so that the production of the methyl glyoxal may occur in reaction mixtures which are near the neutral point.

In water solutions, glucose does not react with benzylamine in the presence of acetic acid, when the amine and acid are in a one to one ratio but when the amount of acid used is very small, then reaction does occur as in alcohol. Glucose-benzylamide in water solution is hydrolyzed very readily to the constituent compounds, and the formation of methyl glyoxal or nitrogen ring compounds was not apparent under these conditions.

SASKATOON, SASKATCHEWAN, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MECHANISM OF THE CHANGE OF ISONITRO TO NITRO COMPOUNDS

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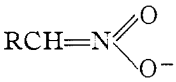
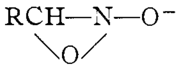
Introduction

It has been shown by Hantzsch[1] that the reversible electrolytic dissociations of nitromethanes are slow enough in both directions to permit the measurement of the rates of change of electrical conductivity when nitromethanes react with bases to form salts or when nitromethanes are formed from their salts by reaction with hydrogen ion. He explained the anomalously slow rates of these homogeneous ionic reactions as due to accompanying changes of structure. The formula RCH_2NO_2 has been accepted as that of the nitromethanes, while the alternative formulas  $RCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix}$ and  $RCH{-}\underset{\diagdown O \diagup}{N}{-}O^-$ have been assigned to the ions. Hantzsch prefers the latter formula. This theory is supported by the existence of an isomeric but unstable form of phenylnitromethane, which can be obtained from solutions of the salts of phenylnitromethane by rapid precipitation with hydrochloric acid.

Hantzsch's measurements of the rates of these reactions are not sufficiently accurate to show the mechanisms of the changes, although they do indicate that these are somewhat complex. We have, therefore, attempted to elucidate the mechanisms of these reactions through more accurate measurements of the rates.

Phenylnitromethane and nitromethane were chosen as examples of aryl-substituted and purely aliphatic nitromethanes, respectively, both of these substances having previously been used by Hantzsch. *p*-Nitrophenol was chosen as an example of a different type of nitro compound

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[1] Hantzsch, *Ber.*, **29**, 2251 (1896); **32**, 607 (1899).

whose behavior as an acid is presumably also accompanied by a change in structure.

The rates were measured only for the reactions in one direction, that of the formation of the nitro compounds by the combination of the ions. They were carried out at two temperatures in each case, in order to see whether the heats of activation for the reactions were markedly different for these types of nitro compounds.

The conditions under which the experiments were carried out, that is, at low temperatures, in dilute solutions, and without excess of acid, were such that secondary decompositions of the nitro compounds, even of nitromethane, were negligible.

Experimental Part

General Method.—Solutions containing equivalent amounts of the sodium salt of the nitro compound in question and of hydrochloric acid were mixed. The normality of each solution was 0.01 and equal volumes of the solutions were used, so that after mixing, the resulting solution was 0.005 *N* with respect to both sodium chloride and the isonitro acid. The solvent for all the solutions was a mixture of methyl alcohol and water, containing 500 cc. of the former substance per liter of the solution. These concentrations are such that no substance crystallizes out during the experiment, even at —24°. The same solvent was used to make up both solutions so as to avoid the heating effects due to mixing methyl alcohol and water. The solutions were cooled to the temperature of the thermostat, and then thoroughly mixed. This process was carried out with the minimum removal of the flasks from the thermostat. Blank experiments showed that this could be done without raising the temperature of the solutions more than 0.1°. When mixed, the solution was rapidly sucked into a conductivity cell, which had also been allowed to reach the temperature of the bath. This cell was essentially a U-shaped tube with two bulbs, into one of which platinum plate electrodes were sealed and afterwards platinized. The ends of the tubes were supplied with stopcocks, so that when these were shut no changes of the level of the liquid could occur during the experiment.

Measurements of the conductivity were then made at different times, over a range corresponding to a 100-fold change of concentration of the pseudo nitro compound. The final conductivity was obtained by allowing the solution to stand until all significant changes of conductivity had taken place, and then measuring the conductivity. This measurement was preferred to that obtained by measuring the conductivity of 0.005 *N* sodium chloride solution, as it avoids the errors and delay which occur when a level has to be adjusted to a mark. Further, the use of the final conductivity instead of that of a 0.005 *N* solution of sodium chloride automatically corrects for any reversibility of the reactions in cases, such as these, in which the reactions are very nearly completed. However, the differences between the final conductivities and that of 0.005 *N* sodium chloride are not greater than those which could be produced by filling the tubes to different levels.

