Attempted ethanolysis of XXVII to the corresponding aminoester, catalyzed by either dry hydrogen chloride or boron trifluoride, gave only starting material.

***trans*-2-Acetamidocyclohexaneacetic Acid (XXVIII).**—Solutions of 3.1 g. of the ester XXVII in 50 ml. of ethanol and 21.45 g. of barium hydroxide octahydrate in 100 ml. of water were mixed and refluxed for 20 hr. under nitrogen. The mixture was cooled, diluted with 100 ml. of water, and carefully neutralized with 3.77 ml. of concentrated sulfuric acid in 60 ml. of water. After filtration of the precipitated barium sulfate, the filtrate was evaporated to dryness. The residue was taken up in 60 ml. of water, acidified to *p*H 4.1 with 0.1 *M* sulfuric acid, filtered, and again evaporated to dryness. The residue, m.p. 148–158°, was recrystallized twice from aqueous methanol, giving 0.94 g. of colorless needles, m.p. 181–183.5°. Mixed with an authentic sample of *trans*-2-acetamidocyclohexaneacetic acid,[16] m.p. 183–184°, it melted at 182.5–184°.

Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 59.95; H, 8.60; N, 7.37.

Esterification of the acid with ethanol saturated with dry hydrogen chloride gave the original ester XXVII, m.p. 101–103°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE 5, TENN.]

A Study of the Rates of Cyclization of Some *o*-Benzoylbenzoic Acids and of *o*-Phenoxybenzoic Acid in Polyphosphoric Acid[1]

BY R. G. DOWNING[2] AND D. E. PEARSON[3]

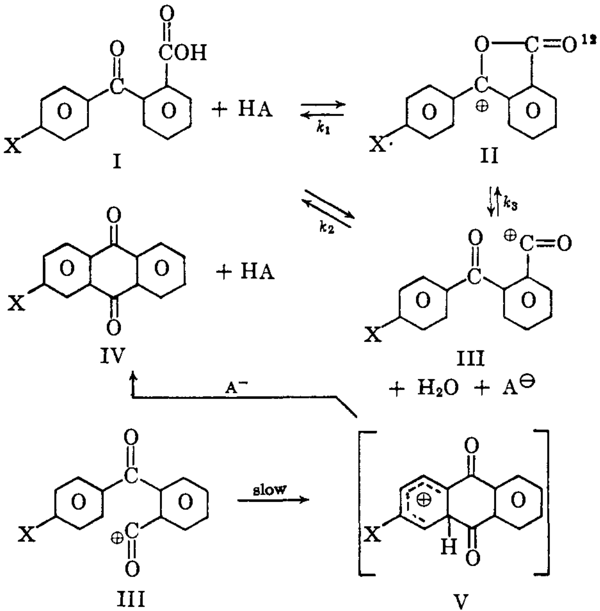
RECEIVED JULY 12, 1962

The rates of ring closure of *o*-benzoyl, *o*-(*p*-chlorobenzoyl)-, and *o*-(*p*-toluyl)-benzoic acids have been determined in polyphosphoric acids of various strengths. Maxima in the rate constants were found in the range 78–83% P_2O_5 content. On the other hand, the rate constants for the closely related ring closure of *o*-phenoxybenzoic acid in PPA did not show a maximum. All four reactions followed first-order kinetics. Explanations of a tentative nature are offered for the sake of provoking interest in this kinetic phenomenon.

The most frequently reported use of polyphosphoric acid (PPA) is cyclodehydration or, more specifically, intramolecular acylation.[4,5] A kinetic study of this type of reaction therefore seemed of practical as well as theoretical interest. Furthermore, earlier studies on the Beckmann rearrangement of acetophenone oximes[6] and on the decomposition of formic acid[7] showed that the rate constants either leveled off or passed through a maximum in increasingly concentrated PPA. It seemed of interest to see if this phenomenon was more general and occurred in other reactions.

To our knowledge only four kinetic studies have been carried out in PPA. Two have been described,[6,7] and two have been concerned with the subject of this paper, intramolecular acylation. Denny and Klemcluk[8] concluded that there was a small deuterium isotope effect in the ring closure of 2-deuterio-2′-carboxybiphenyl to fluorenone. Goldberg and Wragg[9] gave rate constants for the cyclization of *o*-phenoxybenzoic acid to xanthone in PPA of 81.6% P_2O_5 content. On re-examination of this reaction in this Laboratory, we found that the rate constants of reference 9 were too small by a factor of about 1000 and probably represented the rates of solution of the *o*-phenoxybenzoic acid in PPA rather than its rates of cyclization. Neither of these acylation studies was concerned with effects of changing the concentration of the medium on the reaction rates.

Since there are many similarities in acylation reactions in PPA and sulfuric acid, mechanism studies in sulfuric acid furnish an important basis for comparisons with the work reported here. Newman and co-workers[10,11] have shown that the intramolecular acylation of *o*-benzoylbenzoic acid to anthraquinone (X = H) in sulfuric acid may be represented by the following equations which will serve also for discussion of the mechanism in PPA.



