formed. These are as much as one-fourth inch (6.3 mm.) long and one thirty-second inch (0.4 mm.) in cross section and were adapted for the complete X-ray structure analysis heretofore unknown, which will be reported elsewhere.

Preliminary crystallographic examination indicates that these red lead crystals are prismatic in habit. They are entirely transparent and under polarized light show pleochroism, yellow to red. Extinction is inclined 13° to the long axis. They have well-marked cleavage, prismatic in type, making angles of 120° with one another with conchoidal fracture transverse to the long axis. The crystals belong to the monoclinic system, are characterized by almost square cross sections and with great length in proportion to their diameter, terminating in a combination of basal pinacoid and dome with a very high angle beta. Some prisms are terminated by a basal pinacoid with a 101 dome and two faces of the 011 dome, making a four-sided pyramidal termination. In other cases the termination is wedge shaped with the domes 011. Still another termination showed basal pinacoid and the dome 011 terminating the prism 110 and the orthopinacoid 100.

Finally a lead–sodium–oxygen compound was obtained in the bomb at 250–260° by heating 10 g. of lead dioxide, 3.24 g. of sodium peroxide, 10 cc. of hydrogen peroxide and 5 cc. of water. On analysis this compound, heretofore unknown, gave the following composition: lead, 80.9, 80.8%; active oxygen, 5.54, 5.57; sodium, 3.635 and 3.66. This compound is also formed as a by-product when Pb_2O_3 or Pb_5O_8 is prepared according to the procedures given above. The pattern is shown in Fig. 2f. Boiling with water gradually decomposes it giving lead dioxide.

Summary

The oxides Pb_2O_3 and Pb_5O_8 have been prepared by a pressure bomb technique at temperatures of 260–275° and 295–310°, respectively. These have been identified by microscopic examination and X-ray diffraction patterns. The large crystals obtained by Simon and reported to be pure PbO_2 are identical with the Pb_2O_3 crystals prepared in this work. Pb_3O_4 in the form of very large crystals was also prepared in the bomb at 355–375° and identified by its X-ray pattern. A new lead–sodium–oxygen compound is also prepared in the bomb.

Urbana, Illinois Received August 16, 1937

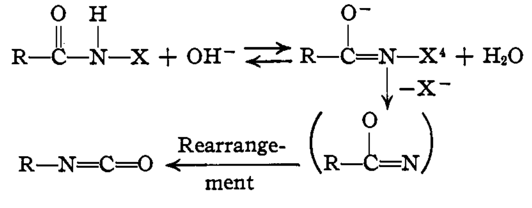
[Contribution from the Chemical Laboratory of Duke University]

The Relative Rates of Decomposition of the Potassium Salts of Certain Meta and Para Substituted Dibenzhydroxamic Acids. A Study of the Lossen Rearrangement[1,2]

By W. B. Renfrow, Jr., and Charles R. Hauser

The Stieglitz mechanism for the Hofmann and Lossen reactions has been widely accepted for a number of years, but increased knowledge of electrons and valence naturally has introduced modifications in the representation of the process. The following equations are considered to illustrate the best mechanism[3] for these reactions.

The halogen amide or dihydroxamic acid reacts with a base to form a salt. The anion of the salt then releases a negative halogen or carboxylate ion and rearranges to an isocyanate. No evidence has been obtained for the existence of the intermediate "univalent nitrogen" compound, but such a compound might have a very brief existence. On the other hand, the release of X and the rearrangement might be simultaneous processes.



$$R-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle H}{|}}{N}-X + OH^- \rightleftarrows R-\overset{\overset{\textstyle O^-}{|}}{C}=N-X^{4} + H_2O$$
$$\downarrow -X^-$$
$$R-N=C=O \xleftarrow[\text{ment}]{\text{Rearrange-}} \left(R-\overset{\overset{\textstyle O}{|}}{C}=N\right)$$

The factors affecting the ease with which a compound will undergo the Hofmann type of rearrangement were first investigated by Jones and

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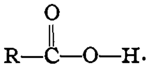
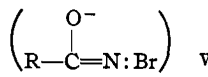
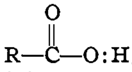
[1] This paper embodies a part of the material presented by W. B. Renfrow, Jr., to the Graduate School of Duke University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

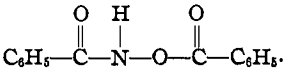
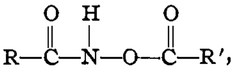
[2] This paper is considered as the third in the series entitled "The Removal of HX from Organic Compounds by Means of Bases."