Source of Chemicals.—The phenylnitromethane was prepared by the action of benzyl bromide on silver nitrite. It was purified by precipitating its sodium salt from an ethereal solution of the phenylnitromethane with a solution of sodium methylate in methyl alcohol. The salt was then taken up in water, and the aqueous solution was freed from practically neutral substances, for example, benzyl alcohol, by washing it with ether. The phenylnitromethane was precipitated from the aqueous solution of its salt with carbon dioxide. It was then fractionally distilled in a vacuum.[2]

The nitromethane, a Kahlbaum preparation, was purified by fractional distillation. A fraction which distilled between 100.5 and 101.5° was used.

The *p*-nitrophenol was also a Kahlbaum preparation. It was purified by crystallization from water; m. p., 114°.

The standard solutions of the salts of the nitro compounds were prepared by dissolving weighed quantities of the nitro compounds in 0.01 *N* solutions of sodium hydroxide. The sodium hydroxide was standardized against the hydrochloric acid solutions, using phenolphthalein as the indicator. The sodium hydroxide used contained traces of carbonate, but this was an advantage, as the presence of the carbonate prevents any appreciable excess of either hydrogen ion or of the negative ion of the isonitro compound, which might be produced by a failure to measure out or mix exactly equivalent amounts of the acid and alkali.

Measurement of the Conductivities.—The usual conductivity set was used. It consisted of an Edison potassium hydroxide battery giving 6.7 v., 1000-cycle Leeds and Northrup oscillator, a standard four-dial resistance box with a maximum resistance of 9999 ohms, a Kohlrausch slide-wire bridge of Leeds and Northrup make and a set of Murdock headphones.

Preliminary runs were always made, during which the cell was balanced for capacity, so that during the experiments sharp minima could be obtained without delay.

The conductivities were measured with an accuracy of about 0.1%. However, as the conductivities are only partly due to the conductivities of the isonitro acids the actual accuracy of any measurement is much less, more especially near the end of a run.

Temperature Control.—A gallon (3.8-liter) Dewar flask was used as a thermostat. The bath liquid in every case was in equilibrium with a solid phase, and was stirred mechanically throughout the runs, except during the times when the minima of sound in the phones was being observed. The constant-temperature systems used were carbon tetrachloride in equilibrium with solid carbon tetrachloride, water in equilibrium with ice, benzene in equilibrium with solid benzene, and a mixture

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[2] We thank Messrs. M. A. Joslyn and C. Judah, students at this university, for this preparation of our phenylnitromethane.

of methyl alcohol and water, 1 to 10 by volume, in equilibrium with ice. Although this last is a two-component system, it gave a temperature as constant as the other systems, due to the fact that the heat flow through the Dewar flask during the experiment was equivalent to the heat of solution of an amount of ice quite negligible with respect to the water present in the liquid phase. The temperatures were measured from time to time during the runs, and at different parts of the bath. During none of the runs reported in this article was any variation of temperature greater than 0.05° with respect to both time and place observed.

Owing to the great dilution of the reagents, the heat of the reaction is quite small with respect to the heat capacity of the reacting solutions, so that no rise in temperature greater than 0.1° could have taken place through the mixing of the reagents. The heat of mixing methyl alcohol and water was avoided by making up the solutions with the already mixed solvents.

Experimental Results

The results obtained are shown graphically in eight curves. In these curves the common logarithms of the conductivities due to the isonitro acids are plotted against the times which have elapsed after mixing. In each case the conductivity of the final solution is taken as the unit of conductivity. In every case except Curve 8 the final solution was a 0.005 *N* solution of sodium chloride. In Curve 8 a slight excess of hydrochloric acid was present. The conductivity of the isonitro acid, expressed in terms of the final solution, was obtained by subtracting the final conductivity from the measured conductivity and dividing the result by the final conductivity. Throughout this paper, this quantity is represented by the letter *c*.

The value of *c* is proportional to the concentration of the negative ion of the isonitro acid during any run, as the changes of mobility of the ions are negligible during an experiment (the solutions are very dilute) and the total conductivities never change more than 40%. The results of a typical experiment are shown in Table I.

TABLE I

RATE OF FORMATION OF *p*-NITROPHENOL FROM ITS IONS AT —23.6°

Initial concentrations: *p*-isonitrophenol, 0.005 *N*; sodium chloride, 0.005 *N*

Time, min.	Conductivity, mhos × 10^{-4}	*c*	Time, min.	Conductivity, mhos × 10^{-4}	*c*
2	2.350	0.2730	11	1.872	0.0141
3.25	2.140	.1593	14	1.857	.0060
6	1.976	.0704	17	1.850	.0022
8	1.914	.0368	22	1.846	.0000
9	1.891	.0243	Infinity	1.846	.0000