X = H,CH$_3$,Cl

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[1] Presented in part at the Organo-Phosphorus Symposium, American Chemical Society Meeting in Chicago, Ill., Sept. 8, 1961.

[2] Based on a portion of the Ph.D. thesis of R. G. D., 1961. Present address: E. I. du Pont de Nemours and Co., Wilmington, Del.

[3] To whom correspondence should be directed.

[4] F. D. Popp and W. E. McEwen, *Chem. Revs.*, **58**, 321 (1958); *Trans. Kansas Acad. Sci.*, **63**, No. 3 (1960).

[5] F. Uhlig and H. R. Snyder in "Advances in Organic Chemistry," Vol. I, R. A. Raphael, E. C. Taylor and H. Wynberg, editors, Interscience Publishers, Inc., New York, N. Y., 1960.

[6] D. E. Pearson and R. M. Stone, *J. Am. Chem. Soc.*, **83**, 1715 (1961).

[7] A. I. Gel'bstein, G. G. Shcheglova and M. J. Temkin, *Zhur. Fis. Khim.*, **30**, 2267 (1956); *C. A.*, **51**, 9272 (1957).

[8] D. B. Denny and P. P. Klemcluk, *J. Am. Chem. Soc.*, **80**, 3285 (1958).

[9] A. A. Goldberg and A. H. Wragg, *J. Chem. Soc.*, 4227 (1958).

[10] M. S. Newman, *J. Am. Chem. Soc.*, **64**, 2324 (1942).

[11] M. S. Newman, H. C. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

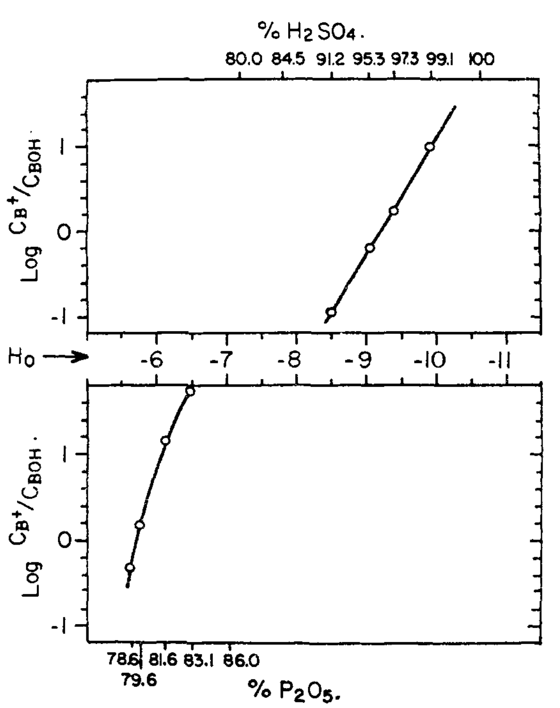
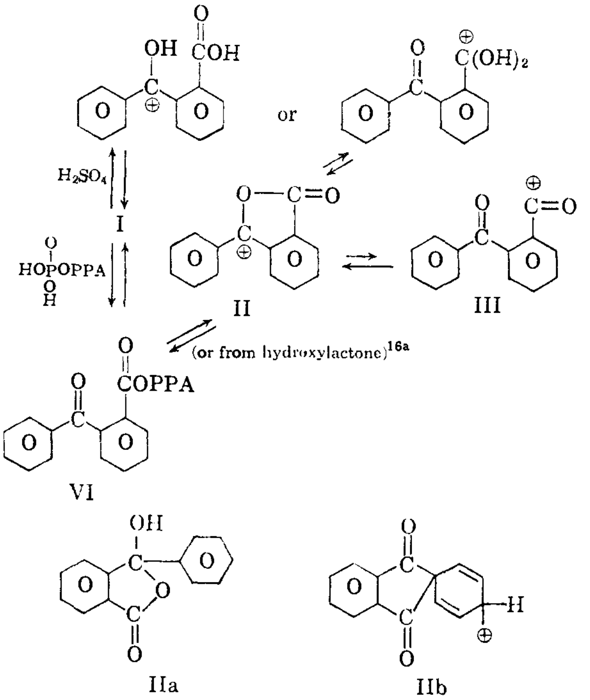


Fig. 1.—Comparison of ionization of *o*-benzoylbenzoic acids in sulfuric acid[13] and PPA. Logarithm of ratio of concentration of cyclic carbonium ion to concentration of unionized form *versus* H_0.

The cyclic carbonium ion II is stable in strong acid solutions at room temperature. Vinnik and co-workers[13] have determined equilibrium concentration of the free acid I and the cyclic ion II in sulfuric acid by the spectroscopic method. They demonstrate that the ratio II/I increased from zero in 85% sulfuric acid to infinity in 100% acid and that over this range the first-order rate constants were directly proportional to the concentration of II. In fuming sulfuric acid Deane[14] has shown the rate constants to remain unchanged from 100% H_2SO_4 to 14% oleum where the rate constants begin to increase further. The rate-determining step is undoubtedly the conversion of the cyclic ion II, or some species in equilibrium with it such as the open chain acylium ion III to anthraquinone. Deane[14] showed the cyclization to be a true first-order reaction. Also all attempts to show that the rate constants are the usual simple function of the H_R or H_0 acidity scales have failed.

