approaches that of water, so that interionic effects in formic acid solutions are relatively small. Hence it is possible to gain some information with regard to the molecular state of ionized solutes in this solvent from the magnitude of the freezing point depressions produced by them.

From a large scale plot of the freezing point depressions obtained by Kendall and Adler[2a] for sodium formate solutions, as well as of those here observed, it was found that the lowerings produced by the formate are almost equal to those calculated for a completely dissociated ideal solute; the acetate, however, gives depressions about $^3/_2$ as great as the ideal values. Thus, for example, the depression obtained by interpolation for a 1 molal solution of sodium acetate is 8.06°, as compared with 5.13° for sodium formate at the same concentration, and 5.34°[12] for an ideal binary salt. Thus the lowering due to the acetate is 1.57 times as large as for the formate, or 1.51 times the ideal value. Since the interionic effects would not diverge widely, in this solvent, for two salts of the same valence type, the most probable explanation of this large difference in cryoscopic effects appears to be that based upon solvolysis. Specifically, we may conclude that the solvolytic reaction represented by the equation

$$Na^+ + C_2H_3O_2^- + HCHO_2 \longrightarrow HC_2H_3O_2 + Na^+ + CHO_2^-$$

takes place to a very considerable extent (if, indeed, it does not go practically to completion) in these dilute solutions. Hence the separation, at somewhat higher concentrations, of a solvated sodium *formate* as solid phase, is readily accounted for.

Summary

1. A temperature–concentration curve has been obtained for equilibrium between solid and liquid phases in the binary system sodium formate–acetic acid.

2. Two new compounds, $NaCHO_2 \cdot 2HC_2H_3O_2$ and $NaCHO_2 \cdot HC_2H_3O_2$, have been isolated from these solutions, and their compositions confirmed by analysis.

3. The behavior of sodium formate in acetic acid solution has been shown to be markedly similar to that of sodium acetate in the same solvent.

4. Evidence is presented that sodium acetate is extensively solvolyzed in formic acid solution.

LAWRENCE, KANSAS RECEIVED JANUARY 20, 1941

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[12] This is twice the molal freezing point constant, 2.67, calculated from the melting point, 8.4°, and the heat of fusion, 2713 calories ("International Critical Tables," Vol. V, p. 132).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Acylation of Aldoximes. VI. The Relative Ease and Mechanism of Conversion of Benzoyl-*syn*-aldoximes to Nitriles in the Presence of Pyridine and Pyridinium Chloride[1]

BY CHARLES R. HAUSER AND GERTRUDE VERMILLION

Although benzoyl-*syn*-aldoximes are stable in pure pyridine, they are gradually converted into nitriles (and benzoic acid) on standing in solutions of pyridine containing pyridinium chloride.[2] This conversion is considered to involve the intermediate formation of benzoyl-*anti*-aldoximes, which, like other acyl *anti*-derivatives,[3] would doubtless be decomposed readily by pyridine to form nitriles. The isomerization of benzoyl-*syn*-aldoximes to their *anti*-isomers is assumed to take place through the medium of their acid salts, the precedent for this being the well-known isomerization of the acid salts of *syn*-aldoximes.[4] The reactions may be represented by the following ionic equations, in which Y represents a meta or para substituent.

The effect of various meta and para substituents (Y) in benzoyl-*syn*-benzaldoximes, on their ease of conversion to nitriles has been determined by allowing a series of the compounds in pyridine solutions containing pyridinium ion to stand under the same conditions and then isolating unchanged *syn*-benzoates; in cases in which the nitriles formed were solids they also were isolated. The percentage yields of these substances

