[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE REACTION VELOCITY OF REARRANGEMENT OF POTASSIUM DIBENZHYDROXAMATE

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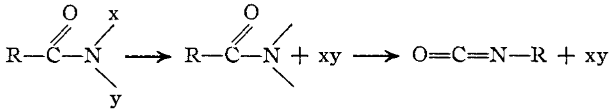
Several theories have been advanced to explain the rearrangement of hydroxamic acids (Lossen[1]), halogen amides (Hofmann[2]), acyl azides (Curtius[3]), and other similar classes of compounds. The most successful interpretation of all rearrangements of this character was proposed by Stieglitz;[4] he assumed the intermediate formation of univalent nitrogen derivatives. Thus,

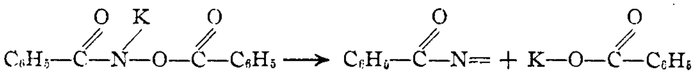


$$R—\overset{O}{\overset{/\!/}{C}}—N\begin{smallmatrix}\diagup x\\ \diagdown y\end{smallmatrix} \longrightarrow R—\overset{O}{\overset{/\!/}{C}}—N\begin{smallmatrix}\diagup\\ \diagdown\end{smallmatrix} + xy \longrightarrow O{=}C{=}N—R + xy$$

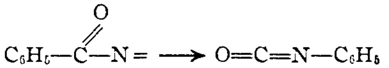
So far, no attempt has been made to determine the order of reaction in rearrangements of this kind by measurements of their velocities. It seemed desirable to follow closely the course of a reaction of this character with time so as to gain information concerning the extent and influence of side reactions.

For this purpose, the potassium salt of dibenzhydroxamic acid was chosen. The following equations represent the stages in the rearrangement of the compound and the reactions which accompany the principal change.

Rearrangement:



$$C_6H_5—\overset{O}{\overset{/\!/}{C}}—\overset{K}{N}—O—\overset{O}{\overset{/\!/}{C}}—C_6H_5 \longrightarrow C_6H_5—\overset{O}{\overset{/\!/}{C}}—N{=} + K—O—\overset{O}{\overset{/\!/}{C}}—C_6H_5 \qquad (1)$$



$$C_6H_5—\overset{O}{\overset{/\!/}{C}}—N{=} \longrightarrow O{=}C{=}N—C_6H_5 \qquad (2)$$

Accompanying reactions:

$$C_6H_5—N{=}C{=}O + 2KOH \longrightarrow C_6H_5—NH_2 + K_2CO_3 \qquad (3)$$

$$C_6N_5—N{=}C{=}O + C_6H_5—NH_2 \longrightarrow (C_6H_5—NH)_2{=}CO \qquad (4)$$

These equations represent the chief reactions. Mohr[5] found that a solution of the potassium salt of dibenzhydroxamic acid in water, when heated alone or with an excess of potassium hydroxide, gave symmetrical diphenyl urea, aniline and benzoic acid as the chief decomposition products; but, in addition to these substances, he obtained tests for monobenzhydroxamic acid, for phenyl isocyanide and for phenyl isocyanate. He

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[1] Lossen, *Ann.*, **161**, 358 (1872); **175**, 268 (1875).

[2] Hofmann, *Ber.*, **14**, 2721 (1881); **15**, 408 (1882).

[3] Curtius, *Ber.*, **27**, 778 (1894).

[4] Stieglitz, THIS JOURNAL, **18**, 751 (1896).

[5] Mohr, *J. prakt. Chem.*, **71**, 133 (1905).

stated that the quantity of alkali present determined the relative amounts of aniline and urea formed, and that the actual concentration of the alkali also was an important factor.

We have found that the temperature is an additional factor; that is, the lower the temperature the greater the amount of urea produced. This, of course, would be expected, since the formation of the urea must be dependent chiefly upon the stability of phenyl isocyanate in the solution. At the temperature used by Mohr (70°) the reaction was complete in two hours. This was too rapid a reaction to permit its progress to be examined with time. Therefore, the conditions were altered; the temperature was lowered and a greater dilution of the reactants was chosen so that the reaction was not complete until about 100 hours had passed.

Under these conditions, experiments made at 25° with 5.5 g. of potassium salt of dibenzhydroxamic acid and one equivalent of potassium hydroxide dissolved in 1000 cc. of water showed that there was little change in the appearance of the transparent, colorless solution until about 15 hours had elapsed. At this time, the solution became a light purple in color, and an unmistakable odor of phenyl isocyanide was noticed. The amount of phenyl carbylamine must be exceedingly small. Its formation during a reaction in which phenyl isocyanate is certainly the chief intermediate product is noteworthy. The reaction mixture gave tests for aniline and for monobenzhydroxamic acid almost from the beginning. About 25 hours after the reaction began, a fine precipitate of symmetrical diphenyl urea made its appearance, and the liquid became darker, until finally it assumed a brownish-red tint. The amount of the urea increased gradually as the reaction progressed to the end.