Curves 1, 2, 3, 4, 5 and 6 represent experiments in which the initial concentrations were 0.005 *N* with respect to the isonitro acid and to sodium chloride. Curves 1 and 2 represent experiments on phenylisonitromethane at 0 and 5.2°, respectively. Curves 3 and 4 represent experiments on isonitromethane at —23.8 and 0°, respectively. Curves 5 and 6 represent experiments on p-isonitrophenol at —23.6 and —9.8°, respectively. Curve 7 represents an experiment on phenylisonitromethane at 0° in which the initial concentration of the isonitro acid was 0.002 N, while that of the sodium chloride was 0.005 N. Curve 8 represents an experiment in which about 10% excess of hydrochloric acid was present,

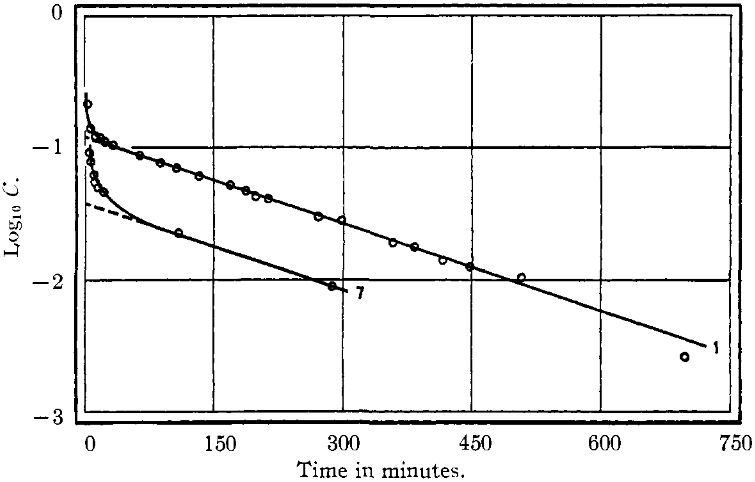


Fig. 1.—Change of conductivity during the formation of phenylnitromethane from its salt at 0°. Initial concentration, 1, 0.005 N; 7, 0.002 N.

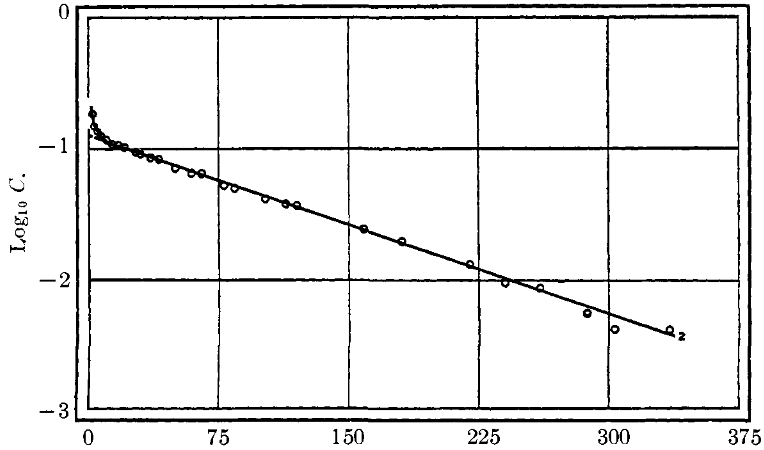
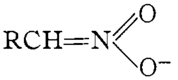
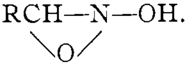
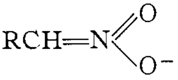


Fig. 2.—Change of conductivity during the formation of phenylnitromethane from its salt at 5.2°. Initial concn., 0.005 N.

but which otherwise was identical with the experiment represented by Curve 4.

The curves are all twofold in character. They are concave upwards at the start, but become straight lines as the reactions proceed. The curved portions of the graphs must represent reversible formations of isonitro compounds by combinations of ions, and an accompanying change of structure, as the reactions are not instantaneous. These reactions may be represented by the type equation,  $\mathrm{RCH{=}N}{\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O^-}}}$ + $H^+ \longrightarrow$  $\underset{\diagdown \mathrm{O} \diagup}{\mathrm{RCH{-}N}}\mathrm{{-}OH}$. The linear portion of the graphs must represent isomeric changes of the ions, whose reversals are prevented by very rapid combinations with hydrogen ion to form the true nitro compounds. These changes may be represented by the type equations,  $\mathrm{RCH{=}N}{\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O^-}}} \longrightarrow$ $\mathrm{R\overline{CH}NO_2}$, and $\mathrm{R\overline{CH}NO_2} + H^+ \longrightarrow RCH_2NO_2$. The reasons why the experiments show these steps in the reactions are discussed in the following section.