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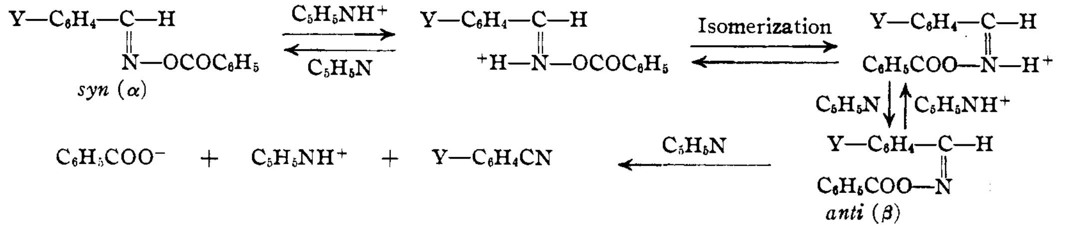
[1] Presented before the division of Organic Chemistry of the American Chemical Society, Detroit Meeting, September, 1940.

[2] See Vermillion and Hauser, THIS JOURNAL, **62**, 2939 (1940).

[3] See Hauser and Jordan, *ibid.*, **58**, 1772 (1936).

[4] See, for example, Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Company, New York, N. Y., 1937, p. 361.

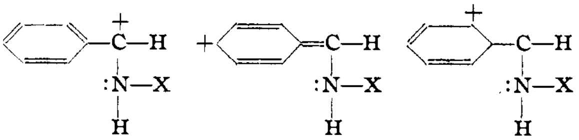


are given in Tables (II) and (III). From these results it may be concluded that the ease of conversion of benzoyl-*syn*-benzaldoximes to nitriles decreases in the following order as the meta or para substituent (Y) is varied: p-OCH_3 > p-CH_3 > H > m-OCH_3 > p-Cl > m-NO_2, p-NO_2. It should be pointed out that while there is no doubt that the position of the three substituents, p-CH_3, H and m-OCH_3, is between the substituents, p-OCH_3 and p-Cl, the relative positions of the three substituents is not established with as much certainty, since the yields of recovered *syn*-benzoates in these cases differ by only 3–5% (Table II) and the yields are probably reproducible to within approximately 5%.

The ease of conversion of benzoyl-*syn*-aldoximes to nitriles in solutions of pyridine–pyridinium ion is evidently not dependent upon the last reaction represented above, involving the elimination of the elements of benzoic acid from the *anti*-benzoates, since if this were the case the reverse order for the effects of substituents should be found. The reverse order has been found for the ease of elimination of benzoic acid from para substituted benzoyl-*syn*-benzaldoximes[5] in the presence of hot triethylamine; thus, as the para substituent is varied the ease of the elimination reaction decreases in the following order: p-NO_2 > p-Cl > p-OCH_3.

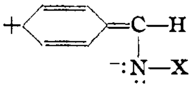
Apparently, the ease of conversion of *syn*-benzoates to nitriles in solutions of pyridine–pyridinium ion is dependent upon the ease with which the *syn*-benzoates are converted to *anti*-benzoates and this should be dependent upon the concentrations of the acid salts of the *syn*-benzoates and/or upon the rates of the isomerization of the acid-salts. If the equilibrium of the acid–base reaction of the *syn*-benzoates with the pyridinium ion is on the side of these reactants, and this seems quite likely, the concentrations of the acid salts would be determined by the basicities of the oxime nitrogens. The decreasing order found for the ease of conversion of the *syn*-benzoates to nitriles is probably also the decreasing order for the basicities of the oxime nitrogens; this seems likely because the strengths of the corresponding benzoic acids, YC_6H_4COOH, increase in this order.[6]

The rates of the isomerization of the acid salts of the *syn*-benzoates may be considered to be dependent upon the single bond character of the carbon–nitrogen group. The single bond resonance forms of the acid salt of benzoyl-*syn*-benzaldoxime may be represented as follows



Substituents in the ring may increase or decrease the contributions that such single bond resonance forms make to the structure of the molecule; for example, the methoxy group in the para position (and also in the ortho position) should increase, while the nitro group should decrease, the single bond character of the carbon–nitrogen group. These effects are directly related to the order found for the effects of substituents on the ease of conversion of *syn*-benzoates to nitriles in solutions of pyridine–pyridinium ion.