[3] In this connection see Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, 1936, pp. 363–371.

[4] A resonance form of this ion may be represented by the formula $\left(R-\overset{\overset{\textstyle O}{\|}}{C}-N^{-}-X\right)$, but for simplicity it will be represented only in the enolic form. The ion probably has an intermediate structure. See Sidgwick, *J. Chem. Soc.*, 694 (1937).

his students,[5] who showed that esters of triphenylacethydroxamic acid, $(C_6H_5)_3CCONHOH$, underwent the Lossen rearrangement more readily than esters of diphenylacethydroxamic acid, $(C_6H_5)_2CHCONHOH$. The generalization was made that "the ease of rearrangement is dependent upon the tendency of the radical in the univalent nitrogen derivative to exist as a free radical." Recently,[6] evidence has been presented that R does not exist as a free radical during the Hofmann rearrangement.

In a previous paper,[7] we have shown that the rates of decomposition of a series of meta and para substituted bromobenzamides in alkaline solution are inversely related to the ionization constants of the corresponding carboxylic acids. This relationship was anticipated from the mechanism represented above and from consideration of the ionization constants of meta and para substituted benzoic acids as measures of the electron attraction of R in the general formula  $R-\overset{O}{\overset{\|}{C}}-O-H$. The line of reasoning which led to the anticipation of this relationship was as follows. The formation of salts of the bromoamides could not be the rate determining step in the reaction, because these salts have been isolated in certain cases. Neither is it likely that the rate of rearrangement of the univalent nitrogen compound is the rate determining step because all attempts to isolate a compound of this type have failed. Therefore, the rate of decomposition of a bromoamide in alkaline solution should be determined by the ease of release of bromide ion from the negative ion of the bromoamide salt. Since bromine is released with a complete octet of electrons from the bromoamide ion  $\left(R-\overset{O^-}{\overset{|}{C}}=N:Br\right)$ whereas a proton is released without any electrons from the acid,  $R-\overset{O}{\overset{\|}{C}}-O:H$, an inverse relationship was expected between the rates of decomposition of a series of substituted bromobenzamides and the ionization constants of the corresponding carboxylic acids.

In this investigation a study has been made of the rates of decomposition of the potassium salts of a series of substitution products of dibenzhydroxamic acid,  $C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$. These particular compounds were selected because substituents may be placed in both ends of the molecule and the resulting effect on the reaction velocity measured. It was anticipated that an inverse relationship would exist between the rates of decomposition of the salts of a series of dihydroxamic acids,  $R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-R'$, and the ionization constants of the carboxylic acids corresponding to R, provided that R′ was maintained the same. A direct relationship was expected between reaction velocities and the ionization constants of the acids corresponding to R′ when R was held constant.

Rates of Decomposition.—Dougherty and Jones[8] previously have conducted experiments on the rate of decomposition of dibenzhydroxamic acid in the presence of two equivalents of potassium hydroxide, but were unable to obtain satisfactory constants over the entire course of the reaction. The phenyl isocyanate formed in the reaction was hydrolyzed by the excess alkali to aniline. As soon as aniline was present in the solution, it reacted with phenyl isocyanate to form the highly insoluble diphenyl urea, which had to be filtered off before the unchanged dibenzhydroxamic acid could be precipitated. The excess alkali not only hydrolyzed the phenyl isocyanate but also hydrolyzed some of the potassium dibenzhydroxamate to potassium benzoate and potassium benzhydroxamate according to the equation

$$(C_6H_5CONOCOC_6H_5)K + KOH \longrightarrow C_6H_5COOK + C_6H_5CONHOK$$

In this investigation, the above difficulties have been eliminated by measuring the rates of decomposition of the potassium salts of the dihydroxamic acids in 0.10 *N* ammonia solution. The ammonia reacts with phenyl isocyanates to form soluble phenylureas, but does not increase the hydroxyl ion concentration to an extent that will cause appreciable hydrolysis of the dihydroxamic acids. The concentration of the potassium salts was 0.025 molar and the temperature was 30 ± 0.02°.

Velocity constants were calculated from the first order rate of reaction equation

$$K = \frac{2.303}{t}\log\frac{a}{a-x}$$

in which *a* is the grams of dihydroxamic acid per 100 cc. at the time the first aliquot was removed

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[5] See Porter, "Molecular Rearrangements," The Chemical Catalog Co., New York, 1928, p. 20–25.