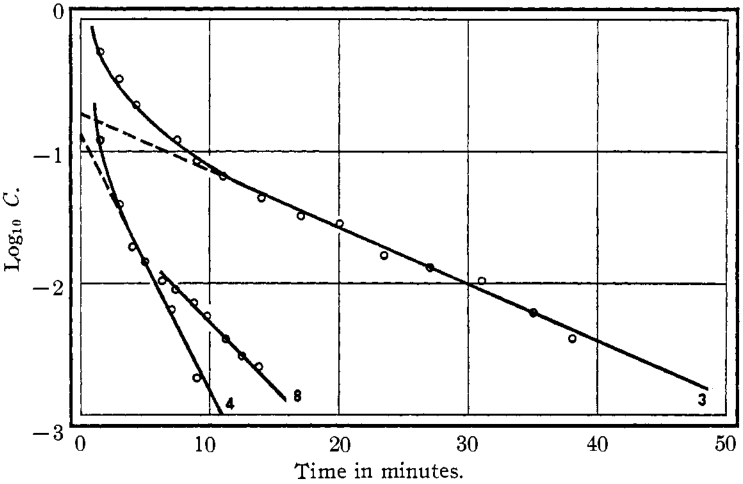


Fig. 3.—Change of conductivity during the formation of nitromethane from its salt: 3, initial concn., 0.005 *N*, *T*, −23.8°; 4, initial concn., 0.005 *N*, *T*, 0°; 8, initial concn., 0.005 *N*, *T*, 0°, HCl present.

Discussion of Results

If the isonitro acids are partially ionized and change irreversibly to the un-ionized nitro compounds, the courses of the reactions may be followed by conductivity measurements, but the rates of decrease of the conductivities are not proportional to the rates of formation of the un-ionized compound, because the fraction of any reactant which is ionized increases as its concentration decreases. However, if we assume that the mobilities of the ions are constant during the reaction, that the activities are proportional to the concentrations and that the purely ionic reactions are rapid with respect to the reactions involving changes of structure,[3] then we can obtain equations expressing the rate of change of conductivity as a function of the conductivity, in which the nature of the function depends on the mechanism of the reaction. Thus, if the rate-determining reaction is a monomolecular change of the ion of the isonitro acid to an ion which immediately combines with a hydrogen ion to form the nitro compound, the equation will be

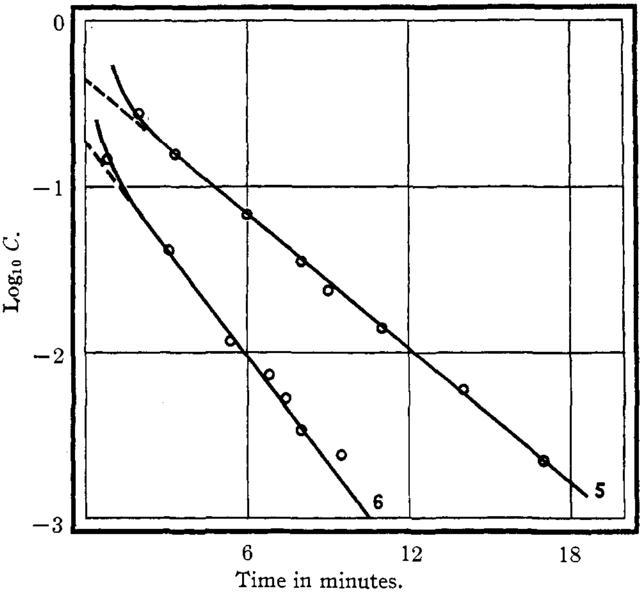


Fig. 4.—Change of conductivity during the formation of *p*-nitrophenol from its salt: 5, initial concn., 0.005*N*, *T*,—23.6°; 6, initial concn., 0.005*N*, *T*,—9.8°.

$$-dc/dt = kc/[(2c/KR) + 1] \qquad (1)$$

where c is the conductivity due to the isonitro acid, k is the rate of reaction constant, K is the dissociation constant of the isonitro acid, while R is a proportionality constant connecting the conductivity, c, with i, the concentration of the ion of the isonitro compound, by the equation

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[3] All of these assumptions are valid when the solution is very dilute and the change of conductivity during the reaction is small, and both of these conditions exist in our measurements.

$c = Ri$. On the other hand, if the master reaction is a monomolecular change of the undissociated isonitro acid to the nitro compound, then the equation connecting the rate of change of conductivity with the conductivity is

$$-\mathrm{d}c/\mathrm{d}t = k/KR \cdot [(2c/KR) + 1] \tag{2}$$

These equations would give different types of curves if log c were plotted against time. The curve corresponding to Equation 1 would be concave downwards at high values of c, but would become a straight line as c decreases. On the other hand, the curve which would be obtained from Equation 2 would be a straight line at the beginning, but would become concave upwards, eventually corresponding to the curve of a second-order reaction. Whether the plot of an actual series of measurements would show these peculiarities would depend on the range of values over which c was measured, and on the values of R and K.