These facts concerning the behavior of *o*-benzoylbenzoic acid in sulfuric acid were quite helpful in studying its behavior in PPA. In general, we believe the mechanism in PPA is the same as that proposed by Newman in sulfuric acid, but there are important differences.

Although the equilibrium I $\rightleftarrows$ II is present in PPA, the mode by which PPA forms the cyclic carbonium ion is strikingly different from that in sulfuric acid. Considering *o*-benzoylbenzoic acid as an indicator of the "dehydration" ability of the two media, Fig. 1 illustrates that at equal values of the ratio C_{II}/C_I the acidity of the two media is vastly different. The common abscissa in Fig. 1 is the H_0 acidity scale.[15] Thus in the range where PPA of about 82% P_2O_5 content and 100% sulfuric acid have about the same "dehydration" ability (log C_{B^+}/C_{BOH} = *ca.* 1), PPA is about 2000 times weaker as an acid than sulfuric acid. Such a great difference in acidity under circumstances where both acids perform a function with equal efficiency supports the view that this dehydration in PPA is the result of reaction of the substrate hydroxyl group with an anhydride linkage of the PPA to give a mixed anhydride VI which then cleaves to the carbonium ion (II, III). In sulfuric acid the "dehydration" is believed to take place by simple protonation and elimination of water.



Dissociation of the mixed anhydride VI to a resonance-stabilized anion, $^{-}$OPPA, is the driving force for PPA "dehydration."[17]

Another phenomenon was observed in the equilibrium reaction I $\rightleftarrows$ II. When *o*-benzoylbenzoic acid was dissolved in PPA, the usual yellow color of the carbonium ion developed. If a small drop of water was added, the yellow color of the ion

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[12] Compounds II and III have a most unusual and interesting relationship. They would be canonical forms except that they also differ from each other in the degree of rotation of the aromatic group about the carbon atom connecting the two rings.

[13] M. I. Vinnik, R. S. Ryabova and N. M. Chirkov, *Zhur. Fiz. Khim.*, **33**, 1992 (1959).

[14] C. W. Deane, *J. Am. Chem. Soc.*, **59**, 849 (1937); C. W. Deane and J. R. Huffman, *Ind. Eng. Chem.*, **35**, 684 (1943).

[15] An apparent H_0 acidity scale for PPA has been determined recently by the present authors, *J. Am. Chem. Soc.*, **83**, 1718 (1961).

[16] (a) The hydroxylactone IIa may be involved in place of I. It does not change the point being made here, however, of the difference in mode of action between PPA and sulfuric acid; IIa, if present, is protonated by sulfuric acid and then loses water, or is esterified by PPA and then eliminates the PPA anion to give II. Another intermediate (IIb) may participate in the above equilibria as indicated in the Hayashi rearrangement.[16b] The authors are indebted to a referee for pointing out the possibilities mentioned in this footnote. (b) M. S. Newman and K. G. Ihrman, *J. Am. Chem. Soc.*, **80**, 3652 (1958).

[17] John R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 437–440, 590.

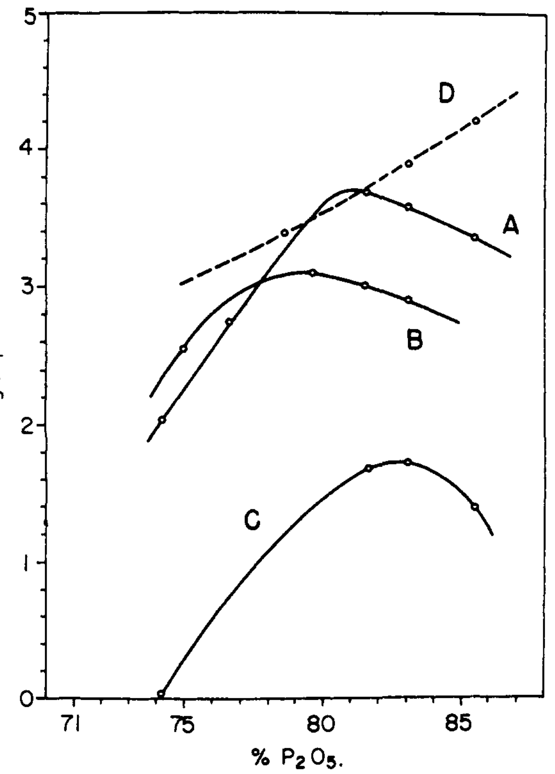

Fig. 2.—Variation of logarithm of first-order rate constants with concentration of PPA: A, *o*-benzoylbenzoic acid at 80°; B, *o*-(*p*-toluyl)-D, *o*-phenoxybenzoic acid at 44°.

disappeared and then, on standing, slowly reappeared. No such phenomenon was observed in sulfuric acid. Our interpretation is that the water reacts more rapidly with the carbonium ion than with PPA. The regenerated acid I is then slowly reconverted to the carbonium ion by PPA—a relatively slow process compared to the rapid protonation and removal of free water from the reaction sphere by the strongly acidic sulfuric acid.