If the reaction proceeds according to the above equations, a unimolecular velocity constant should be obtained, since the steps indicated by 3 and 4 are known to be very rapid under the prevailing conditions. However, it was problematical, in view of the complicating side reactions, whether a method for the measurement of the rearrangement alone could be devised. Yet with the exception of monobenzhydroxamic acid, only traces of products, probably not coming from the normal rearrangement, have ever been isolated. Therefore it is possible that the hydrolysis of the potassium dibenzhydroxamate is the only side reaction which could appreciably affect the measurement of the rate of rearrangement. Since the reaction could be stopped at any time by the addition of a mineral acid, and the unchanged dibenzhydroxamic acid could be precipitated practically quantitatively from the solution of its potassium salt, it was possible to measure the rate at which the dibenzhydroxamic acid itself was being consumed in the rearrangement and in the accompanying side reactions. When the figures obtained in this way were inserted in the equation for a first order reaction, it was found that a diminishing value for K was obtained for a period of 25 hours, at the beginning of the reaction.

TABLE I

SHOWING A DIMINISHING VALUE FOR K FOR THE FIRST PART OF THE REACTION

$K = \frac{1}{t} \times \frac{1}{0.4343} \log \frac{a}{a-x}$ where a is the g. of dibenzhydroxamic acid per 100 cc. at the start, and x is the g. of dibenzhydroxamic acid consumed at time t.

Time in hours	0	1.75	5.9	7.75	19.75
$a - x$	0.4233	0.3539	0.2593	0.2346	0.1634
K	....	.0999	.0830	.0761	.0482

Beyond that stage, during approximately 75% of the course of the reaction, a fairly satisfactory constant was obtained.

TABLE II

RESULTS OF TWO EXPERIMENTS SHOWING CONSTANCY OF K OVER THE LAST 75% OF THE REACTION

Expt. 1

Time in hours	0	23	41.8	46.9	66.9	71.6	95.8	115
$a - x$	0.4794	0.2221	0.1201	0.0890	0.0442	0.0316	0.0163	.0060
K	0	.0334	.0331	.0359	.0356	.0379	.0353	.0380

Expt. 2

Time in hours	0	28.75	47	55	64.1	75.5	81.5	97.5
$a - x$	0.4794	0.1479	0.1047	0.0822	0.0400	0.0386	0.0290	0.0134
K	0	.0409	.0324	.0321	.0387	.0333	.0344	.0367

The average deviation from the mean in these experiments is from 4 to 8%. Since the results were based upon actual weighings of materials separated from solution, the error is large, particularly toward the end of each run. However, the fact that results obtained repeatedly gave fairly good constants for the last 75% of the reaction indicates that, over this range at least, we are dealing with a unimolecular reaction which in all probability proceeds according to the equations given.

It was thought that the anomalous behavior during the first 25-hour period might be explained principally by the hydrolysis of dibenzhydroxamic acid to give monobenzhydroxamic acid and benzoic acid. This hydrolysis was measured by taking advantage of the fact that a molecule of dibenzhydroxamic acid, as it rearranges, yields one molecule of benzoic acid, but when a molecule of dibenzhydroxamic acid is hydrolyzed, a molecule of monobenzhydroxamic acid is formed in addition to one molecule of benzoic acid. Consequently, the increase in acidity of the reaction mixture over that normally required by the rearrangement may be considered a measure of the hydrolysis. It was actually found that the hydrolysis, while quite large at first, slowed down in the neighborhood of 25 hours to the point where it would not affect the results of the rearrangement appreciably.

TABLE III

GRAMS OF DIBENZHYDROXAMIC ACID HYDROLYZED AFTER T HOURS

T	1	2.75	6.9	8.75	20.75	29
D. per 100 cc. hydrolyzed g...	0.0184	0.0326	0.0554	0.0648	0.1031	0.1057

However, when account was taken of this hydrolysis in the reaction-velocity equation for the rearrangement, it was found that K still decreased in value for the first 25 hours. Therefore, other complications must enter in. Chief among them was the fact that the free potassium hydroxide in the reaction mixture was constantly diminishing, and diminishing rapidly in the early stages before symmetrical diphenyl urea began to form. It was being consumed to neutralize carbon dioxide which resulted from the hydrolysis of the isocyanate, as well as to hydrolyze the dibenzhydroxamic acid. But, as soon as the urea began to form (which occurred in the neighborhood of the 25-hour mark), the potassium hydroxide was no longer consumed to the same extent, because a large part of the phenyl isocyanate was not being hydrolyzed to aniline; it was reacting with aniline to form symmetrical diphenyl urea. Consequently, up to about 25 hours, we may expect a continually diminishing velocity due to decrease in the concentration of the potassium hydroxide. On account of the experimental difficulties involved it was not possible to measure with any degree of accuracy, the alkalinity of the reaction mixture at any given time.