Finally, the well-known fact that the *syn-anti* isomerization in the oxime series is greatly facilitated by converting oximes or derivatives into their acid salts is readily explained on the basis that the addition of a proton to single bond resonance forms, such as



should stabilize them, thereby causing them to contribute relatively more to the structure of the molecule.

Experimental

Preparation and Purification of Compounds and Reagents.—Eastman Kodak Co. pyridine was dried over

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[5] Vermillion and Hauser, THIS JOURNAL, **63**, 1227 (1941).

[6] See Dippy and co-workers, *J. Chem. Soc.*, 357 (1938), and earlier papers.

"Drierite" and distilled; the fraction boiling at 114–115° was collected for use. Eastman benzoyl chloride was vacuum distilled before use. Pyridinium ion solution was prepared by passing dry hydrogen chloride gas over dry pyridine in an Erlenmeyer flask until a permanent precipitate of pyridinium chloride remained after shaking the mixture. The flask was stoppered and sealed with paraffin until ready for use. The clear solution above the precipitate was removed as needed by means of a dry pipet.

Benzoyl derivatives were prepared by a modification of the procedure described previously.[2] To 1 g. of *syn*-aldoxime dissolved in 5 cc. of pyridine contained in a three-necked, bolt-headed flask fitted with a thermometer, mercury-sealed stirrer and dropping funnel, was added slowly with stirring a solution of one equivalent of benzoyl chloride in 5 cc. of pyridine. The temperature of the reaction mixture was kept at 0° by cooling the reaction flask in an ice-bath. The addition of benzoyl chloride required approximately five minutes. After standing at 0° for ten minutes longer the mixture was poured into 20 g. of crushed ice; the benzoyl derivative was filtered off and washed free from pyridine with cold water. An alternative procedure consisted in pouring the pyridine mixture into 14 cc. of cold concentrated hydrochloric acid containing 30 g. of crushed ice; the benzoyl derivative was filtered off and washed with water. In order to remove any oxime the benzoyl derivative was treated with a little 2 *N* sodium hydroxide, followed by water. In order to remove any nitrile the derivative was washed with 10 cc. of alcohol. After recrystallization from alcohol or a mixture of alcohol and acetone, the melting points of the benzoyl derivatives of *syn*-benzaldoxime, and of *syn*-4-methoxy-, 3-nitro-, and 4-nitro-benzaldoximes agreed with those reported in the literature.[7] The melting points and analytical data[8] of the benzoyl derivatives not previously recorded are given in Table I. The yields of pure derivative appeared to be good in all cases, that from *syn*-4-methoxybenzaldoxime being 77% of the theoretical amount.

Table I

Melting Points and Analytical Data for Benzoyl Derivatives of Substituted *syn*-Benzaldoximes

Substituent	M. p., °C.	Empirical formula	Percentage nitrogen Calcd.	Percentage nitrogen Found
4-Methyl-	129–130	$C_{15}H_{13}NO_2$	5.85	5.83
3-Methoxy-	108–109	$C_{15}H_{13}NO_3$	5.49	5.40
4-Chloro-	143–144	$C_{14}H_{10}NO_2Cl$	5.40	5.70

Procedure for Determining Ease of Conversion of Benzoyl-*syn*-aldoximes to Nitriles.—To 0.0025 mole of benzoyl-*syn*-aldoxime dissolved in 5 cc. of anhydrous pyridine in a test-tube was added 2 cc. of pyridinium ion solution. The test-tube was stoppered tightly, sealed with paraffin and placed in a thermostat at 30 ± 0.1°. After seventy-two hours, the contents of the tube were poured on approximately 20 g. of crushed ice. Five grams of crushed ice and water were used to rinse out the test-tube. The precipitate was filtered on a sintered glass crucible and washed with cold water until free of pyridine. The solid in the crucible consisted of either or both, benzoyl-derivative and nitrile; these were separated by taking advantage of the greater solubility of the nitrile in alcohol. In general 10 cc. of 95% alcohol was allowed to run slowly through the solid, suction being used only after most of the alcohol had passed through the crucible; the solid was then washed with a second portion of 5 cc. of alcohol in a similar manner. In most cases the solid remaining in the crucible was practically pure derivative and the residue, obtained by evaporation of the alcohol filtrate, practically pure nitrile but in certain cases further treatment was required to completely separate these compounds. An additional amount of nitrile was generally obtained from the original pyridine filtrate. The latter was acidified with 6 *N* hydrochloric acid, extracted twice with ether, and once with 2 *N* sodium hydroxide (in order to remove benzoic acid). Nitrile was obtained by evaporation of the ether solution. In cases in which the nitrile was a liquid no attempt was made to isolate it quantitatively.