Table I

Summary of Rate Constants[a] for Intramolecular Acylations in PPA

% P_2O_5	*t*, °C.	*o*-BBA[b]	*o*-(*p*-ClB)-BA[b]	*o*-(*p*-T)-BA[b]	*o*-PBA[b]
85.48	80	0.228	0.00248	...	...
	44	...	...	...	1.66
	25	...	...	...	0.213
83.05	80	.380(2)	.00528	0.0812	...
	70	.129	...	...	...
	60	.0360	...	...	...
	44	...	...	...	.798
	35	...	...	...	.292(2)
	25	...	...	...	.088
81.6	80	.489	.00491	.104	...
79.6	80	...	...	.128	...
78.6	44	...	...	...	.248
76.6	80	.0557(4)	...	...	...
75.0	80	...	...	.0355	...
74.2	80	.0110	.0	...	...

[a] First-order rate constants expressed in hours^{-1}; numbers in parentheses indicate number of kinetic runs averaged. [b] *o*-BBA, *o*-benzoylbenzoic acid; *o*-(*p*-ClB)-BA, *o*-(*p*-chlorobenzoyl)-benzoic acid; *o*-(*p*-T)-BA, *o*-(*p*-toluyl)-benzoic acid; *o*-PBA, *o*-phenoxybenzoic acid.

A kinetic study was made of the intramolecular acylation of *o*-benzoylbenzoic acid, its *p*-chloro- and *p*-methyl-substituted analogs, and of *o*-phenoxybenzoic acid in PPA of various strengths. All four reactions follow first-order rate kinetics which are recorded in Table I. Figure 2 illustrates how the logarithms of the rate constants vary with the concentration of the phosphorus pentoxide in PPA. The surprising result is that the rate constants of all three *o*-aroylbenzoic acids go through a maximum in the range 79–82% P_2O_5 content while the rate constants for *o*-phenoxybenzoic acid do not. The maximum for *o*-benzoylbenzoic acid, curve A, cannot be pinpointed with accuracy, but it appears to be at about 81.0% P_2O_5 content. Similarly, the maximum for *o*-(*p*-toluyl)-benzoic acid, curve B, is about 79.5% P_2O_5. For *o*-(*p*-chlorobenzoyl)-benzoic acid, curve C, the maximum may be set more accurately in PPA at about 82.5% P_2O_5 content. All three maxima occur at the point where the equilibrium has shifted completely toward the cyclic ion II. Figure 2 shows that in PPA of less than 77.7% P_2O_5 content the magnitude of the first-order rate constants for the cyclization of *o*-aroylbenzoic acids are in the order *p*-toluyl- > benzoyl > *p*-chlorobenzoyl-. This is the same order as the reactivity of the nuclei to electrophilic substitution and is the order expected if the substitution is the rate-determining step. However, above 77.7% P_2O_5 the rate constants for *o*-benzoylbenzoic acid become larger than those for *o*-(*p*-toluyl)-benzoic acid. Also in 95.6% H_2SO_4, Oda and Tamura[18] reported the rate constants for *o*-benzoylbenzoic acid to be larger than that of *o*-(*p*-toluyl)-benzoic acid. The reversal of the rate constants in the more concentrated acids furnishes important evidence for the mechanism proposed below. In this mechanism, the attack on the aromatic nucleus is still assumed to be rate determining and the observed reversal in magnitude of the rate constants is due to change in stability in the cyclic carbonium ion II, which is in equilibrium with the true reactive species III. The concentration of III in relation to the cyclic ion II is decreased more in the *p*-toluyl case than in the benzoyl case as the PPA concentration increases. Therefore at higher acid concentration the influence of the methyl substituent is more pronounced in equilibria preceding the rate-determining step than it is in the rate-determining step itself.

Further evidence for the stabilizing influence of the *p*-methyl and *p*-chloro substituents on the cyclic carbonium ion may be found by comparing the spectra of these ions, Table II. The substituents

Table II

Spectral Characteristics of Ionized *o*-Aroylbenzoic Acids in 83.05% PPA

Benzoic acid	λ_{max}, mμ	ε
o-Benzoyl-	406	27,865
o-(*p*-Toluyl)-	432	35,000
o-(*p*-Chlorobenzoyl)-	440	41,260

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[18] R. Oda and K. Tamura, *Sci. Papers. Inst. Phys. Chem. Research (Tokyo)*, **32**, 263 (1937).

cause a large bathochromic shift and furnish evidence for a structure of the ion which allows substantial interaction of the substituent with the π-electron system of the ion.

