of THF, reaction occurred over a period of a few minutes, resulting in an orange solution with a small amount of precipitate. A portion of the solution was removed for nmr analysis, and the remainder was placed in a vacuum sublimator. The nmr spectrum could not be examined below 4 ppm because of the strong THF peaks, but the aromatic and olefinic region was rather similar to that obtained for 9, although poorly resolved. There were two broad olefinic peaks at 5.7 and 6.4 and a series of diffuse aromatic peaks from 6.8 to 7.8. The solvent was evaporated from the sample in the sublimator and the apparatus evacuated to below 0.005 mm. The sample was heated at 100° for 24 hr, but there was no trace of sublimate at the end of this period. Since 9 is known to sublime readily under these conditions, it may be concluded that none was formed by the reaction. A second reaction was run on the vacuum line in degassed THF at −60 to −65°. The initial red color changed to orange over a period of 30 min. After stirring for 5 hr, a small amount of orange solid gradually formed, although the appearance of the solution remained about the same. The solvent was removed under vacuum, and the resultant orange solid was left below 0.01 mm overnight.

Addition of deuteriochloroform to the solid gave an orange solution with an insoluble residue. The residue was largely inorganic, as determined by an ignition test. The nmr spectrum of the solution was virtually identical with the previous spectrum in the olefinic and aromatic regions. Residual THF gave rise to multiplets at 1.8 and 3.7, but additional small, broad aliphatic peaks could be discerned at 3.1 and 4.1.

Pyrolysis of Benzoyl-α-benzaldoximes.
I. The Effect of Substitution, Solvents, and Catalysts
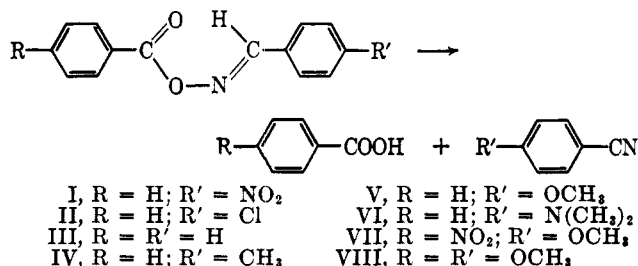
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The pyrolytic elimination of benzoic acid from eight substituted benzoyl-α-benzaldoximes to yield the corresponding substituted benzonitriles shows first-order kinetics in five solvents. The plot of log k_1 vs. σ is linear for this reaction in the solvents tetralin, o-dichlorobenzene, dimethyl sulfoxide, and N-methylacetamide but not N,N-dimethylformamide, in which competing base catalysis by the solvent occurs. Thermodynamic parameters and small negative values for ρ indicate that the reaction mechanism is essentially synchronous. Catalysis by a wide range of metal salts was observed.

Of the many reactions available for the conversion of oximes to nitriles the pyrolysis of acyl-α-aldoximes (*syn* isomers) has been one of the least used.[2] This reaction occurs at moderate temperatures (100–150°) and has been shown to be first order when carried out in xylene using several different acyl groups.[3,4] The relatively low temperatures required for this pyrolysis allowed us to study further the kinetics of this reaction in a range of solvents. In addition, the effect of substituents and catalysts on the kinetics of reaction was investigated by us to gain insight into the reaction mechanism. We chose the benzoyl derivatives for this investigation because they are easily prepared and purified, and the benzoic acid produced on pyrolysis can be readily titrated in aqueous solution.

The benzoyl-α-benzaldoximes, I–VIII, used in this study were prepared by previously described methods[5] and, with the exception of VI which was photosensitive, were stable when stored *in vacuo* over potassium hydroxide. Pyrolyses were carried out at 123° and 142° in the absence of any solvent and at these same two temperatures after solution in each of five solvents: tetralin (TET), o-dichlorobenzene (DCB), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methylacetamide (NMA).