Two series of experiments were carried out as described above with the benzoyl derivatives listed in Table II. Although the actual yields of nitrile and of unchanged derivative obtained from certain derivatives differed in the two series by as much as 5%, the relative order of the yields in the two series was the same. The yields given in Table II are average values obtained in the two series of experiments. The melting points on which the yields are based are also given in Table II. A blank run with benzoyl-*syn*-4-methoxybenzaldoxime in 5 cc. of pyridine (but none of the pyridinium ion solution) after seventy-two hours at 30° gave no nitrile, 96% of unchanged benzoyl derivative being recovered.

Table II

Percentage Yields of Products from Benzoyl Derivatives of Substituted *syn*-Benzaldoximes in Pyridine and Pyridinium Ion Solution

	Recovered derivative			Nitrile		
Substituent	Yield, %	M. p., °C. Found[a]	Lit. m. p., °C.	Yield, %	M. p., °C. Found[a]	Lit. m. p., °C.
4-Methoxy-	15	105–109	109–110	80	53–56	60–61
4-Methyl-	23	128–130	129–130[b]			
Hydrogen	26	98–99	101–102			
3-Methoxy-	31	107–109	108–109[b]			
4-Chloro-	48	138–143	143–144[b]	23	89–91	92

[a] The melting points of products were raised by recrystallization to those reported in the literature. [b] See Table I.

Because the benzoyl derivatives of *syn*-3-nitro and *syn*-4-nitrobenzaldoximes would not dissolve completely in the proportions of solvents used in the experiments described above, the ease of conversion of these two benzoyl derivatives together with that of *syn*-4-chlorobenzaldoxime (the most stable derivative listed in Table II) was carried out in the following manner. The benzoyl derivative (0.0024 mole) was dissolved in 30 cc. of pyridinium ion solution and kept at 31° for forty-five hours. The mixture was worked up essentially as described above. The yields of nitrile and unchanged derivative recovered together with the melting points of the products on which the yields are based are given in Table III. Experiments with the benzoyl derivatives of *syn*-4-chloro- and *syn*-3-nitro-benzaldoximes were carried out also under slightly different conditions, the relative yields of products being approximately the same as those found in the experiments described above. Since data for the *syn*-4-chloro- derivative

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(7) See Brady and McHugh, *J. Chem. Soc.*, **127**, 2415 (1925).

(8) Microanalysis by Arlington Laboratories, Chagrin Falls, Ohio.

TABLE III

PERCENTAGE YIELDS OF PRODUCTS FROM BENZOYL DERIVATIVES OF SUBSTITUTED *syn*-BENZALDOXIMES IN PYRIDINIUM ION SOLUTION

	Recovered derivative			Nitrile		
Sub-stituent	Yield, %	M. p., °C. Found[a]	Lit. m. p., °C.	Yield, %	M. p., °C. Found[a]	Lit. m. p., °C.
4-Chloro-	18	141–143	143–144	65	89–92	92
3-Nitro-	35	162–163	164	55	110–113	115
4-Nitro-	35	186–188	196	52	133–137	147

[a] The melting points of products were raised by recrystallization to those reported in the literature.

are found in both Tables II and III it is possible to arrange all of the derivatives studied in the order of their stabilities.

Summary

1. The relative ease of conversion of the benzoyl derivatives of a series of substituted *syn*-benzaldoximes to nitrile in the presence of pyridine and pyridinium ion has been determined.