We propose that the maxima observed in Fig. 2 are due to medium effects on the cyclic carbonium ion II. The fact that *o*-phenoxybenzoic acid does not exhibit a maximum is congruent with the lack of a stable carbonium ion intermediate such as observed for the *o*-aroylbenzoic acids. The exact nature of these medium effects can be the subject of much discussion and several possibilities are explored below.

If it is assumed that the intramolecular attack of the open-chain acylium ion III on the aromatic nucleus and not proton elimination is the rate-determining step, then it is attractive to assume that changes in the activity of III is the cause for the variation of rate constants with changes in medium concentration. Qualitatively, as the acid strength and "dehydration power" of the medium is increased, the activity of III and of the corresponding acylium ion of *o*-phenoxy–benzoic acid increases. This is reflected in increasing rate constants for all four reactions in PPA up to 80% P_2O_5 content and above 80% for *o*-phenoxybenzoic acid. However, for the *o*-aroylbenzoic acids in PPA above 80% P_2O_5 the incursion of the stable intermediate II, in equilibrium with III, causes a decrease in the concentration of III as the acid strength increases and consequently causes a reduction in reaction rate constants. Briefly, if the medium effects are regarded simply as solvation effects, the Brönsted equation for the effects of changes in the medium on the rate-determining step may be used to develop[2] the following equation for the first-order rate constant.

$$k_1 = \frac{k'K_2}{K_1(\text{II} + \text{I})} \times \text{II} \times \frac{f_{\text{II}}}{f^*} \qquad (4)$$

The K's are equilibrium constants in reaction 1 and f_{II} and f^* are activity coefficients for the cyclic ion and the transition state of the rate-determining step which may be envisaged as structure V. The first term on the right in eq. 4 is constant. The second term increases to its maximum as the PPA concentration increases up to about 80% P_2O_5 content. The maxima must be explained by assuming the third term begins to decrease around 80% PPA and continues to decrease as the PPA concentration is increased. The net result is that the first-order constant, k_1, increases under the dominating influence of the second term until about 80% P_2O_5 where the decrease in the third term becomes the dominating factor. This demands large variation in the ratio f_{II}/f^* in order to explain the results; for example, a change from a value of 1.0 at 80% P_2O_5 to a value of 0.3 at 86% would approximately fit the data for *o*-benzoylbenzoic acid. The literature furnishes no information about the behavior of activity coefficients in PPA except our work[15] on the H_0 of PPA which shows that the activity coefficients of the free base and conjugate acid forms of 2,4-dinitroaniline and 2-bromo-4,6-dinitroaniline do not behave ideally; *i.e.*, the ratio $f_{\text{A}}f_{\text{BH}^+}/f_{\text{B}}f_{\text{AH}^+}$ is not constant and equal to one as in the case of sulfuric acid (a medium of high dielectric constant). If the ratio $f_{\text{BH}^+}/f_{\text{AH}^+}$ for the chemically similar indicators mentioned above is not constant as the PPA concentration is changed, then it is not surprising the ratio f_{II}/f^* for dissimilar structures is not constant.

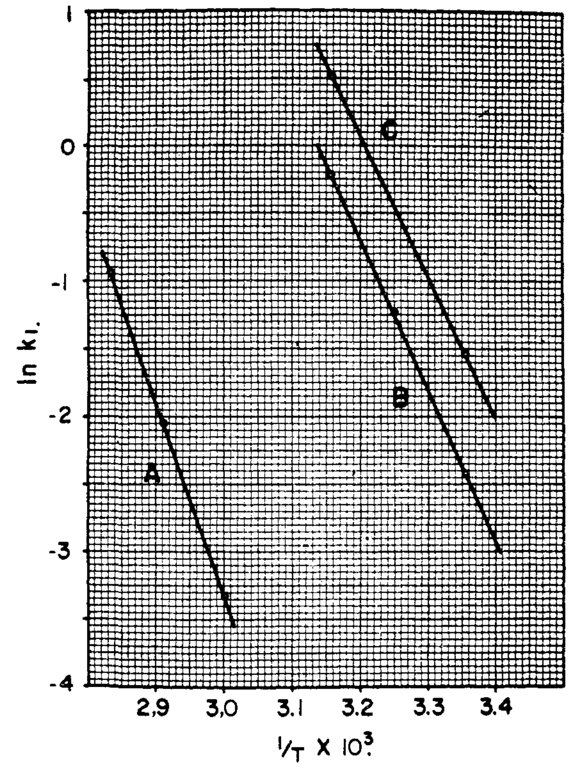

Fig. 3.—Arrhenius plot: A, cyclization of *o*-benzoylbenzoic acid to anthraquinone in 83.05% PPA, E_a = −27,600 cal./mole, ΔS^* = +1.33 e.u. at 80°; B and C, cyclization of *o*-phenoxybenzoic acid in 83.05% and 85.48% PPA respectively, E_a = −22,100 and −20,580 cal./mole, ΔS^* = −5.70 and −9.03 e.u. at 44°.