Experimental Part

In a liter of potassium hydroxide solution containing 2.26 g. of potassium hydroxide was dissolved 4.794 g. of dibenzhydroxamic acid. A stirrer was placed in the flask and the latter was immersed in a water thermostat at 25°. From time to time 100cc. portions of this solution were withdrawn and filtered rapidly; the solid was washed with 50 cc. of cold water; any insoluble symmetrical diphenyl urea remained behind on the filter paper. The filtrate was sufficiently dilute to prevent the precipitation of benzoic acid when it was acidified. To the filtrate 46.8 cc. of hydrochloric acid (1 cc. of which was equal to 0.00483 g. of potassium hydroxide) was added; this amount of acid is equivalent to 0.226 g. of potassium hydroxide. The free dibenzhydroxamic acid formed as a flocculent, white precipitate. The solution and precipitate were stirred and allowed to stand for an hour, after which the solid acid was collected in a Gooch crucible, washed, and dried at 75–80° until constant weight was reached.

The second filtrate and washings contained benzoic acid, potassium chloride, monobenzhydroxamic acid, carbon dioxide and a trace of dissolved dibenzhydroxamic acid. (There was a slight solubility error due to the dibenzhydroxamic acid which was taken into account in the calculations.) Before determining the acidity due to organic acids, it was necessary to eliminate the carbon dioxide. It was found that this could be accomplished by bubbling a stream of dry, carbon dioxide-free air through the solution at a pressure of about 10 cm. of water for 15 minutes. (It was determined by experiment that no benzoic acid was lost in this way.) Finally, the solution was titrated with a standard solution of potassium hydroxide using phenolphthalein as an indicator. If no hydrolysis of potassium dibenzhydroxamate had taken place, the acidity due to benzoic acid should correspond with the amount of dibenzhydroxamic acid consumed. Since the acidity in excess of this amount is caused by the monobenzhydroxamic acid, it furnishes a measure of the hydrolysis of the potassium dibenzhydroxamate.

Summary

The rearrangement of the potassium salt of dibenzhydroxamic acid has been studied and a description given of the changes in the reaction mixture as time progressed. The velocity of the rearrangement has been measured and found to correspond with that of a unimolecular reaction for the last 75% of the reaction time. An explanation has been given as to why a first order reaction constant was not obtained for the first 25% of the reaction.

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NOTE

Graham and Carr's Supposed Calcium-Nicotine Combinations.—In a recent article[1] Graham and Carr mention the difficulty which they had in securing complete recovery, by any available analytical method, of all the nicotine present in various products to which calcium salts had been added, and attribute their difficulty to the probable formation of hypothetical combinations of calcium with nicotine which are insoluble in the solvents used in the several analytical processes they employed. While there can be no doubt as to the fact of failure to recover all nicotine originally present in such mixtures, the explanation suggested by these authors is altogether untenable in the light of theoretical considerations and of experimental evidence as to the effect of various calcium compounds upon nicotine-containing materials which has been published recently.

In studies of the effect of various chemicals upon the volatility of nicotine from various compounds and mixtures used for insecticide purposes, Thatcher and Streeter,[2] Headlee and Rudolfs,[3] and de Ong[4] have found that nicotine, in its reactions with other chemicals, behaves in a way exactly analogous to the behavior of ammonia, and that nicotine compounds react with various calcium salts in the same way as do ammonium compounds, in so far as the volatility of the resulting product is concerned. Hence, it is very difficult to conceive the formation of stable insoluble compounds of the strong base nicotine with the strongly basic element calcium.

The investigations referred to above have shown that carbonates of the alkali and alkaline earth metals are especially effective in increasing the volatility of nicotine from insecticide mixtures. In fact, mixtures of nicotine sulfate (Black-leaf Forty) with calcium or sodium carbonate, when exposed in the open air, lost by volatilization every trace of nicotine

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[1] Graham and Carr, THIS JOURNAL, **46**, 695 (1924).

[2] Thatcher and Streeter, *N. Y. (Geneva) Agr. Expt. Sta. Bull.*, **501** (1923).

[3] Headlee and Rudolfs, *N. J. Agr. Expt. Sta. Bull.*, **381** (1923).

[4] de Ong, *J. Econ. Entomology*, **16**, 486 (1924).