When heated in the absence of solvent at 142° for about 48 hr, all the benzoyl-α-benzaldoximes yielded stoichiometric amounts of benzoic acid, which was assayed by titration. Gas chromatography of the residues left after extraction of the benzoic acid with dilute carbonate showed that only one component was present in each residue. This component had the same retention time as the expected authentic nitrile. The benzoic acid free residues showed no N—H or C=O absorptions in the infrared, thus ruling out the formation of amides during pyrolysis by a Beckmann type of rearrangement. Heating for 48 hr in the presence of solvents also yielded essentially stoichiometric amounts of benzoic acid. When the solvent was water miscible (DMF, NMA, DMSO), work-up of the reaction consistently yielded better than 85% of the expected nitrile, the infrared spectrum of which was always superimposable on that of the corresponding authentic nitrile. Pyrolyses in water-immiscible

I, R = H; R' = NO₂
II, R = H; R' = Cl
III, R = R' = H
IV, R = H; R' = CH₃
V, R = H; R' = OCH₃
VI, R = H; R' = N(CH₃)₂
VII, R = NO₂; R' = OCH₃
VIII, R = R' = OCH₃

(1) Abstracted in part from the B.S. Thesis of L. D. Schmookler, William Smith College, 1965.
(2) P. W. Neber, K. Hartung, and W. Ruopp, *Ber.*, **58**, 1239 (1925).
(3) D. Ambrose and O. L. Brady, *J. Chem. Soc.*, 1243 (1950).
(4) O. L. Brady and H. A. M. Sharawy, *ibid.*, 4083 (1953).

(5) O. L. Brady and G. P. McHugh, *ibid.*, **127**, 2420 (1925); C. R. Hauser and C. T. Sullivan, *J. Am. Chem. Soc.*, **55**, 4611 (1933).

TABLE I

RATE CONSTANTS ($k_1 \times 10^4$ sec^{-1}) FOR THE PYROLYSIS OF BENZOYL-α-BENZALDOXIMES

Compd	Temp, °C	TET	DCB	DMF	DMSO	NMA
I	123	0.31 ± 0.01	0.46 ± 0.01	3.56 ± 0.06	0.29 ± 0.01	0.27 ± 0.02
	142	2.54 ± 0.03	3.14 ± 0.01	18.90 ± 0.20	1.72 ± 0.02	1.66 ± 0.03
II	123	0.80 ± 0.01	1.04 ± 0.02	0.99 ± 0.02	0.53 ± 0.02	0.37 ± 0.01
	142	6.12 ± 0.08	6.09 ± 0.03	5.74 ± 0.04	3.21 ± 0.02	2.32 ± 0.01
III	123	1.02 ± 0.02	1.45 ± 0.02	0.80 ± 0.02	0.72 ± 0.02	0.47 ± 0.02
	142	8.14 ± 0.07	10.10 ± 0.04	4.81 ± 0.05	4.42 ± 0.03	2.84 ± 0.02
IV	123	1.28 ± 0.02^a	1.61 ± 0.04^b	0.78 ± 0.02	0.77 ± 0.01	0.56 ± 0.02
	142	9.24 ± 0.02	10.81 ± 0.05	4.64 ± 0.02	4.72 ± 0.05	3.61 ± 0.03
V	123	1.54 ± 0.02^c	1.84 ± 0.02^d	0.75 ± 0.01	0.84 ± 0.01	0.65 ± 0.01
	142	11.70 ± 0.07	12.90 ± 0.04	4.81 ± 0.04	5.18 ± 0.10	3.82 ± 0.06
VI	123	3.44 ± 0.04	3.74 ± 0.04	1.19 ± 0.03	1.51 ± 0.03	1.15 ± 0.02
	142	22.40 ± 0.20	22.78 ± 0.08	7.67 ± 0.01	8.97 ± 0.03	7.09 ± 0.10

The following are values determined from infrared data: ^{a} 1.22 ± 0.20; ^{b} 1.58 ± 0.15; ^{c} 1.51 ± 0.15; ^{d} 1.80 ± 0.22.

solvents (DCB, TET) were assayed for nitriles by comparison of the infrared spectra of reaction aliquots with those of standard equimolar mixtures of the expected nitrile and benzoic acid at the absorbance maximum due to C≡N (ca. 2230 cm^{-1}). Nitriles were produced in at least 90% yield in every case. These results indicate that no appreciable side reactions take place during pyrolysis.