No explanation of the occurrence of maxima in PPA is free from arguments, including the one presented above. For example, the identity of the rate-determining step is based on precedent and not fact, and the true reactive intermediate may not be an open-chain acylium ion but rather a mixed anhydride. Furthermore, the view taken above explains the maxima or peculiar properties of the *o*-aroylbenzoic acid and disregards the possibility that it is the PPA which causes the maxima. Explanations based on some general property of PPA must rationalize the fact, however, that *o*-phenoxybenzoic acid does not exhibit a maximum. For example, if one assumes that proton elimination, reaction 3, is the rate-determining step and that the decrease in rate constants is due to lack of a base to accept the proton in the highly acidic solutions, then why should *o*-phenoxybenzoic acid be an exception? Other explanations based on the specific effects of some component of PPA which changes in concentration as the total P_2O_5 content changes suffer the same drawback. Of course, if the mechanisms of cyclization of *o*-phenoxybenzoic and *o*-aroylbenzoic acids are different, these explanations become more valid.

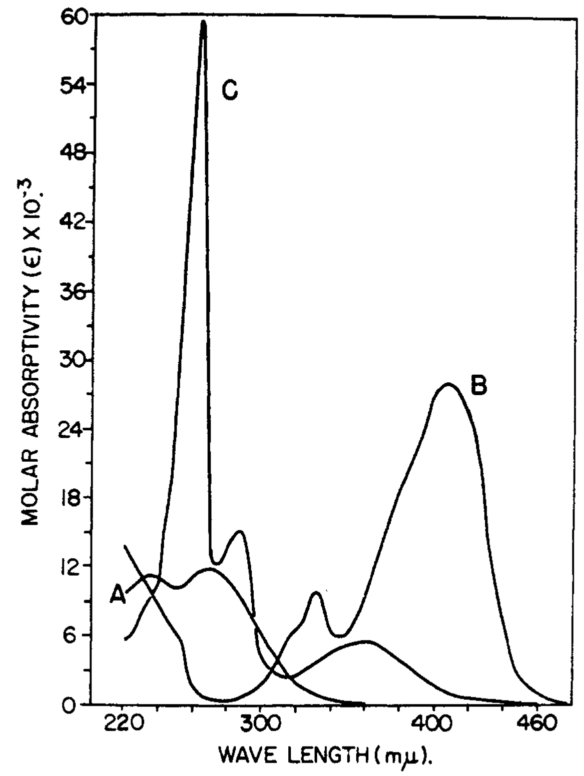

Fig. 4.—Ultraviolet absorption spectra of *o*-benzoylbenzoic acid (free acid and cyclic carbonium ion forms) and of anthraquinone: A, free acid form in 72.0% PPA; B, cyclic carbonium ion form in 83.0% PPA; C, anthraquinone in 81.6% PPA.

Recently it was suggested[6] that the great increase in viscosity of PPA in the region around 80% P_2O_5 content was responsible for the slacking off of the rates of rearrangements of acetophenone oximes. In order to test the possibility that the viscosity of the medium was causing the maxima, an Arrhenius plot, Fig. 3, was made. Since the viscosity of PPA changes greatly over the 20° range studied, an abnormal plot would be expected if viscosity were important. We assume this to be true because the Arrhenius equation ignores the effect of viscosity or at least implies that viscosity changes with temperature are always the same. The plots were normal, however, and tend to indicate that the high viscosity of PPA does not influence the kinetics of these intramolecular reactions.

Experimental

General.—The highly viscous, hygroscopic nature and low (or sluggish) solubilizing powers of PPA necessitated the use of special laboratory techniques. All aliquots and dilutions were made on a weight–weight basis and were converted to volumetric dimensions when necessary by means of reported densities.[19a,b]

The spectroscopic method of analysis demanded that low concentrations, 10^{-4} to 10^{-5} *M*, of reactants be present in PPA. Stock solutions of powdered reactants were made to about 10^{-2} *M* in PPA of 72 to 80% P_2O_5 content. Aliquots from the stock solutions were then diluted about 100-fold to make reaction mixtures and standard solutions in PPA of the desired strength.