[6] Wallis and Moyer, THIS JOURNAL, **55**, 2598 (1933); Bell, *J. Soc. Chem. Ind.*, **52**, 584 (1933).

[7] Hauser and Renfrow, THIS JOURNAL, **59**, 121 (1937).

[8] Dougherty and Jones, *ibid.*, **46**, 1535 (1924).

and $a - x$ is the grams per 100 cc. after time t. Two sets of measurements have been made with each compound. The yields of amines produced by rearrangement and hydrolysis of the intermediate isocyanates also were determined.

The velocity constants for potassium dibenzhydroxamate are given in Table I. In Table II are tabulated the average values of the rate constants obtained for the potassium salts of a series of meta and para substituted dibenzhydroxamic acids. In the latter table are given also the yields of amines obtained in each case.

Table I

Rates of Decomposition of Potassium Dibenzhydroxamate (0.025 *M*) in 0.10 *N* Ammonia at 30°

Time, min.	Run 1 ppt., g.	*K*	Time, min.	Run 2 ppt., g.	*K*
0	0.5726		0	0.5457	
115	.4886	0.00138	130	.4554	0.00139
378	.3396	.00138	438	.2992	.00137
576	.2595	.00138	760	.1925	.00137
736	.2055	.00139	1376	.0822	.00138
1338	.0912	.00137			
	Average	.00138		Average	.00138

In order to determine the effect of ammonia concentration on the velocity of the reaction, the rate of decomposition of 0.025 *M* potassium dibenzhydroxamate in 0.20 *N* ammonia solution was measured. The values for the velocity constants obtained in this way decreased slightly during the course of the reaction, and the average value in 0.20 *N* ammonia was 5% higher than the average value in 0.10 *N* ammonia. This discrepancy is greater than can be attributed to experimental error, and it seemed probable that the hydroxyl ion concentration in 0.20 *N* ammonia was sufficient to cause appreciable hydrolysis of the potassium dibenzhydroxamate. The yield of aniline was found to be 5.6% lower in a 0.20 *N* ammonia solution than in a 0.10 *N* solution, indicating that more hydrolysis does occur in the more concentrated solution. The presence of the ammonia in a 0.10 *N* solution may have a slight effect on the reaction velocities, but, since all rate measurements were made in solutions of the same concentration, we consider the results to be comparable.

The method used in this investigation for determining the rates of decomposition of potassium dihydroxamates is very satisfactory for compounds that decompose to yield a benzoic acid which is soluble in water to the extent of at least 0.025 mole per liter. The method can be used in cases where a less soluble acid is produced, but constants cannot be obtained for the entire course of the decomposition.

The average values of the velocity constants were reproducible to within 3% in all cases except that of *p*-methoxybenzoyl benzhydroxamate. The insolubility of *p*-anisic acid made it possible to obtain constants only over the first 15% of the decomposition, and the maximum deviation in these constants amounted to 6%.

Discussion of Results

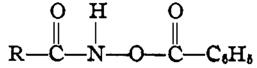
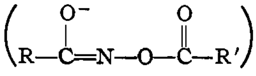
In Fig. 1, the negative logarithms of the velocity constants for the rates of decomposition of the potassium salts of a series of dihydroxamic acids of the general formula  $R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$ have been plotted against the negative logarithms of the ionization constants of the carboxylic acids corresponding to R. It may be seen that the derivative of the acid with the smaller dissociation constant has the greater velocity constant.

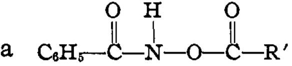
Table II

Velocity Constants and Yields of Amines Obtained in the Decomposition of Potassium Dibenzhydroxamates of the General Formula

 $\left(R-\overset{O^-}{\overset{|}{C}}=N-O-\overset{O}{\overset{\|}{C}}-R'\right)K^+$ in 0.10 *N* Ammonia at 30°

Substituent in R	Substituent in R′	*K*	Percentage yields of amines
p-CH_3O	*m*-NO_2	0.0390	83[a]
p-CH_3	*m*-NO_2	.0150	85[a]
p-CH_3O	None	.00943	96
None	*m*-NO_2	.00575	91
m-CH_3	*m*-F	.00436	93
p-CH_3	None	.00359	90
None	*m*-F	.00272	91
m-CH_3	None	.00216	94
None	None	.00138	92
m-CH_3O	None	.000926	93
None	*p*-CH_3O	.000821	97

[a] Salts of these compounds were more unstable than any others prepared, and probably were contaminated with potassium *m*-nitrobenzoate. This would account for the low yield of amine isolated. The presence of a small amount of potassium *m*-nitrobenzoate should not appreciably affect the rates of decomposition of the dihydroxamic acid salts.