The kinetics of these pyrolyses were followed by potentiometric titration of the benzoic acid present in aliquots taken from sealed ampoules. Each aliquot was diluted with approximately ten volumes of 50% aqueous ethanol before titration. A procedure employing measurement of the intensity of infrared absorption due to C≡N at ca. 2230 cm^{-1} was used in addition to the potentiometric titrations with III and V in both TET and DCB. Rate constants calculated from the infrared data agreed with those calculated from the titration data. The spectroscopic method was less precise than the titrimetric method and was judged to be less convenient.

Table I presents the kinetic data obtained. Excellent first-order kinetics were observed to at least three half-lives for II–VIII. Reactions of I were followed only to about one half-life as pyrolysis of this compound was very slow.

In each solvent used, except DMF, the reaction rates showed a regular increase from I, the slowest, through VI, the fastest. For all compounds the best linear Hammett correlation was obtained using values for σ rather than σ^+. The values of ρ obtained from plots of log k_1 vs. both σ and σ^+ are summarized in Table II. Figure 1 presents the log k_1 vs. σ plots.

TABLE II

THE EFFECT OF SOLVENTS ON ρ VALUES FOR THE PYROLYSIS OF BENZOYL-α-BENZALDOXIMES

Solvent	Temp, °C	$\rho(\sigma)$	r^a	$\rho(\sigma^+)$	r^a
TET	123	-0.644	0.998	-0.393	0.969
	142	-0.582	0.996	-0.356	0.967
DCB	123	-0.557	0.997	-0.338	0.961
	142	-0.534	0.993	-0.322	0.951
DMSO	123	-0.440	0.997	-0.267	0.960
	142	-0.442	0.995	-0.267	0.954
NMA	123	-0.398	0.990	-0.251	0.978
	142	-0.397	0.988	-0.249	0.976

^{a} Correlation coefficient.

In DMF the log k_1 vs. σ correlation was not linear but was instead a U-shaped plot (Figure 2) showing
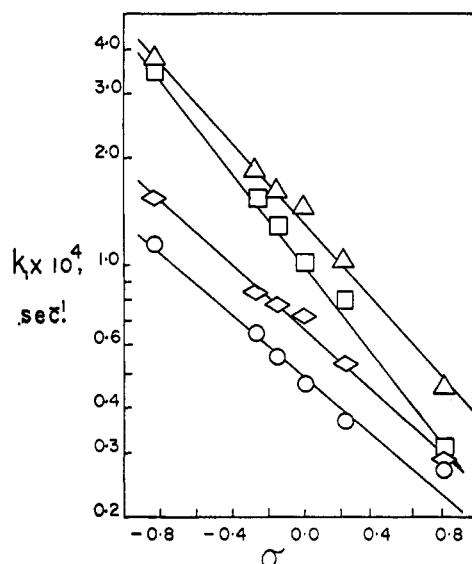

Figure 1.—Hammett plot for the pyrolysis of various benzoyl-α-benzaldoximes at 123° in tetralin (□), o-dichlorobenzene (△), dimethyl sulfoxide (◇), and N-methylacetamide (○).
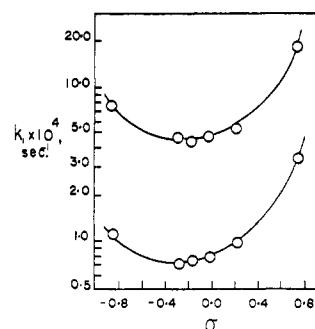

Figure 2.—Hammett plot for the pyrolysis of various benzoyl-α-benzaldoximes in N,N-dimethylformamide. Upper curve at 142°, lower curve at 123°.

that the p-nitro (I) and p-chloro (II) substituents did not retard the reaction, as was the case with the other solvents used, but instead appeared to accelerate it.