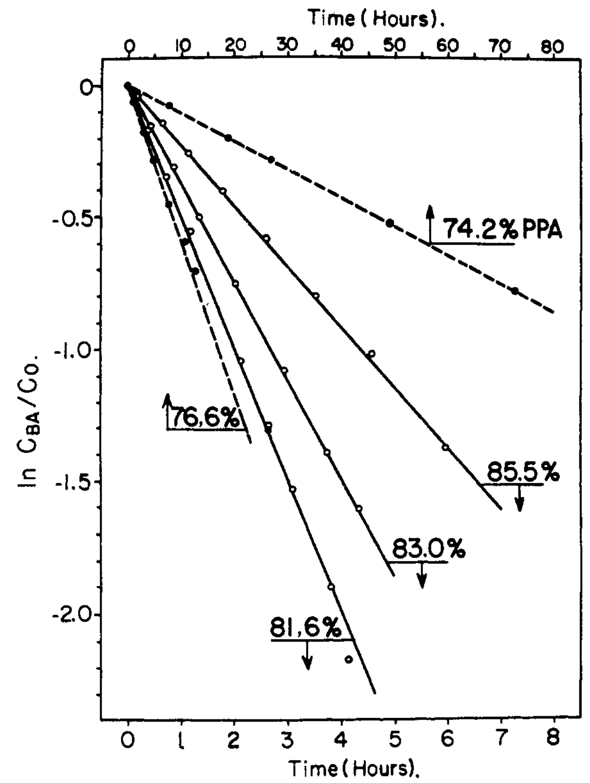

Fig. 5.—Typical first-order plots of cyclization of *o*-benzoylbenzoic acid to anthraquinone at 80° in PPA of various concentrations. The solid lines with open circles are to be used with the lower time scale.

For preparation of standard solutions used for calibration of the spectroscopic method, representative samples of stock solutions were pipetted into tared, glass-stoppered flasks which were quickly stoppered and weighed. To these aliquots PPA of the desired concentration was added, and the contents mixed by stirring with a stirring rod if too viscous to mix by swirling. Gentle heating to decrease the viscosity was a great aid when it could be employed without causing reaction. Mixing of solutions of about 85% PPA at room temperature without the introduction of excessive amounts of small air bubbles was accomplished by

Table III

Kinetics of Cyclization of *o*-Benzoylbenzoic Acid to Anthraquinone in 85.48% PPA at 80.06 ± 0.02°

Hours	C_{BA}[a]	C_{AQ}[a]	$C_{BA} + C_{AQ}$[a]	k_1[b]
0	16.97[c]	0	...	...
0.18	16.84	0.29	17.13	0.212
0.67	15.11	1.99	17.10	.220
1.15	13.45	3.63	17.08	.229
1.79	11.62	5.24	16.86	.229
2.61	9.76	7.23	16.99	.224
3.53	7.85	9.30	17.15	.227
4.57	6.30	10.93	17.23	.224
5.93	4.42	12.67	17.09	.232
20.33	0	16.92	16.92	...

Constants used in eq. 1 are $\epsilon_{406}^{BA} = 28{,}400$, $\epsilon_{262}^{BA} = 1{,}650$, $\epsilon_{406}^{AQ} = 2{,}474$ and $\epsilon_{262}^{AQ} = 54{,}750$. Graphically determined first-order rate constant is 0.228/hr. and the half-life is 3.04 hr. [a] Actual molarities times 10^6. [b] Calculated first-order rate constants using 17.50×10^{-6} *M* as the initial concentration of the starting material, determined by extrapolating a first-order plot to zero time. [c] C_0, calculated from amount of starting material added.

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(19) (a) J. R. Van Wazer, ref. 17, p. 771; (b) R. M. Stone, Ph.D. Dissertation, Vanderbilt University, 1959; *Diss. Abs.*, **20** (4), 1196 (1959).

TABLE IV

SUMMARY OF ANALYTICAL ABSORPTION BANDS AND MOLAR ABSORPTIVITIES[a]

Compound[b]	P_2O_5, %			
	85.48	83.05	81.6	79.6
o-BBA[c]	406; 28,400	406; 27,865	406; 26,500	...
	262; 1,650	262; 1,707	262; 1,870	...
AQ[d]	406; 2,474	406; 1,887	406; 1,650	...
	262; 54,750	262; 56,224	262; 56,250	...
o-(*p*-ClB)-BA	440; 41,560	440; 41,260	440; 37,000	...
	268; 1,419	267; 1,646	267; 2,200	...
2-ClAQ	440; 1,041	440; 310	440; 380	...
	268; 49,450	267; 51,670	267; 53,700	...
o-(*p*-T)-BA[e]		432; 35,000	432; 34,000	432; 31,000
		267; 1,475	267; 2,500	267; 2,730
2-MAQ[f]		432; 2,620	432; 2,000	432; 1,000
		267; 43,500	267; 43,500	267; 43,500
o-PBA[g]	250.75; 8,500[i,j]	250.75; 8,500[i,j]		
	250.75; 9,000	250.75; 8,500[i,k]		
		250.75; 9,000		
X[h]	250.75; 48,000[i,j]	250.75; 51,000[i,j]		
	250.75; 53,500	250.75; 48,000[i,k]		

[a] First entry is wave length in mμ and the second is ε at 25°. [b] See Table I for abbreviation legend; AQ is anthraquinone; 2-MAQ is 2-methylanthraquinone, etc. [c] At 76.6% P_2O_5: 353; 935. At 74.2%: 353; 344. [d] At 76.6%: 353; 5,950. At 74.2%: 353, 58,000. [e] At 75.0%: 267; 6810. [f] At 75.0%: 267; 43,500. [g] At 78.6[i,j]: 251; 8500. [h] At 78.6%[i,j]: 251; 48,000. [i] Values determined with Beckman DU rather than Cary spectrophotometer. [j] ε at 43.76°. [k] ε at 34.74°.

rotating (not stirring) a large stirring rod in the liquid for long periods of time.