The experimental curves (1, 2, 3, 4, 5, 6) belong to neither of these types. They are all concave upwards at the beginning and then become linear, these changes being too abrupt for the curves to represent a combination of Equations 1 and 2. Variations in temperature of sufficient magnitude to produce the effects observed were quite impossible. The only explanation of such curves is that there are two simultaneous reactions or mechanisms of reaction, one of which becomes subordinate to the other as the reaction proceeds. This disappearance of one of the reactions may be either due to its higher order, or because it reaches a steady state, and since, in every case, the two reactions differ markedly in rate, the steady states must be approximately equal to the true equilibria.

These two alternatives are very easily distinguished, for if equilibrium is reached only after a lapse of time, the slope of the curve depends not only on the conductivity, but also on the time, as long as this time is short. On the other hand if the disturbing reaction becomes insignificant because it is a high-order reaction, then the slope of the curve depends only on the conductivity.

To settle this point Expt. 7 was performed. In this experiment all of the conditions were identical with those of Expt. 1, except the initial concentrations of phenylisonitromethane. A comparison of the curves obtained from the two experiments (Fig. 1) shows that they are not superimposable at the beginning, but that after sufficient time has elapsed to allow the steady state to be established, the two curves become identical. This experiment shows conclusively that there is an equilibrium reaction as well as the irreversible change in the case of the phenylisonitromethane, and since all of the curves belong to the same type, presumably also in the cases of the other substances.

In each case, as the change of conductivity due to the reversible reaction becomes negligible, the rate of change of the conductivity becomes proportional to the conductivity, and this proportionality continues over the rest of the range of conductivities measured. This is shown by the linear portions of the curves.

If this phenomenon were due to a monomolecular change of an un-ionized substance to the true nitro compound or, to what is equivalent to this, a second-order reaction of the ions to the nitro compound, then a bend in the curve of log c against time (see Equation 2) should have been noticeable, unless the value of R is very much greater than the corresponding values for organic acids in aqueous solution; for, if in any case the acid were so weak that, throughout the range of concentrations measured, the amount of the substance ionized is negligible, then the conductivities would have fallen over a lower range than those measured. The values of R were measured for phenylisonitromethane and isonitromethane at 0° in the 50% methyl alcohol, and were found to be lower than those of acetic acid in aqueous solution at 0°.

$R = (c_{\text{sodium salt}} + c_{\text{HCl}} - c_{\text{NaCl}})/N$, where $c_{\text{sodium salt}}$, c_{HCl} and c_{NaCl} are the conductivities of the sodium salt of the nitro compound, of hydrochloric acid and of sodium chloride, respectively, all measured at the same very low concentrations. As all of these substances are strong electrolytes, 0.005 N is a low enough concentration for 10% accuracy. In the units in which the conductivities have been expressed in this paper, $c_{\text{HCl}} = 2.84$, $c_{\text{NaCl}} = 1$, c for the sodium salt of phenylnitromethane = 0.69 and c for the sodium salt of nitromethane = 0.90.[4] Hence, $R = 506$ and 548 for phenylisonitromethane and isonitromethane, respectively.

With such values of R, the variations from apparently monomolecular curves, predicted by Equation 2, would have been noticed for acids which would give log $c = -1.2$ when the concentration = 0.005 N. Since such a value of log c is less than those which would be obtained by extrapolating the linear portions of the curves to zero time, the first-order character of the curves cannot be attributed solely to monomolecular reactions of un-ionized molecules, nor to second-order reactions of ions.

On the other hand, if the linear portions of the curves are due to first-order reactions of the ions, the downward concavities of the curves demanded by Equation 1 could be obliterated by the upward concavities due to the reversible reactions, more especially, if the amounts of the true nitro compounds formed before the equilibrium reactions have become negligible are large. This would be the case if the nitro compounds are formed directly from the ions of the isonitro salt and not from those of the substances produced in the reversible reactions, for in that case the

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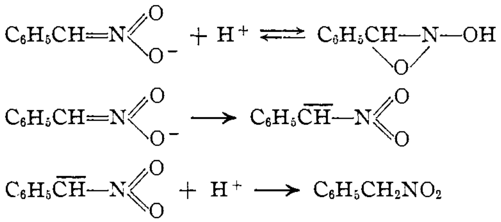
[4] No correction has been made in these measurements for the hydrolysis of the salt, so that these figures are somewhat too high.

concentrations of the reacting ions at the beginning of the reactions are much higher than those corresponding to the steady state.[5]

Further, if there are any accompanying reactions of the un-ionized molecules, there would be a further obliteration of the downward concavities of the curves expected from Equation 1; but whatever the cause for the great range over which the curves are straight lines, the slopes of the lines at the lower concentrations must represent the rates of reactions which are first order with respect to the ions.