The pyrolysis of acetyl-α-benzaldoxime is reported to be catalyzed by metallic copper.[3] In our experiments the addition of 40 mg of copper powder to ampoules containing about 4 ml of 0.1 M III with either DCB or DMF as the solvent reduced the half-life of the pyrolysis by a factor of approximately 20. However, since such a heterogeneous system does not yield

acceptable quantitative data, we tried a homogeneous system containing cupric ion in a concentration range of 1×10^{-5} to 5×10^{-2} with either NMA or DMF as the solvent. This system was found to catalyze the pryolysis of III. These results and others related to metal ion catalysis of the pyrolysis are presented in Table III.

TABLE III
THE EFFECT OF METAL SALTS ON THE RATE OF PYROLYSIS OF BENZOYL-α-BENZALDOXIME (III)[a] IN N-METHYLACETAMIDE (NMA) OR N,N-DIMETHYLFORMAMIDE (DMF) AT 123°

Salt	Concn, M	$k_1 \times 10^4 \text{ sec}^{-1}$	
		NMA	DMF
$Cr(NO_3)_3$	1×10^{-3}	5.18	
$FeCl_3$	1×10^{-3}	4.44	
$Cu(OCOCH_3)_2$	1×10^{-5}	0.68	0.81
	1×10^{-4}	1.18	1.48
	1×10^{-3}	2.40 (2.35)[b]	3.62
	1×10^{-2}	5.92	7.42
	5×10^{-2}	13.33	22.30
$Ni(NO_3)_2$	1×10^{-2}	4.97	
$Co(NO_3)_2$	1×10^{-2}	2.71	
EDTA[c]	1×10^{-4}	0.46	
DBP[d]	1×10^{-3}	0.45	

[a] 0.1 M. [b] Also 1×10^{-3} M in DBP. [c] Ethylenediaminetetraacetic acid sodium salt. [d] 2,6-i-Dt-butylphenol.

To rule out the possibility of catalysis by adventitious traces of metal ions in the systems to which no metal ions had been deliberately added, several reactions were carried out without added salts and in the presence of ethylenediaminetetraacetic acid sodium salt (EDTA). This addition did not change any of the reaction rates significantly.

Oximes and their derivatives are known to be excellent ligands and it is reasonable to assume that the catalytic activity of the metal salts results from formation of a complex between the metal ion and the benzoyl-α-benzaldoxime. Many different types of reactions involving complexed ligands are known,[6] the two most important of which involve participation of the-metal ion either as an intermediate in a one-electron transfer process[7a] or as a Lewis acid.[7b] The presence of 1×10^{-3} M 2,6-di-t-butylphenol (DBP) during pyrolysis of III dissolved in NMA did not affect the catalytic efficiency of added 1×10^{-3} M cupric acetate. This concentration of DBP was found to be without effect on the noncatalyzed reaction. Since DBP is an efficient radical chain suppressor it is reasonable to conclude that the pyrolysis does not proceed by a radical mechanism. This is further supported by the experiment in which III alone or in the presence of cupric acetate was ineffective in initiating the polymerization of styrene when styrene was used as a reaction solvent; the viscosities of pure styrene and the various reaction mixtures after pyrolysis for 3 hr at 123° were essentially the same. On the other hand the pyrolysis of III in NMA at 123° in the presence of any one of several metal salts showed that the catalytic efficiency of the salts paralleled their complex-forming ability and the stability of their com-

plexes.[8] The order $Cr^{3+} > Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+}$ found in the present study was similar to that found for the metal ion catalyzed decarboxylation of oxalosuccinic acid[9] and acetone dicarboxylic acid.[10] Since these latter reactions are known to involve Lewis acid catalysis by metal ions it is reasonable to assume that a similar mechanism pertains to the metal ion catalysis observed in the pyrolyses.