In Fig. 2 the negative logarithms of the velocity constants for the rates of decomposition of the potassium salts of a series of dihydroxamic acids of the general formula  $C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-R'$ have been plotted against the negative logarithms of the ionization constants of the carboxylic acids corresponding to R′. An excellent direct relationship is exhibited.

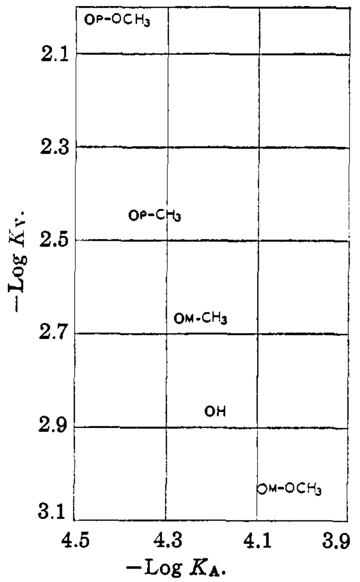
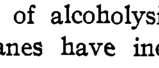


Fig. 1.

These results are in agreement with the mechanism presented above for the Lossen reaction, and support the view that the rate determining step in a Hofmann or Lossen reaction is the release of X as a negative ion from the anion of the salt $(R—CONX)^- K^+$. X in this general formula may be halogen or the group  $R'—\overset{\overset{O}{\|}}{C}—O—$.

The results obtained by Jones and Hurd[6] with derivatives of di- and triphenylacethydroxamic acids are also considered to be in accord with these views. Although the triphenylmethyl group might be expected to be more strongly electron attracting than the diphenylmethyl group, recent measurements[9] of the rates of alcoholysis of a series of phenylchloromethanes have indicated that the triphenylmethyl group is not as strongly electron attracting as the diphenylmethyl group. This order of reactivity was attributed to resonance.

The Effect of Substituents on the Rate of the Reaction.[10]—The Lossen reaction affords a favorable case for a study of the effects of substituents on reaction velocity. According to the mechanism presented above, the reaction measured is quite definite and consists in breaking a single bond in such a way that one of the products takes both of the original bond electrons.

$$A:B \longrightarrow A + :B$$

The rearrangement of A prevents the reversal of the reaction. In the substituted dibenzhydroxamic acid salts, various substituents may be placed in both A and B, and the resulting effects on the reaction velocity can be measured with considerable precision.

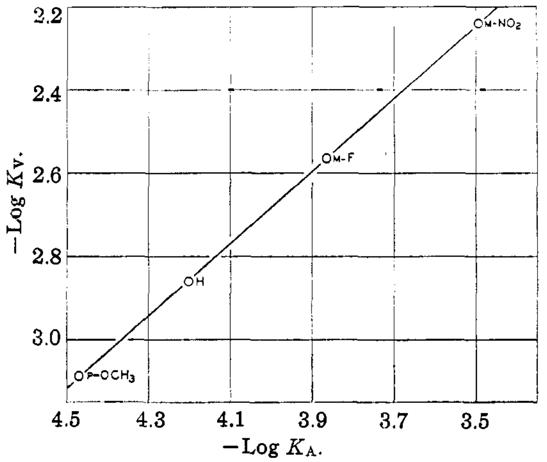


Fig. 2.

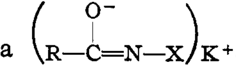
Perhaps the most convenient method for comparing quantitatively the effect of a substituent on the ionization of a benzoic acid with the effect of the same substitutent on a reaction velocity is to utilize the equation recently suggested by Hammett[10]

$$\log K = \log K_0 + \sigma\rho$$

or

$$\rho = \frac{\log K - \log K_0}{\sigma}$$

in which K is the velocity constant for a substituted reactant, K_0 is the velocity constant for the corresponding unsubstituted reactant, σ is the difference between the logarithm of the ionization constant of benzoic acid and the logarithm of the ionization constant of the substituted benzoic acid corresponding to the substituted reactant, and ρ is a constant, dependent upon the reaction, the medium and the temperature. The constancy of the values of ρ calculated for a series of substituted reactants affords a measure of the rigor of the relationship.