That the linear portion of the curve is to be attributed to a reaction monomolecular with respect to the negative ion was further verified in the case of nitromethane by Expt. 8. In this experiment excess of acid was used, which by its mass-action effect should reduce the rate of the reaction due to the negative ion. That this is the case is strikingly shown by a comparison of Curves 4 and 8.

The mechanism for these isomerization reactions shown by the rate measurements can be represented by the following equations, in which phenylnitromethane has been chosen as the substance depicted.



(A)

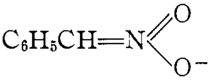
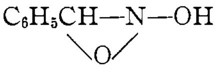
(B)

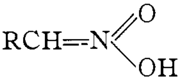
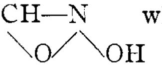
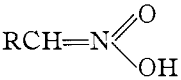
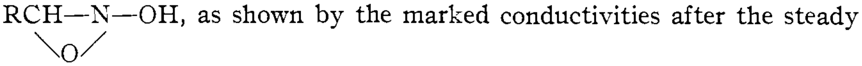
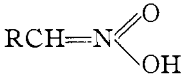
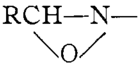
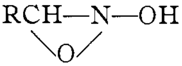
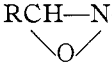
(C)

Equation A represents the reversible reaction which produces the first rapid change of conductivity, and which soon reaches a steady state. Equation B is the rate determining step of the changes which produce phenylnitromethane, and the reaction whose rate is measured by the slope of the linear portion of the curve, while Equation C is a rapid follow reaction, whose rate even in the most dilute solutions measured, must be great in comparison with that of the reverse of Reaction B.

It must be noted that rate measurements do not give direct evidence

[5] This conclusion is supported by the fact that the extrapolations of the linear portions of the curve to zero time apparently do not give the true value of the ion concentrations corresponding to the steady state at initial total concentrations, for in the case of phenylnitromethane at 0° these values are not proportional to the square root of the initial concentrations, but seem to depend upon how quickly the steady state is reached; while in the case of the other two substances these extrapolations lead to higher values at lower temperatures, and the differences are greater than those which might be expected from changes in the value of *R* due to changes of temperature. This would mean that either the steady states are reached when the total concentrations of isonitro compounds are markedly less than the initial concentrations, or that the degree of ionization increases as the temperature decreases; this latter is unlikely, as generally the formation of a weakly ionized substance from ions is an exothermic process.

for the structural formulas of the substances involved, and that the formulas assigned to the substances involved in these equations are chosen only because they do not involve anomalous valences. While the authors consider that the structures  $C_6H_5CH{=}N\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix}$ and  $C_6H_5\underset{\diagdown O \diagup}{CH{-}N}{-}OH$ probably represent the negative ions of the sodium salt of phenylisonitromethane, and the substance formed by the reversible reaction, respectively, and that this latter substance is probably the isomer of phenylnitromethane which is precipitated from the salt with hydrochloric acid, they do not consider that the formula $C_6H_5CH^-$ —NO_2 truly represents the negative ion which combines with hydrogen ion to form the true nitro compound. In the case of nitromethane, the heat of activation is so small (less than 10,000 cal.) that it seems very unlikely that it could represent the energy necessary to shift an electron from an oxygen to a carbon atom.

It may be noted that the formulation suggested for the reaction removes an anomaly which previously existed. Hantzsch, from his measurements, judged that the isonitromethanes were somewhat stronger acids than acetic acid, but the suggested formula,  $RCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ would be expected to represent acids as strong as sulfurous acid, that is 1000-fold stronger than acetic acid because of the pentavalent nitrogen atom, while there is no reason to believe that the other formula suggested for isonitromethanes, namely,  $\underset{\diagdown O \diagup \diagdown OH}{RCH{-}N}$ which has neither double bonds nor pentavalent nitrogen, would be as strong as acetic acid. However, our experiments have shown that the original acid  $RCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ changes much too rapidly to permit of an estimate of its strength by such measurements as these, while the acidic properties of the substances  $\underset{\diagdown O \diagup}{RCH{-}N}{-}OH$, as shown by the marked conductivities after the steady state has been reached, are due to its tautomeric equilibrium with the more acidic  $RCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ and not to its ionization to H^+ and  $\underset{\diagdown O \diagup}{RCH{-}N}{-}O^-$ The over-all strength of the pseudo acids of the type  $\underset{\diagdown O \diagup}{RCH{-}N}{-}OH$ cannot be judged by extrapolation of the linear portions of the curves, as the values so obtained depend on the relative rates of the reactions of Types A and B, as well as on the acidity of the intermediate compounds of the type .

In the cases of phenylnitromethane and *p*-nitrophenol, the final products of the reactions are indubitably the nitro compounds, as these substances can be obtained in large yields from their salts under more drastic conditions than those of these experiments. But nitromethane is much more sensitive to hydrolysis, and it was thought necessary to test experimentally whether the reaction which was measured is an irreversible hydrolysis or the formation of a pseudo acid from its salts, although Hantzsch has assumed it to be of the latter type. The following experiment with its result shows that Hantzsch's assumption is justified.