Of the several pathways that seem probable for the noncatalyzed pyrolytic elimination of benzoic acid from benzoyl-α-benzaldoximes those that involve radicals can be disregarded. The general tendency in all solvents (except DMF, which is discussed later) for electron-donating groups on the benzaldoxime moiety to facilitate the reaction suggests the participation of an electron-deficient nitrogen during the breaking of the O-N bond. This could involve structures ranging from a full ion pair to an essentially concerted process. It seems apparent that large charge separation is not involved since the value of ρ in all cases is quite small and a better Hammett correlation is afforded by σ than by σ^+. In reactions involving ion pairs the opposite is usually found to be the case.[11]

Significant evidence of an essentially synchronous process comes from the effect of solvents on reaction rates. The solvents used can be classified into two main groups: those of low solvating power and low dielectric constant (TET and DCB) and those of high solvating power and high dielectric constant (DMSO and NMA). Reaction rates determined in the former are only two to four times greater than in the latter, which indicates the insensitivity of the pyrolysis to large changes in solvent properties. Furthermore the effect of solvent on reaction rates is opposite to that expected if the reaction were to involve ion pairs that could be stabilized by solvation. Thus the mechanism of the noncatalyzed reaction can be described as one in which fission of the O-N bond is facilitated by electron-donating groups but which does not involve intermediates in the rate-determining step with sufficiently large charge separation to require significant stabilization by solvation.

The calculated thermodynamic parameters for the pyrolysis are presented in Table IV. The activation entropies become more negative as solvent polarity increases and activation enthalpies are somewhat greater (about 2-4 kcal/mole) in the solvents of low solvating power than in those of high solvating power. It seems reasonable that the starting materials are mostly intramolecularly hydrogen bonded in solvents of low solvating power, resulting in a six-membered cyclic configuration analogous to the geometry of the transition state for a cis elimination. As the pyrolysis proceeds, the O-N bond weakens and eventually breaks as the O-H interaction becomes fully bonding. Such a process, resulting in the formation of products from an already highly ordered structure without need of much, if any, reorientation, should result in a relatively positive activation entropy. In solvents of

(6) See M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 376, for a description of seven classes of complexed ligand reactions.

(7) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1960, p 336; (b) p 332.

(8) R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and R. P. Block, J. Phys. Chem., 59, 170 (1955).

(9) A. Kornberg, S. Ochoa, and A. H. Mehler, J. Biol. Chem., 174, 159 (1948).

(10) J. E. Prue, J. Chem. Soc., 2331 (1952).

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 203.

TABLE IV

THERMODYNAMIC PARAMETERS FOR THE PYROLYSIS OF
BENZOYL-α-BENZALDOXIMES IN VARIOUS SOLVENTS

Compd	TET	DCB	ΔH*, kcal/mole DMF	DMSO	NMA
I	35.3	32.1	27.9	29.8	30.4
II	34.1	31.7	29.2	30.1	30.7
III	34.9	32.5	30.0	30.4	29.7
IV	33.1	31.9	29.8	30.4	31.2
V	34.0	32.6	31.1	30.5	29.4
VI	31.4	30.2	31.2	29.8	30.4

Compd	TET	DCB	ΔS*, eu DMF	DMSO	NMA
I	+9.4	+1.0	−4.5	−4.7	−3.4
II	+7.2	+2.8	−3.7	−2.8	−1.9
III	+10.7	+5.4	−2.2	−1.4	−3.9
IV	+7.5	+2.3	−2.8	−1.2	+0.1
V	+8.2	+6.1	+0.4	−0.8	−4.0
VI	+4.7	+1.5	+1.7	−1.3	−0.4

high solvating power the starting materials are most likely to be held in an open configuration, rather than in a cyclic one, because of intermolecular hydrogen bonding with the solvent. During pyrolysis the cyclic transition state develops by reorientation of the molecule in its solvent cage. The result should be a negative activation entropy relative to that observed with a solvent of lower solvating power.