In Table III are listed the values of ρ for variation of X in a series[11] of dihydroxamic acid salts of the general formula  $\left(R—\overset{\overset{O^-}{|}}{C}=N—X\right)K^+$. It can

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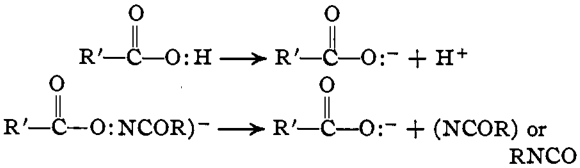
[9] Nixon and Branch, THIS JOURNAL, **58**, 496 (1936).

[10] In this connection see especially Hammett, *ibid.*, **59**, 96 (1937).

[11] This series includes compounds that could not be plotted in Graphs I or II because they contain substituents in both R and X.

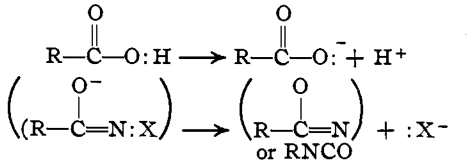
be seen from Table II that the values of ρ are constant within the limits of experimental error. It should be noted that, both in the ionization of a benzoic acid and in the decomposition of the dihydroxamate ions in which the effect of substituents in X alone is being considered, the portion of the molecule which is being varied keeps both of the original bond electrons when the bond is broken. This can be represented by the following equations, in which X is $R'-\underset{\underset{O}{\|}}{C}-O-$.



$$R'-\overset{\overset{O}{\|}}{C}-O{:}H \longrightarrow R'-\overset{\overset{O}{\|}}{C}-O{:}^- + H^+$$

$$R'-\overset{\overset{O}{\|}}{C}-O{:}NCOR)^- \longrightarrow R'-\overset{\overset{O}{\|}}{C}-O{:}^- + (NCOR) \text{ or } RNCO$$

In Table IV are listed the values of ρ for variation of R in a series[11] of dihydroxamic acid salts of the general formula $\left(R-\overset{\overset{O^-}{|}}{C}=N-X\right)K^+$, and the discrepancies may be seen to be entirely too great to be attributed to experimental error. Here the analogy between the ionization of a benzoic acid and the decomposition of the dihydroxamate ion is not as close as in the previous case.



$$R-\overset{\overset{O}{\|}}{C}-O{:}H \longrightarrow R-\overset{\overset{O}{\|}}{C}-O{:}^- + H^+$$

$$\left(R-\overset{\overset{O^-}{|}}{C}=N{:}X\right) \longrightarrow \underset{\text{or } RNCO}{\left(R-\overset{\overset{O}{|}}{C}=N\right)} + {:}X^-$$

In the latter reaction the portion of the molecule which is varied loses both of the bond electrons when the reaction takes place, while in the ionization of the acid it keeps both electrons.

The discrepancies between the values of ρ for variation of R may be due to resonance[9] or tautomeric[12] effects in the benzene ring. Since such effects may be regarded as polarizations, it might be expected that they would be induced to a greater extent by a strongly electron-attracting carboxyl group, which takes the bond electrons when reaction occurs, than by a relatively weakly electron-attracting proton. A further investigation of this subject is now in progress.

TABLE III

RELATIONSHIP BETWEEN IONIZATION CONSTANTS AND REACTION VELOCITIES FOR VARIATIONS OF X IN DIBENZHYDROXAMATE IONS OF THE GENERAL FORMULA $\left(R-\underset{\underset{O^-}{|}}{C}=N-X\right)$

Substituent in R	Substituent in X	ρ
None	m-NO_2	0.874
None	m-F	.876
None	p-CH_3O	.844[a]
p-CH_3O	m-NO_2	.870
p-CH_3	m-NO_2	.875
m-CH_3	m-F	.905[a]

[a] In these cases, experimental difficulties rendered the constants less accurate.