A 0.01 *N* solution of the sodium salt of isonitromethane was mixed with an equal volume of 0.01 *N* hydrochloric acid at 0°, and allowed to stand for 20 minutes. An equivalent of 0.01 *N* sodium hydroxide solution was then added, and again the solution was allowed to stand for 20 minutes. It was again mixed with an equivalent of 0.01 *N* hydrochloric acid and the conductivity was measured from time to time. The same solvent and the same precautions were used in this experiment as in the other measurements. The conductivity was found to decrease in the same way as in Expt. 4. The value of c, 2.67 minutes after mixing, was 0.03, which is comparable with $c = 0.04$ after three minutes in Expt. 4, as the solution is only half as concentrated with respect to the isonitro acid in this experiment, owing to the double neutralization.

However, the final solutions obtained in the experiments on nitromethane gradually increase in conductivity on standing at 0°, but this change is slow compared to the changes of conductivity reported in this paper, and cannot produce significant errors.

The Velocity Constants and Heats of Activation

The velocity constants of the reactions are measured by the slopes of the linear portions of the curves, multiplied by 2.3 and divided by 60 to bring the units to reciprocal seconds. The values are given in Col. 3 of Table II. In each case they are the average values obtained from several independently drawn curves. They are velocity constants for the Type B reactions.

The heats of activation per mole of these same reactions are obtained from the rate constant measured at different temperatures by the usual equation, $Q = -R\Delta \ln k/\Delta(1/T)$, where k is the velocity constant and Q the heat of activation. The heats of activation in calories per mole are given in Col. 4 of Table II.

In Table II the values of B, another constant characteristic of reactions, are given in the last column. The logarithm of a monomolecular-reaction constant may be expressed by the equation $\log_{10}k = B - Q/(2.3 \times RT)$. The reaction is thus determined by the constants B and Q.

TABLE II

VELOCITY CONSTANTS AND HEATS OF ACTIVATION

Substance	Temp., °C.	Velocity constant, sec. $^{-1}$	Heat of activation per mole	B
Phenylnitromethane	5.2	1.78×10^{-4}	22000 ± 2000	13.56
Phenylnitromethane	0	8.34×10^{-5}		
Nitromethane	0	7.45×10^{-3}	8450 ± 600	4.66
Nitromethane	−23.8	1.68×10^{-3}		
p-Nitrophenol	− 9.8	8.44×10^{-3}	4250 ± 800	1.47
p-Nitrophenol	−23.6	5.37×10^{-3}		

Inspection of Table II shows that Q and B vary widely for the different reactions. Q and B are both greatest for the slowest reacting substance, phenylnitromethane, and smallest for the fastest reacting substance, *p*-nitrophenol, and that B is large when Q is large. The differences in the Q's and B's for the various substances are more significant than a comparison of the rates, for the values of Q and B are such that if the reactions were carried out above 50°, the phenylnitromethane would be the fastest reacting of the three substances, and *p*-nitrophenol the slowest.

Addenda

In the body of the paper the equations

$$-\mathrm{d}c/\mathrm{d}t = kc/\left(\frac{2c}{KR} + 1\right) \quad (1) \qquad -\mathrm{d}c/\mathrm{d}t = k/KR.\ c^2/\left(\frac{2c}{KR} + 1\right) \quad (2)$$

are given without derivation. The mathematical derivations are quite simple. The fundamental assumptions that the mobilities of the ions are constant and that the mass law is valid for the electrolytic dissociation may be expressed by

$$c = Ri \tag{3}$$

and

$$i^2/u = K \tag{4}$$

respectively, where i is the concentration of the ionized reactant, u that of the undissociated reactant, R is the proportionality constant between the concentrations of the ions and the conductivity of the solution due to the isonitro acid and K is the dissociation constant of the acid.

Since one mole of reactant forms one mole of resultant, the rate of formation of the resultant is equal to the rate at which the total reactant is used up, that is,

$$\mathrm{d}x/\mathrm{d}t = -\mathrm{d}(i + u)/\mathrm{d}t \tag{5}$$

where x is the concentration of the resultant.