Solvents of low solvating power are unable to stabilize appreciably any charge separation developed in the transition state during pyrolysis, with the result that higher activation enthalpies should be observed in these solvents than in those of higher solvating power if any charge separation is involved in the rate-determining step. The results show a small effect in this direction. For the reactions in polar solvents the interplay between enthalpy and entropy appears to be such that the reduction in enthalpy is counteracted by a more negative entropy, resulting in a net decrease in reaction rate. It is interesting to note that the values of ρ are solvent dependent and that apparently the dispersal of charge in the more polar solvents gives rise to a less negative value of ρ than in the less polar solvents.

The introduction of substituents into the benzoic acid moiety (VII and VIII) results in a slight acceleration of the reaction by those substituents that increase the electrophilicity of the carboxyl oxygen.

In contrast to the other solvents investigated, reactions in DMF did not give a linear log k_1 vs. σ correlation. An increasing divergence from the expected rate (compared to that in DMSO and NMA) occurred as the substituent on the benzaldoxime moiety became more electron withdrawing. This resulted in a U-shaped Hammett plot. Curvature of this kind is frequently ascribed to duality of mechanism.[12] Thus, in DMF, it is likely that concurrent with the pyrolytic elimination already described another reaction that produces nitrile and carboxylic acid by a first-order or pseudo-first-order process also occurs. Although hydrolysis of benzoyl-α-benzaldoximes with a base is known to yield mainly benzoic acid and benzaldoximes,[13] it has been reported that reaction of benzoyl-

α-benzaldoximes with anhydrous triethylamine quantitatively produces benzoic acid and benzonitrile through a base-induced E2 elimination.[14] The ease of this reaction parallels the acidity of the methine hydrogen on the oxime derivative. This suggests that the competing reaction during pyrolysis in DMF may result from the basicity of the solvent. However the order of basicity of the solvents used is DMSO > NMA > DMF ≫ TET, DCB.[15,16] Examination of the Hammett plot of the reactions in NMA (Figure 1) shows that electron withdrawal by the nitro group in I produces an acceleration of the reaction similar, but much less marked, to that observed with electron-withdrawing substituents in DMF. This effect is not observed in DMSO. Therefore the order of solvent basicity is counter to what, by analogy to the effect observed with triethylamine, may be a base-induced E2 reaction. A tentative rationalization of this effect, which we now offer, is that electron density, and hence Lewis basicity, on the amide nitrogen is greater in DMF than in NMA as a result of electron release from the attached methyl groups.[17] If this basic center on nitrogen were specifically involved in proton abstraction in the E2 reaction then the observed order of reactivity would be the expected order. This suggestion also explains why the observed ΔS* for the reaction of I (and II) in DMF is not more positive than in NMA and DMSO. Hydrogen bonding between the solvent oxygen and the methine hydrogen occurs in each case, but when the methine hydrogen is abstracted by the amide nitrogen in the case of DMF (and to a lesser extent by NMA) or when cis elimination in NMA or DMSO occurs, there is substantial reorientation of the solvent–substrate associate with disruption of the intermolecular hydrogen bond between the methine hydrogen and the solvent oxygen leading to either the E2 reaction or the cyclic transition state and subsequent cleavage, with the result that a negative ΔS* is observed. The reaction in DMF is thus a composite of the first-order pyrolysis and the pseudo-first-order, solvent-induced elimination of benzoic acid, with the latter being important in the case of I and to a lesser extent with II and III.

