereas the concentration of oxidizable (CH_2) groups decays with time. This again leads to an apparent first order law. But instead of the sulfuric acid concentration appearing implicitly in equations 7 and 8, the sum of the sulfonic acid concentrations, equal to the initial aniline concentration, is to be introduced. In this case the calculated temperature independent factor k_0' should be multiplied by a/c, c being the molar concentration of concentrated sulfuric acid (18.8 *M*). For our standard initial concentration of 0.4 *N*, we obtain $k_0' = 10^{9.1}$, and for Bredig's concentrations, correspondingly lower values. A direct calculation of collision frequencies gives approximately the same result. Of course, by this correction, derived from conclusive evidence, the agreement with the observed value of $10^{11.9}$ has become worse; but the assumption of 4 internal degrees of freedom, plausible for the large molecules involved, can account for this difference.

Part II. Selenium Catalysis.—When selenium is added to concentrated sulfuric acid, it dissolves slowly above 100°, more rapidly above 200° to form colorless selenious acid. When a drop of aniline sulfate in sulfuric acid is added to the colorless selenious acid solution, a deep blackening occurs, followed by a rapid evolution of gas. This decays gradually as the black color disappears. These observations support the accepted opinion[3] that selenium catalysis proceeds by way of an oxidation of selenium by sulfuric acid, and of aniline or its derivatives by selenious acid, according to

$$Se + 2H_2SO_4 \longrightarrow H_2SeO_3 + 2SO_2 + H_2O \quad (9)$$

$$A + H_2SeO_3 \longrightarrow Se + P \quad (9a)$$

where A represents aniline or its oxidizable derivatives, and P the products of the reaction.

When 1 cc. of 1.2 *N* aniline, 2 cc. of concd. sulfuric acid and moderate amounts of selenium (above 2 mg.) are heated together above 200° a very rapid autocatalytic reaction is first observed during which a stationary Se/H_2SO_4 ratio is developed. This stationary state results in the remainder of the reaction following the ordinary course of logarithmic decay. Quantities of selenium less than 2 mg. (<0.008 *M*) give 90% of the reaction of the latter type. Quantities of 0.016 mg. (7×10^{-5} M) and 0.008 mg. (3.3×10^{-5} *M*) selenium give no acceleration. In Table I the "stationary" decay constants *k* are given for different selenium concentrations and temperatures.

Table I

°C.	Exptl. values, $k \times 10^2$ 8 mg. Se	2 mg. Se	0.8 mg. Se	$k_{spont.} \times 10^2$	Calcd. values, $k \times 10^2$ 8 mg. Se $10^2\alpha$ = 0.88	2 mg. Se 1.12	0.8 mg. Se (1.75)
282		4.2		1.7		3.95	
274		3.2		1.12		3.37	
270	6.9[a]			0.86	7.9		
269	6.86[a]			.81	7.86		
262			1.9	.51			(1.9)
257	6.4[a]			.35	7.39		
246	8.66			.16	7.20		
245		2.3		.15		2.4	
244	5.9[a]			.14	7.18		
240	7.94			.11	7.15		
224	8.66			.03	7.07		
213	7.44			.014	7.05		

[a] Experiments of series 2.

It will be observed that with 8 mg. of selenium, where the spontaneous reaction is almost negligible, the temperature coefficient is almost zero (values denoted by footnote *a;* unmarked values belong to another series of experiments). By subtracting the values for the constant of the spontaneous reaction, $k_{spont.}$ as taken from Fig. 3, values practically independent of temperature are obtained. Thus the total velocity may be represented by

$$k_T = (k_{spont.})_T + \alpha[Se] \quad (10)$$

where α is a constant expressing the catalytic action of 1 mg. of Se in 3 cc. The values calculated in columns 6, 7 and 8, using the values of α indicated in the heading, agree satisfactorily with the observed constants. The value of α increases slightly with decreasing selenium concentration, but this is beyond the accuracy of the measurements. The mean value of $\alpha = 1 \times 10^{-2}$, as defined above, represents the data satisfactorily. For atomic concentrations of selenium, natural logarithms and seconds, $\alpha = 0.097$ $sec.^{-1}$ gram $atoms^{-1}$.