Combining Equations 4 and 5 and eliminating u,

$$\mathrm{d}x/\mathrm{d}t = -\mathrm{d}i/\mathrm{d}t\ [(2i/K) + 1] \tag{6}$$

Now dx/dt depends upon the mechanism of the reaction, and for monomolecular reactions of the negative ion or of the undissociated acid,

$$dx/dt = ki \tag{7}$$

or

$$dx/dt = ku \tag{8}$$

Hence,

$$-di/dt = ki/\left(\frac{2i}{K} + 1\right) \quad \text{or} \quad -di/dt = k/K.i^2/\left(\frac{2i}{K} + 1\right)$$

Substituting c for i in these equations gives

$$-dc/dt = kc/\left(\frac{2c}{KR} + 1\right) \quad \text{and} \quad -dc/dt = k/KR.c^2/\left(\frac{2c}{KR} + 1\right)$$

When c is small, these equations become equivalent to the usual equations for monomolecular and dimolecular reactions, respectively.

In Expt. 8 excess of acid is present. If the concentration of the excess acid is called a, then Equation 4 becomes $i(i + a)/u = K$, while the other fundamental equations remain unchanged. Consequently $dx/dt = -(di/dt)[(2i/K) + (a/K) + 1]$ instead of $dx/dt = -(di/dt)[(2i/K) + 1]$. When i becomes very small compared to a, then $dx/dt = -di/dt[(a/K) + 1]$, so that if the reaction is monomolecular with respect to the ions, then

$$-di/dt = \left[k/\left(\frac{a}{K} + 1\right)\right] i, \quad \text{or} \quad -dc/dt = \left[k/\left(\frac{a}{K} + 1\right)\right] c.$$

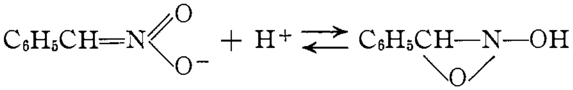
The reaction is thus still first order, but the constant is reduced from k to $k/[(a/K) + 1]$.

Summary

The isomerization of isonitromethane, phenylisonitromethane and *p*-isonitrophenol to the corresponding nitrocompounds has been investigated by measurements of the rates of the changes of electrical conductivity which occur when solutions of the sodium salts of these substances are mixed with hydrochloric acid.

In all these cases the rates of decrease of the conductivity were found to diminish very rapidly at first, and after some time were observed to become proportional to the conductivities, due to the isonitro compounds, and to remain so to as low values as it was possible to measure.

The twofold character of the curves corresponding to these results has been explained by assuming another type of isonitro compound which is formed by reversible reactions as, for instance, such a reaction as



$$C_6H_5CH{=}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-} + H^+ \rightleftarrows C_6H_5CH{-}N{-}OH$$

The persistent proportionality between the rates of change of the conductivities and the conductivities of the isonitro acids has been taken as a strong indication that formations of the true nitro compounds occur through comparatively slow changes of the ions of the isonitro acids to ions which combine rapidly with hydrogen ion to form the nitro compounds.

The velocity constants of these second reactions have been measured at two temperatures for each of the substances. The heats of activation of these reactions have been calculated from the results.

The heats of activation have been found to differ very markedly for the three substances, that for phenylisonitromethane being more than 10,000 cal. greater than that for nitromethane.

The heat of activation in the case of *p*-isonitrophenol has been found to be very small, being less than 5000 cal.

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[CONTRIBUTION FROM THE GOODYEAR TIRE AND RUBBER COMPANY]

RESEARCHES ON THIAZOLES. II. THE NITRATION AND REDUCTION OF 2-MERCAPTOBENZOTHIAZOLE AND ITS SUBSTITUTED DERIVATIVES

BY JAN TEPPEMA AND L. B. SEBRELL

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In a previous paper[1] a new method of preparation for 2-mercaptobenzothiazole was given. This method was extended to the preparation of several new 2-mercaptobenzothiazoles which had hitherto not been described.

It is the purpose of the present paper to outline the results obtained by nitration and subsequent reduction of 2-mercaptobenzothiazole and its derivatives as given in the first paper.

Bogert[2] has shown that the nitration of 2-phenylbenzothiazole gives 6-phenyl-2-mercaptobenzothiazole. We were unable to fix the position of the nitro group in nitro-2-mercaptobenzothiazole by use of the procedure followed by Bogert. However, we were able to prove by another way that the nitro group is in Position 6.

The work of Kwaysser[3] and Mylius[4] has made available 2-amino-5-nitrothiophenol. After reduction this compound, treated with sodium hydrosulfide and carbon disulfide according to our previously described method gave 6-amino-2-mercaptobenzothiazole; m. p., 263°. The reduction product of nitrated 2-mercaptobenzothiazole after purification melted at 260°. A mixed-melting-point determination gave no decrease in melting point. We, therefore, conclude that on nitration the nitro group enters the ring in 2-mercaptobenzothiazole in Position 6.

These reactions are

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[1] Teppema and Sebrell, THIS JOURNAL, **49**, 1748 (1927).

[2] Bogert, *ibid.*, **44**, 826 (1922).

[3] Kwaysser, *Ann.*, **277**, 240 (1893).

[4] Mylius, *Dissertation*, University of Berlin, **1883**.