TABLE IV

RELATIONSHIP BETWEEN IONIZATION CONSTANTS AND REACTION VELOCITIES FOR VARIATIONS OF R IN DIBENZHYDROXAMATE IONS OF THE GENERAL FORMULA $\left(R-\underset{\underset{O^-}{|}}{C}=N-X\right)$

Substituent in R	Substituent in X	ρ
p-CH_3	None	−2.44
p-CH_3	m-NO_2	−2.45
m-CH_3	None	−2.81
m-CH_3	m-F	−2.96
p-CH_3O	None	−3.11
p-CH_3O	m-NO_2	−3.10
m-CH_3O	None	−1.50

Experimental

Preparation of Hydroxamic Acid Salts.—The potassium salts of benzhydroxamic, p-methoxybenzhydroxamic, p-methylbenzhydroxamic, m-methylbenzhydroxamic and m-methoxybenzhydroxamic acids were prepared by a modification of the method of Jeanrenaud.[13] Separate solutions of 46.7 g. (0.667 mole) of hydroxylamine hydrochloride in 240 cc. of methyl alcohol, and of 56.3 g. (1 mole) of potassium hydroxide in 140 cc. of methyl alcohol were prepared at the boiling point of the solvent. Both were cooled to 30–40° and the one containing alkali added with shaking to the hydroxylamine solution. Any excessive rise of temperature during the addition was prevented by occasional cooling in an ice-bath. After all of the alkali had been added, the mixture was allowed to stand in an ice-bath for five minutes in order to ensure complete precipitation of potassium chloride. One-third of a mole of the ethyl or methyl ester of the appropriate benzoic acid was then added with thorough shaking, and the mixture filtered with suction immediately. The residue in the funnel was washed with a little methyl alcohol. The filtrate was transferred to an Erlenmeyer flask which was then tightly stoppered and allowed to stand for three days at room temperature. Due to the ease with which hydroxylamine is oxidized by atmospheric oxygen, the solution was protected from air as much as possible during the above manipulations.

The potassium salts of benzhydroxamic, p-methoxybenzhydroxamic, and p-methylbenzhydroxamic acids were only partially soluble in alcohol and consequently precipitated from the reaction solution. The potassium salts of m-methylbenzhydroxamic and m-methoxybenzhydroxamic acids were soluble in the amount of alcohol used for their

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[12] See Dippy, Watson and Williams, *J. Chem. Soc.*, **348** (1935).

[13] Jeanrenaud, *Ber.*, **22**, 1272 (1889).

preparation. In the case of benzhydroxamic acid, the potassium salt was filtered from the solution, washed with a little alcohol and dried. The yield of potassium benzhydroxamate was 70% of the theoretical amount. In the case of the other hydroxamic acids, the alcoholic solutions were poured into three times their volume of water and stirred until clear solutions were obtained. Any salt that had precipitated from the alcohol solution was dissolved in the alcohol–water solution. The solution was made acid with concentrated hydrochloric acid and 40.8 g. (0.167 mole) of $BaCl_2 \cdot 2H_2O$ dissolved in it. Upon addition of concentrated ammonia a dense precipitate of the barium salt of the hydroxamic acid was formed. Ammonia was added until no further precipitation was produced. The barium salt was filtered, washed with water and allowed to dry in the air. As soon as the salt was fairly dry it was placed in a desiccator. The yields were as follows: barium *m*-methylbenzhydroxamate, 78%; barium *p*-methylbenzhydroxamate, 73%; barium *m*-methoxybenzhydroxamate, 65%; barium *p*-methoxybenzhydroxamate, 75% of the theoretical amount.

In addition to the 70% yield of potassium benzhydroxamate, a 15% yield of the barium salt of benzhydroxamic acid was obtained by treating the alcoholic filtrate from the potassium salt with water, acid, barium chloride and ammonia in the manner described above. The total yield of salt in this case was 85% of the theoretical amount.

Preparation of Dihydroxamic Acids.—Ten to twenty grams of the appropriate barium or potassium benzhydroxamate was finely pulverized and suspended in 50 to 100 cc. of dioxane. The calculated amount of benzoyl or substituted benzoyl chloride was added to the dioxane suspension and the mixture stirred and boiled for five minutes. After the mixture had cooled to about room temperature it was poured in a fine stream into 800 to 1000 cc. of distilled water. The resulting precipitate of dihydroxamic acid was filtered, washed with water, and crystallized from alcohol. Ninety-five per cent. ethyl alcohol was generally used for the crystallizations, but, in cases where the substance was fairly soluble in alcohol, water was added to the hot solution until precipitation started. The solution was then heated until all material was dissolved, after which it was allowed to cool slowly to room temperature. One crystallization was usually sufficient to yield a pure compound, but two or three were sometimes necessary. The yields of purified products were 60–80% of the theoretical amounts. Since the dihydroxamic acids melted with decomposition, their melting or decomposition points were taken by immersing the capillary tube containing the substance in a bath 3–5° below the melting point and heating slowly until a clear liquid was obtained. Analytical data and melting points are given in Table V.