The task is to find a suitable reaction mechanism based upon equations 9 and 9a. Postulating reaction 9a as rate determining is precluded by, (a) direct evidence of the individual reaction velocities, (b) the fact that elemental selenium cannot exist in homogeneous solution, (c) that a bimolecular (pseudo-unimolecular) reaction without measurable activation energy ought to have a velocity of 10^{11} and not 10^{-1} as found. The solution is found in the assumption that the rate determining step is a *diffusion* process. In the initial period, selenium is formed by direct reduction of selenious acid by aniline and coagulates into droplets (m. p. 217°) of a stationary average size. During the remainder of the reaction these droplets are superficially oxidized by sulfuric acid, the oxidizable species, A, reaches this surface by diffusion and reacts with the selenious acid there with immeasurably high velocity. The picture is that of a heterogeneous reaction governed by a diffusion velocity.

This mechanism is amenable to an approximate quantitative treatment. Let the concentration of A in moles per cc. be *c*, and the *x* dimension be the distance from the center of a spherical selenium droplet. Then the spherical analog of the second Fick equation[5] gives

$$\left(\frac{dc}{dt}\right)_x = D\left(\frac{d^2c}{dx^2} - \frac{2dc}{xdx}\right)_t \qquad (11)$$

The solution for the stationary state ($dc/dt = 0$) and the marginal conditions $c_{x=r} = 0$ and $c_{x=\infty} = c_0$ (r being the droplet radius) is

$$dc/dx = rc_0/x^2 \qquad (12)$$

This, substituted in the first Fick equation

$$dm/dt = -Dq dc/dx \qquad (13)$$

with $q = 4\pi x^2$ and dm/dt being the number of moles A passing through q in a second, gives

$$dm/dt = -4\pi Drc_0 \qquad (14)$$

and for n selenium droplets

$$dm/dt = -4\pi nDrc_0 \qquad (14a)$$

In a total solution volume V_0 is

$$k' = -(1/c_0)(dc_0/dt) = (4\pi nDr)/V_0 \qquad (15)$$

or

$$nr = k'V_0/4\pi D \qquad (16)$$

On the other hand, g grams of selenium of a density ρ have a volume

$$(4/3)\pi r^3 n = g/\rho \qquad (17)$$

From (16) and (17)

$$r = \sqrt{3D\rho/gk'V_0} \qquad (18)$$

We estimate D from

$$D = (\kappa T)/6\pi\eta r' \qquad (19)$$

$\kappa = 1.37.10^{-16}$ being the Boltzmann constant, T 523° a mean absolute temperature, $\eta = 0.005$ the viscosity of sulfuric acid at this temperature from (7a) and $r' = 5.10^{-8}$ cm. the molecular radius of the diffusing species A. This gives D 1.45×10^{-5} sec.$^{-1}$ cm.^{2} = 1.3 day^{-1} cm.^{2}, a plausible value.

In equation 18, ρ is 3.9 for liquid selenium,[6] $g = 0.008$ g., and k' in the respective experiments was found to be $2.3 \times 0.07/60 = 0.0027$ sec.$^{-1}$, and V_0 3 cc. This gives an average radius of the selenium droplets of 3.3×10^{-3} cm. A less accurate estimation, assuming a linear concentration gradient across a Nernst–Brunner adhering layer of 3×10^{-3} cm. thickness gives the same result, as does a microscopic examination of the reaction mixture quenched from the stationary state.

The reaction mechanism postulated on the basis of the low velocity and absence of activation energy is thus confirmed by the absolute magnitude of the velocity and the size of the selenium particles.

Part III. Copper Catalysis.—Bredig and Brown[2] report that copper salts at 0.034 *M* concentration with aniline concentrations of 0.009 *N* increase the velocity at 275° about 12-fold, nearly as much as the equivalent quantity of mercury. In their case copper is in excess, so that all the aniline could have been present as a copper complex. With our higher aniline to copper ratio, 44:1, no acceleration was observed, hence the catalyzed reaction is negligible under these conditions.

Part IV. Mercury Catalysis.—Bredig and Brown[2] found that at 275° and with 0.009 *N* aniline, the reaction velocity increases linearly with the mercury concentration between 0.00335 and 0.0531 *M*, but that the influence of mercury concentration lower than 0.00335 *M* is considerably greater. As with copper, their mercury concentrations were commensurate or even greater than the concentration of aniline. We tried mercury in the order of concentrations used by these authors, but with aniline concentrations as high as 0.4 *N*, and at various temperatures. The results are collected in Fig. 5 in which log k is plotted *vs.* $1/T$. Mercury concentrations as low as 3×10^{-6} *M* had no effect, but in the range of 10^{-3} *M* the velocity was considerably increased.