In summary, three mechanisms seem to be available for the formation of benzoic acid and a nitrile from the pyrolysis of a benzoyl-α-benzaldoxime. These are (a) a noncatalyzed pyrolytic elimination which proceeds by a hydrogen bonded, cyclic transition state and which is analogous to the well-known cis eliminations of esters, xanthates, and amine oxides,[18,19] (b) a metal ion catalyzed reaction which may involve a chelated intermediate (IX)[20] and in which the metal behaves as a Lewis acid, and (c) a base-catalyzed reaction in which the solvent acts as a Lewis base. Which of

(12) D. N. Kershaw and J. A. Leisten, Proc. Chem. Soc., 84 (1960); R. F. Hudson and G. Klopman, J. Chem. Soc., 1062 (1962).

(13) C. R. Hauser and E. Jordan, J. Am. Chem. Soc., 57, 2450 (1935); M. Benger and O. L. Brady, J. Chem. Soc., 1221 (1950).

(14) G. Vermillion and C. R. Hauser, J. Am. Chem. Soc., 63, 1227 (1941)

(15) C. D. Leake, Nature, 152, 1646 (1966).

(16) T. Higuchi, C. H. Bernstein, H. Ghassemi, and W. E. Perez, Anal. Chem., 34, 400 (1962).

(17) Whether the oxygen or the nitrogen is the primary basic center in amides is not certain, but a recent review suggests that it may be the carboxyl oxygen. See E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitwieser, and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 270.

(18) C. H. DePuy and R. W. King, Chem. Rev., 60, 431 (1960).

(19) D. J. Cram and C. A. Kingsbury, J. Am. Chem. Soc., 82, 1810 (1960).

(20) Preliminary experiments, using a polarographic method, indicate that the formation constants for complexes of benzoyl-α-benzaldoximes are very small.

these predominates in any case will depend on the reaction conditions used. The three mechanisms can be summarized as in eq 1.

$$R{-}COOH \quad + \quad R'{-}CN \tag{1}$$
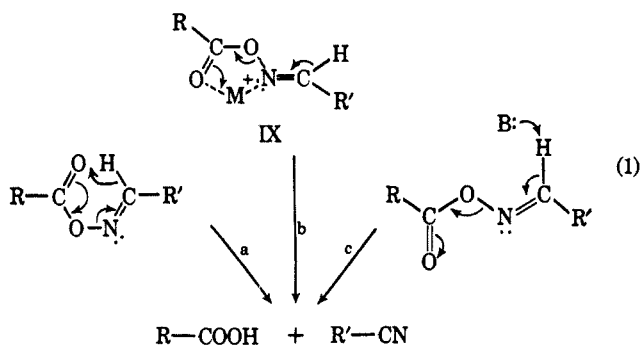
Experimental Section[21]

Materials.—Oximation of the aldehydes in dilute sodium hydroxide containing dioxane followed by direct benzoylation and crystallization of the product from acetone or ethanol yielded the following compounds: benzoyl-α-p-nitrobenzaldoxime (I), mp 203° (lit.[22] 196°); benzoyl-α-p-chlorobenzaldoxime (II), mp 146–147° (lit.[22] 143–144°); benzoyl-α-benzaldoxime (III), mp 102–103° (lit.[23] 101–102°); benzoyl-α-p-methylbenzaldoxime (IV), mp 128–129° (lit.[22] 129–130°); benzoyl-α-p-methoxybenzaldoxime (V), mp 109–110° (lit.[22] 109–110°); benzoyl-α-p-dimethylaminobenzaldoxime (VI), mp 143–144° (lit.[24] 144°); p-nitrobenzoyl-α-p-methoxybenzaldoxime (VII), mp 152–153° (lit.[3] 153°); p-methoxybenzoyl-α-p-methoxybenzaldoxime (VIII), mp 149° (lit.[3] 149°).