TABLE V

ANALYTICAL DATA AND MELTING OR DECOMPOSITION TEMPERATURES FOR THE DIHYDROXAMIC ACIDS STUDIED

Substituent in R	Substituent in R′	Neutral equiv. Calcd.	Neutral equiv. Found	Melting or dec. temp., °C.
None	*m*-NO_2	286.1	286.1	148–150
None	None	241.1	242.0	161–162
None	*p*-CH_3O	271.1	270.8	135–137
p-CH_3O	None	271.1	270.1	162–164
p-CH_3	None	255.1	255.7	161–162
p-CH_3	*m*-NO_2	300.1	297.3	161–162
p-CH_3O	*m*-NO_2	316.1	314.9	124–126
m-CH_3	None	255.1	255.6	123–125
m-CH_3O	None	271.1	271.8	118–120
None	*m*-F	259.1	259.3	140–143
m-CH_3	*m*-F	273.1	274.5	114–116

Analysis of Dihydroxamic Acids.—An accurately weighed sample (0.6–0.8 g.) of the purified acid was dissolved in approximately 100 cc. of 95% ethyl alcohol. One drop of thymol blue indicator solution was added and the solution titrated with 0.1 *N* sodium hydroxide solution until the original yellow color changed to light purple. The titer obtained was substituted in the following equation and the neutral equivalent calculated.

$$\text{N. e.} = \frac{\text{Wt. of sample} \times 1000}{\text{Cc.} \times \text{normality factor}}$$

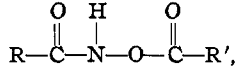
Preparation of Potassium Salts of Dihydroxamic Acids.—Eight to ten grams of the dihydroxamic acid was dissolved in 100–200 cc. of a solution composed of equal volumes of dioxane and absolute alcohol. The solution was cooled below 10° in an ice-bath and the calculated amount of an approximately 2.5 *N* standardized solution of potassium hydroxide in absolute alcohol added rapidly with vigorous shaking. A precipitate of the potassium salt usually formed immediately, but sometimes it was necessary to add a little ether to initiate the precipitation. The mixture was allowed to remain in the ice-bath for five to ten minutes, after which it was filtered and the salt washed first with a little alcohol and finally with about 25 cc. of ether. The salts were dried by pressing on a porous plate, and used immediately.

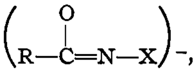
Procedure for Determining Velocity Constants.—A 0.025 molar solution of the freshly prepared potassium salt in 0.10 *N* ammonia was prepared by dissolving the finely pulverized salt in the ammonia solution. A thermometer graduated in tenths of a degree was placed in the flask and the temperature adjusted as rapidly as possible to exactly 30° by shaking the flask containing the solution under a running hot water tap. A bath of ice water was at hand to cool the solution in case the temperature of the reaction solution was inadvertently made too high. When the temperature had been adjusted, the flask was placed immediately in a thermostat at 30 ± 0.02° and 100-cc. aliquots withdrawn at appropriate time intervals and run into a solution of 3 cc. of glacial acetic acid in 15 cc. of water, whereby unreacted dihydroxamic acid was precipitated. The time was recorded when the solution from the pipet was released into the acid solution. The precipitate of dihydroxamic acid was allowed to stand for at least one hour with the solution from which it had precipitated, after which it was transferred quantitatively into a weighed sintered glass crucible, washed thoroughly with water and dried at 70–80° for five to ten hours or until constant weight was reached.

Procedure for Determining Yields of Amine Produced by Rearrangement.—The yields of aniline from *m*-nitrobenzoyl benzhydroxamate, benzoyl benzhydroxamate and *p*-methoxybenzoyl benzhydroxamate were determined by the following procedure. A 0.0250 molar solution of the potassium salt of the dihydroxamic acid in 0.10 *N* ammonia was allowed to remain in a thermostat at 30° for three days. Twenty-five cc. aliquots of this solution were refluxed for seven hours with 15 cc. of concentrated hydrochloric acid, after which the solution was cooled in an ice-bath and made alkaline by the addition of solid sodium hydroxide. The alkaline solution was extracted with two 50-cc. and one 25-cc. portion of ether. The ether extracts were washed with 30 cc. of water and extracted with one 60-cc. and two 20-cc. portions of a solution of 15 cc. of concentrated hydrochloric acid in 85 cc. of water. The acid solution was boiled to expel ether. To the cooled acid solution was added 12 cc. of 10% potassium bromide solution, after which it was titrated with approximately 0.15 *N* standard potassium bromate solution. The end-point was determined by spotting on starch–potassium iodide paper. One cubic centimeter of 0.1 *N* potassium bromate is equivalent to 1.551 mg. of aniline. This method gave results reproducible to within 0.8%.