2. The mechanism of the conversion has been discussed.

DURHAM, N. C.

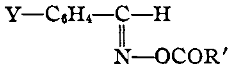
RECEIVED DECEMBER 23, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Relative Ease of Elimination of the Elements of Benzoic Acid from Para Substituted *syn*-Benzaldoxime Benzoates in the Presence of Triethylamine

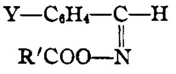
BY GERTRUDE VERMILLION AND CHARLES R. HAUSER

It has been shown that *syn*- or *anti*-benzaldoxime esters, (I) or (II), respectively, may undergo two types of reaction in the presence of a base like sodium hydroxide[1] or potassium amide[1a]; one type of reaction involves the elimination of the elements of acid to form nitrile, while the other type involves the usual hydrolysis or ammonolysis at the carbonyl group of the ester, leading to the formation of the corresponding *syn*- or *anti*-aldoxime.



$$\begin{array}{l} Y{-}C_6H_4{-}C{-}H \\ \qquad\qquad\;\, \| \\ \qquad\qquad\;\, N{-}OCOR' \end{array}$$

(I) *syn* (α)



$$\begin{array}{r} Y{-}C_6H_4{-}C{-}H \\ \| \quad\;\; \\ R'COO{-}N \quad\;\; \end{array}$$

(II) *anti* (β)

Since tertiary amines are incapable of effecting the usual hydrolytic type of reaction at the carbonyl group of esters, it might be expected that if tertiary amines react with *syn*- or *anti*-benzaldoxime esters they would effect only the elimination reaction. Actually, it has already been shown[2] that with pyridine, *anti*-benzaldoxime esters (II) readily eliminate the elements of acid to form nitrile, whereas all of the *syn*-benzaldoxime esters (I) that have been studied thus far are relatively stable in pyridine solution at room temperatures; in fact, this base serves as a convenient reagent for distinguishing *syn*- and *anti*-isomers.[2]

In the present paper it is shown that in the presence of the stronger base, triethylamine, even *syn*-benzaldoxime benzoates (I in which R′ is phenyl) eliminate the elements of benzoic acid to form nitrile (apparently quantitatively) and that the ease of this reaction is dependent upon the activation of the aldehydic hydrogen atom. In Table I are given the yields of unchanged *syn*-benzaldoxime benzoates recovered and the yields of nitriles (and benzoic acid) formed after heating the esters in pyridine solutions in the presence of two equivalents of triethylamine at 89° for three hours.

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM PARA SUBSTITUTED *syn*-BENZALDOXIME BENZOATES WITH TWO EQUIVALENTS OF TRIETHYLAMINE IN PYRIDINE SOLUTION FOR THREE HOURS AT 89°

	syn-Benzoate recovered			Nitrile formed		
Para sub-stituent	Yield, %	M. p., °C. Found[a]	M. p., °C. Lit.	Yield,[b] %	M. p., °C. Found[a]	M. p., °C. Lit.
Methoxy	78	106–108	109–110	12	55–57	60–61
Chloro	41	139–141	143–144	48	83–85	92
Nitro	0	.....	.....	95	145–146	147

[a] These melting points were raised by recrystallization to those reported in the literature. [b] The yields of benzoic acid obtained corresponded to within 2% of the yield of the nitrile.

It can be seen from Table I that the ease of elimination of the elements of benzoic acid from the *syn*-benzaldoxime benzoates in the presence of the tertiary amines decreases in the following order as the para substituent, Y, is varied: $NO_2 > Cl > OCH_3$. This order is related directly to the strengths of the corresponding carboxylic acids. Hence, it may be concluded that in the presence of the base, the elimination reaction is

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(1) See especially (a) Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935); (b) Vermillion, Rainsford and Hauser, *J. Org. Chem.*, **5**, 68 (1940).

(2) Hauser and Jordan, THIS JOURNAL, **58**, 1772 (1936).