Tetralin (TET) was freed from peroxides (FeSO₄), fractionally distilled under reduced pressure, and the fraction with bp 92–93° (25 mm) was collected and stored at 0° in the dark until used. o-Dichlorobenzene (DCB) was fractionally distilled at atmospheric pressure from P_2O_5; the fraction with bp 178–179° was collected. N,N-Dimethylformamide (DMF) was purged at 80° for 3 hr with N_2, stored over a molecular sieve (A-4) overnight, and fractionally distilled at atmospheric pressure and the fraction with bp 152–153° was collected with the usual precautions to exclude moisture. N-Methylacetamide (NMA) was fractionally distilled at atmospheric pressure; the fraction with bp 204–205° was collected. Dimethyl sulfoxide (DMSO) was purged at 40° for 3 hr with N_2, stored overnight over a molecular sieve (A-4), and fractionally distilled under reduced pressure. The fraction with bp 74° (15 mm) was collected.

Product Identification.—Weighed samples (0.3–0.5 g) of the benzoyl-α-benzaldoximes (I–VI) were heated, usually at 142°, in sealed ampoules for about 4 hr. The contents of each ampoule were dissolved in 50% aqueous ethanol and titrated potentiometrically with standard NaOH. In all cases better than 98% benzoic acid was liberated. For compounds I and VI the temperatures used were 150 and 100°, respectively. In another set of experiments the contents of a similar group of ampoules were each extracted into ether, washed thoroughly with dilute Na_2CO_3, and dried with Na_2SO_4. After evaporation of the ether the residues were examined gas chromatographically. With He as a carrier and a 6 ft × 0.25 in. steel column packed with 5% SE-30 on Chromosorb W (60–80 mesh) at 220°, only one peak was obtained from each reaction and in every case it had a retention time identical with that of the authentic expected nitrile.

Similarly, pyrolysis of 0.05–0.1 M solutions of I–VI in DMF, DMSO, or NMA at 142° for 48 hr, followed by dilution with water, basification, extraction with ether, and evaporation, yielded better than 85% by weight of the expected nitrile in every case. Potentiometric titration of diluted aliquots showed better than 97% formation of benzoic acid in every case. Pyrolysis of the same concentrations of I–VI in TET and DCB for 48 hr at 142° yielded better than 90% of the expected nitrile, in every case. Nitrile content was assayed by measurement of the intensity of the C≡N absorption at about 2230 cm⁻¹ in an aliquot of the reaction mixture and compared with calibration curves constructed from standard equimolar mixtures of the expected nitrile and benzoic acid in the appropriate solvent.

Kinetic Procedure.—Solutions of I–VIII (typically 0.05–0.1 M) in the appropriate solvent were placed in ampoules which were then sealed. The time of immersion of the ampoules into the thermostat bath at 123 ± 0.1° or at 142 ± 0.1° was taken as zero time. The ampoules were removed at noted time intervals, cooled immediately in ice, opened, and 2.0-ml aliquots were transferred into 20 ml of 50% aqueous ethanol. The benzoic acid present was titrated potentiometrically with standard NaOH. Reaction mixtures titrated prior to pyrolysis produced negligible values for acidity. All runs were duplicated and those in DMF were triplicated. The rate constants were determined from a least-squares treatment of a plot of $\log a/(a - x)$ vs. t.[25] A satisfactory linear relationship was noted to at least three half-lives in those cases where reactions were carried this far. An alternative procedure using the infrared assay method for nitrile previously described was used to check the results obtained in TET and DCB for IV and V. The infrared method gave results comparable to those from the titrimetric procedure, although the scatter of points in individual runs was appreciably higher.

Thermodynamic parameters were evaluated by the methods described by Bunnett.[26]

(21) Melting points were determined on a calibrated Fisher-Johns apparatus and are corrected. Gas chromatography was carried out on an Aerograph A-90 P3 instrument.

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(25) Thanks are due to Mr. Robert Lamberson for assistance with the least-squares programs used for the determination of ρ and k_1. These calculations were performed on an IBM 1130 computer.

(26) J. F. Bunnett, "Techniques of Organic Chemistry," Vol. VIII, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 199.