The yield of amine from benzoyl *p*-methoxybenzhydroxamate, benzoyl *p*-methylbenzhydroxamate, *m*-nitrobenzoyl *p*-methylbenzhydroxamate, *m*-nitrobenzoyl *p*-methoxybenzhydroxamate, benzoyl *m*-methylbenzhydroxamate, benzoyl *m*-methoxybenzhydroxamate and *m*-fluorobenzoyl benzhydroxamate was determined by dissolving 1 to 2 g. of the potassium salt of the dihydroxamic acid in the amount of 0.1 *N* ammonia calculated to make a 0.025 molar solution and allowing the salt to decompose in the thermostat at 30°. The solution was then made acid with 20 cc. of concentrated hydrochloric acid and refluxed for seven hours. The solution was concentrated to about 50 cc. by distillation, cooled in an ice-bath and made alkaline by addition of solid potassium hydroxide. The alkaline solution was extracted with two 50-cc. and one 25-cc. portion of ether and the combined ether extracts washed with 30 cc. of water. The ether solution was extracted with two 25-cc. portions of 3 *N* hydrochloric acid. The acid solutions were combined in a weighed beaker, evaporated to dryness on a water-bath and finally dried in a desiccator over Drierite until their weight did not change after a day in the desiccator. The yield of amine was calculated from the weight of amine hydrochloride obtained in this way. This method gave results that were reproducible to within 2%.

Summary

1. The rates of decomposition of the potassium salts of a series of meta and para substituted dibenzhydroxamic acids,  $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'}$, have been determined at 30°. A qualitative inverse relationship has been found between the ionization constants of benzoic acids corresponding to R and the rates of decomposition of dihydroxamic acid salts in which the effect of substituents in R alone was considered. A quantitative direct relationship has been found between the ionization constants of benzoic acids corresponding to R′ and the rates of decomposition of dihydroxamic acid salts in which the effect of substituents in R′ alone was being considered.

2. These results support the hypothesis that the rate determining step in a Hofmann or Lossen reaction is the release of X as a negative ion from the anion,  $\left(\mathrm{R{-}\overset{O}{\overset{|}{C}}{=}N{-}X}\right)^-$, of the salt of a halogen amide or dihydroxamic acid.

3. A general method for the preparation of a number of hydroxamic and dihydroxamic acids has been described.

DURHAM, N. C. RECEIVED SEPTEMBER 5, 1937

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

3-Acetoxy-4-chloro-2,5-diphenylfuran

BY ROBERT E. LUTZ, A. H. STUART, F. N. WILDER AND W. C. CONNOR

The two compounds supposed in earlier papers to be acetoxychlorodiphenylfuran, VII, and diacetoxydiphenylfuran[1] have been shown by Kohler and Woodward[1f] to be, respectively, chlorodiphenylfuranone, III, and acetoxydiphenylfuranone, IV. These two compounds were prepared by the action of acetyl chloride and acetic anhydride (with sulfuric acid) on diphenylbutanetrione enol and the open-chain and cyclic ethers. The erroneous furan formulations[1d] were based on these preparations and upon the reactions with phosphorus pentachloride to give dichlorodiphenylfuran, II. The latter reactions are outlined correctly in the diagram.

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[1] (a) Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934); Lutz and Wilder, *ibid.*, **56**; (b) 1987; (c) 2065; (d) 2145 (1934); (e) Lutz and Stuart, *ibid.*, **58**, 1885 (1936); (f) Kohler and Woodward, *ibid.*, **58**, 1933 (1936).

The discussion of results in previous papers dealing with diphenylbutanetrione enol (refs. a–d) are confused by the erroneous formulation of diphenylmethoxy and chlorofuranones (III) as open-chain compounds. The corrections are outlined in a later paper (ref. e) together with discussion of the ring-chain tautomerism involved; simultaneously a similar discussion and rigorous proof of the cyclic formulations of this type was published by Kohler and Woodward (ref. f).