Diagrams showing the influence of different mercury concentrations at constant temperature were constructed on the basis of Fig. 5 by means of linear interpolations or short extrapolations to the chosen temperature. These showed that true catalysis is exerted by mercury, dependent on the absolute concentration only and not on its ratio to the aniline concentration.

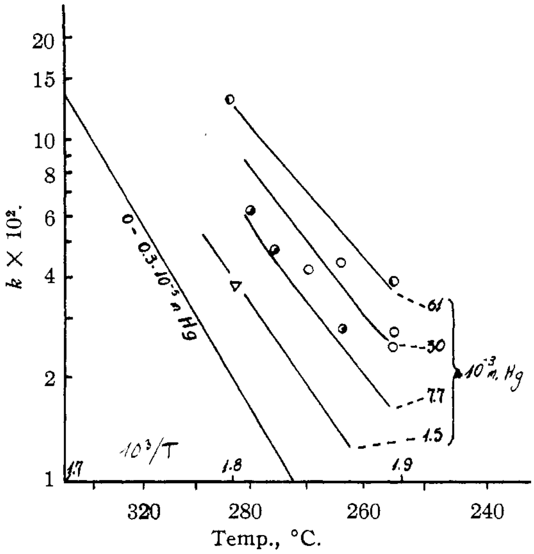

Fig. 5.

The dependence of reaction velocity on the mercury concentration can be expressed analytically, over the entire temperature range covered, by the formula

$$k_{\text{Hg}} = k - k_{\text{spont.}} = \frac{\alpha[\text{Hg}] + \beta[\text{Hg}]^2}{1 + b[\text{Hg}]} \qquad (20)$$

By successive approximations, using the four mercury concentrations of Fig. 5, the best values for the constants α, β and b were found, Table II, for 10^{-3} *M* as the unit of [Hg].

TABLE II

°C.	$10^2\alpha$[a]	$10^2\beta$	b
280	1.5	0.024	0.31
264	0.69	.0136	.31
255	0.44	.010	.31

[a] The probable error of α and β is about 10%, that of b is 3%.

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[5] G.-M. Schwab and J. Philinis, THIS JOURNAL, 69, 2588 (1947). (A misprint in the equation is corrected here.)

[6] Gmelin, "Handbook of Inorganic Chemistry," Verlag Chemie, Berlin, 1942, 8th ed., No. 10 (Se) p. 179.

The temperature dependence of the constants, referred to molarities of Hg, is given by the equations

$$\log \alpha = 11.49 - 26{,}200/4.57T \qquad (21)$$
$$\log \beta = 9.49 - 18{,}000/4.57T \qquad (22)$$

Equation (20) indicates that the influence of the mercury is exerted simultaneously in two ways: One, involving one, and the other, two mercury ions. Of the many reaction schemes of this kind tried, only the following is self consistent with respect to the data of Table II

$$A + K \longrightarrow Z_1 \qquad (1)$$
$$Z_1 \longrightarrow K + P \qquad (2)$$
$$Z_1 + K \longrightarrow Z_2 \qquad (3)$$
$$Z_2 \longrightarrow 2K + A \qquad (4)$$
$$Z_2 \longrightarrow 2K + P \qquad (5)$$

where A is the oxidizable species, K the catalyst, P the gaseous reaction products and Z_1 and Z_2 two intermediate compounds.

Application of Bodenstein's principle of stationary concentration of the intermediates, or of a probability calculation[7] leads to equation (23) which is obviously identical in form to equation (20).

$$\frac{dP}{dt} = [A]\,\frac{k_1[K] + (k_1k_3k_5)/(k_2(k_4 + k_5))\,[K]^2}{1 + k_3/k_2\,[K]} \qquad (23)$$

The α corresponds to the bimolecular constant k_1 and ought to contain the temperature independent factor characteristic of these constants, α^0 2.8×10^{11} sec.$^{-1}$ or log α_0 11.45. The experimental value of log α_0 11.49, or for natural logarithms and seconds, 10.07 in equation (21) is noticeably less which indicates a low steric factor of reaction (2) as is to be expected for the attack on the amino group.

Further, from equations (20 and 23) it follows that $k_3/k_2 = b = 0.31$ and $\alpha b/\beta = 1 + k_4/k_5$. Table III gives the values of k_4/k_5 calculated in this way.

TABLE III

°C.	k_4/k_5
280	18.2
264	15.6
255	13.7

Expressing this temperature dependence by the Arrhenius equation

$$\log k_4/k_5 = 4.33 - 7800/4.57T \qquad (24)$$

we find 7,800 (±1000) cal./mole as the difference of the activation energies (q_4-q_5) of reactions (4) and (5). This gives the difference between the energy terms of Eqs. (21) and (22). Eq. (22) can be exactly valid only if $k_4 \gg k_5$, but this is the case as shown by Table III. The temperature independent term of (24) is somewhat high. If both reactions (4) and (5) are unimolecular it should be about zero, and even if only (5) is pseudo-unimolecular (impacts of solvent molecules) it ought to be about three. It is possible to account for this difference by a participation of more than two degrees of freedom in the activation, about another two being sufficient.

Nothing can be said on the basis of purely kinetic measurements about the chemical nature of the intermediates Z_1 and Z_2, but independent of special assumptions, the essential features of any acceptable mechanism are: (1) That the oxidation of mercurous ion by sulfuric acid and the oxidation of the organic molecule by mercuric ion are faster than the direct action of sulfuric acid or sulfonic acids on the organic molecule. (2) That part of the reaction is accomplished by the successive action of two mercuric ions.

Part V. Mercury–Copper Catalysis.—Although Bredig and Brown[2] first observed that at 275° the action of 0.13 *M* Hg^{++} and 0.09 *M* Cu^{++} exceeds by 30% the sum of the actions of the single catalysts, they did not further study this interesting promoter effect. We carried out this investigation by adding aniline sulfate to sulfuric acid containing various amounts of cupric and mercuric sulfates. Final concentrations of 0.4 *N* aniline sulfate and 7.7×10^{-3}, 31×10^{-3}, and 61×10^{-3} *M* of cupric and mercuric sulfates were used at temperatures between 248 and 270°, the the main work being done at 255°.

The most characteristic feature, not previously observed, was that the reaction was not of first order from the beginning, but rather resembled the selenium experiments. During the first few minutes there was an autocatalytic increase in velocity. After a steep maximum, the velocity decreased quickly to reach a stationary state in which the velocity decayed logarithmically with time as described by the first order law. The initial period of very fast reaction takes only a few minutes, but accounts for 50 to 70% of the total reaction. As with selenium, one must assume that during the initial period the final stationary state is established through reduction of mercuric and/or cupric ions by aniline, or by transition of aniline to some derivative. This is a mechanism radically different from that treated in Part IV.

The above conclusion is confirmed by the curves obtained. In Fig. 6, mean values of the first order constant *k* of the stationary period at 255° are given as a function of the mercury concentration for two copper concentrations (triangles and circles). The lowest curve is that of copper-free mercury catalysis as discussed in Part IV. The character of the curve is entirely changed by the presence of as little as 7.7×10^{-3} *M* of Cu^{++}. Instead of rising continuously with mercury concentration, the velocity constants converge toward a limiting value. This difference has been stated unambiguously by repeated sets of experiments. Attempts to reconcile this behavior with the above mercury mechanism, by ascribing to copper a participation in it, have been without success. An independent treatment of the stationary portion of the copper–mercury catalyzed reaction may be made as

$$k_{\text{Cu, Hg}} = k - k_{\text{spont.}} = \alpha'[\text{Hg}][\text{Cu}]/(1 + b'[\text{Cu}] + c'[\text{Hg}][\text{Cu}]) \qquad (25)$$

where $10^2\,\alpha' = 0.1$, $b' = 0.163$ and $c' = 0.0192$ at 255°, the constants referring to Briggsian logarithms, minutes and 10^{-3} *M* as the concentration unit. The two upper curves in Fig. 6, have been

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(7) See G.-M. Schwab, *Z. physik. Chem.*, **B8**, 141 (1930).

calculated from these values and represent the experimental points satisfactorily. A few additional experiments at other temperatures lead to over-all activation energies around 35 kcal./mole.

Principles previously developed[7] allow the postulation of a reaction mechanism based on Eq. 25.

The only mechanism permitted by these principles is

$$A \longrightarrow Z \qquad (6)$$
$$Z_1' \longrightarrow A \qquad (7)$$
$$Z' + Hg \longrightarrow Z' \qquad (8)$$
$$Z_2' \longrightarrow Z_1' + Hg \qquad (9)$$
$$Z_2' + Cu \longrightarrow P + Cu + Hg \qquad (10)$$

or

$$A \underset{k_7}{\overset{k_6}{\rightleftarrows}} Z_1' \underset{k_9}{\overset{k_8[Hg]}{\rightleftarrows}} Z \xrightarrow[k_{10}[Cu]]{} P + Hg + Cu$$

the notation being the same as for reactions (1)-(5). For the stationary state, this leads to

$$\frac{dP}{dt} = [A] \frac{(k_6k_8k_{10})/(k_7k_9)\ [Hg][Cu]}{1 + k_{10}/k_9\ [Cu] + (k_8k_{10})/(k_7k_9)\ [Cu][Hg]} \qquad (26)$$

Comparison with the numerical values in Eq. 25 gives for 255°

$$k_6 = \alpha'/c' = 5.2 \times 10^{-2},\ k_{10}/k_9 = b' = 0.163 \text{ and } k_8/k_7 = c'/b' = 0.118$$

The mechanism can be described as a rate determining reaction preceded by two equilibria, degenerated into a chain reaction with heavy chain breaking, the latter producing the final products.

Little can be said concerning the confirmation of this analysis by the absolute value of the constants. If, in analogy to the pure mercury reaction, the constants in the denominator are independent of temperature, the measured activation energy is that of the pseudo-unimolecular reaction (6). In this case, one would expect

$$\log k_6 = 10.7 - 35{,}000/4.57 \times 528 = -3.8$$

The experimental value, reduced to natural logarithms and seconds, is −2.7. The agreement seems satisfactory.

As for the chemical significance of our formal mechanism, conjectures only can be made, inasmuch as it is uncertain what happens to the aniline during the initial stage of the fast reaction, and whether one of the catalysts or both are reduced to the monovalent state. Beyond any speculations, the certain characteristic of the reaction mechanism is the successive action of mercury and copper on the reactants. This is faster than the direct oxidation of the oxidizable groups by sulfonic acids because of the lower activation energy (35 instead of 38 kcal./mole), and is faster than the simple mercury mechanism in spite of the higher activation energy, because the faster primary reaction and the more favorable branching ratio.

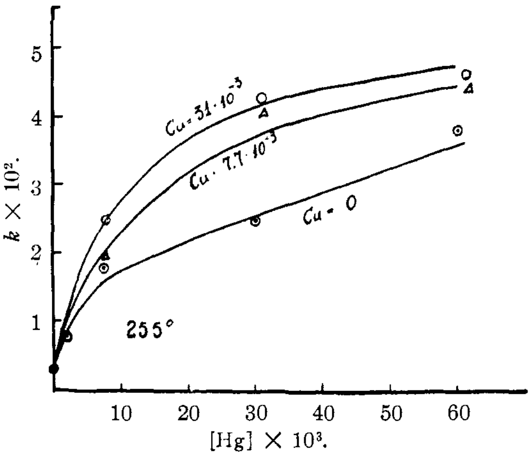

Fig. 6.

Summary

The kinetics of the oxidation of aniline by concd. sulfuric acid (Kjeldahl reaction) has been measured by observing the flow rate of the gaseous products, without a catalyst, with selenium, with copper, with mercury, and with mercury and copper as catalysts. The reaction is of the first order with respect to aniline throughout its course. In the case of selenium and of copper–mercury catalysis, this is true only after a preliminary exaltation of the velocity. Every one of the five cases is different.

1. The spontaneous reaction is accelerated by the intermediate products of the oxidation, these being present in a concentration independent of time. The assumption that intermediate sulfonic acids act as oxidizing agents leads to a satisfactory explanation of the absolute velocity. The activation energy is 38 kcal./mole.
2. The reaction catalyzed by selenium is proportional to the amount of catalyst present and independent of temperature. The reaction is a heterogeneous one in which the organic molecules reach the surface of selenium particles by diffusion and react there instantaneously with selenious acid formed by the action of sulfuric acid on the selenium surface.
3. The reaction catalyzed by mercury proceeds in two ways, one involving the action of one, the other of two successive mercury ions. Activation energies have been calculated and a formal mechanism proposed.
4. Copper, at aniline concentrations of 0.4 *N*, does not exert any perceptible catalysis.
5. With copper and mercury both present, the system is radically changed during an initial exaltation period. The subsequent stationary reaction bears no relation to the above mercury mechanism. Activation energies have been calculated and a formal mechanism proposed.

ATHENS, GREECE

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