Simple techniques were used to avoid excessive moisture absorption without resorting to operation in a dry-box. A Cary recording spectrophotometer, model 14, and 1-cm. matched quartz cells were used for all spectroscopic measurements except as noted.

Typical Rate Determination.—A 250-ml. glass-stoppered erlenmeyer flask containing a weighed amount of PPA of the desired strength was placed in a constant temperature bath. After the PPA had attained the temperature of the bath, an aliquot of a stock solution of the reactant was added to the heated PPA from a weighing buret. Immediately a stirrer was inserted and the mixture manually stirred for 5 to 15 minutes in a manner to avoid introduction of small air bubbles. Zero time was taken as the moment stirring was begun. Samples were taken periodically from the reaction mixture by means of a heated, large-bore pipet and placed directly in the absorption cells to be used in the spectroscopic analysis. The cells were cooled in an ice-bath for 1 or 2 minutes in order to quench the reaction, and the moment of introduction of the aliquot into the ice-bath was taken as termination of the reaction. The samples were allowed to come to room temperature before scanning.

In most cases studied a direct two-component analysis was possible. In Fig. 4 the ultraviolet spectra of *o*-benzoylbenzoic acid (A), of its cyclic carbonium ion (B) and of anthraquinone (C) illustrate this ideal situation between the reactant (B) and the product (C). The following set of simultaneous equations was used to calculate the concentration of unreacted acid C_{BA} and of product C_{AQ} in the samples

$$\begin{aligned} A^{BA}_{\lambda_1} &= \epsilon^{BA}_{\lambda_1} C_{BA} + \epsilon^{AQ}_{\lambda_1} C_{AQ} \\ A^{AQ}_{\lambda_2} &= \epsilon^{BA}_{\lambda_2} C_{BA} + \epsilon^{AQ}_{\lambda_2} C_{AQ} \end{aligned} \qquad (1)$$

The symbols λ1 and λ2 stand for the two analytical wave lengths, *A* for the experimental absorption value, ε for the molar absorptivity, and *BA* and *AQ* for the substituted benzoic acid reactant and anthraquinone product, respectively. Since the initial concentration of the reactant C_0 was also an experimentally determined value, the equation

$$C_{BA} + C_{AQ} = C_0 \qquad (2)$$

was used as a check on the results from eq. 1.

First-order rate constants k_1 were determined graphically from plots like those for *o*-benzoylbenzoic acid in Fig. 5. Table III contains the data for one run illustrated in Fig. 5. Table I summarizes the k_1's for all the compounds studied. Table IV summarizes analytical absorption bands and molar absorptivities in PPA of varying P_2O_5 concentration.

A slightly modified kinetic method was used for *o*-phenoxybenzoic acid due to its more rapid reaction rates. The reaction was started in the same manner as above, but, immediately after mixing, an aliquot was removed and promptly placed in an absorption cell in the constant-temperature cell compartment of a Beckman DU spectrophotometer. Periodic absorption measurements were taken at the analytical absorption band only. In this case, eq. 2 and the following equation were used to determine the concentrations present

$$A_{\lambda_3} = \epsilon^{BA}_{\lambda_3} C_{BA} + \epsilon^{X}_{\lambda_3} C_X \qquad (3)$$

The symbol λ3 represents the analytical absorption band and X stands for the product xanthone.

Polyphosphoric Acid.—Measured volumes of distilled water were added dropwise to a weighed amount of Baker and Adamson phosphorus pentoxide (reagent grade, code 1148) in a 12-liter flask. The flask was heated and stored in its own heating mantle, and withdrawals were made through a permanently installed suction system which was suitably guarded with stopcocks and drying tubes. Several large 15-pound batches were made and standardized by potentiometric titration with standard base. Before use, new batches of PPA were heated at 120–150° for several weeks with agitation until completely homogeneous. Smaller batches of PPA were made by diluting portions of previously standardized PPA with a measured volume of distilled water. Late in this study the refractive index method[15] was used to standardize new batches of PPA.

***o*-Benzoylbenzoic Acids.**—All melting points reported are uncorrected. The commercial product was dissolved in dilute aqueous sodium hydroxide. The sodium salt in solution was then extracted thoroughly with chloroform and partially acidified, the resulting precipitate being discarded. After complete acidification of the remaining solution, the acid was filtered, washed with water, air-dried under vacuum and recrystallized from benzene; m.p. 128.5–129° with the correct neutralization equivalent. With crystallization alone, the neutralization equivalent was too high by one-half to two units.

Anthraquinone.—Matheson #2850 anthraquinone was sublimed under vacuum giving fine needles melting at 279.5–280°.

***o*-(*p*-Chlorobenzoyl)-benzoic acid** was prepared by the Friedel–Crafts reaction of phthalic anhydride and chlorobenzene. After being submitted to the purification described for *o*-benzoylbenzoic acid, the resulting compound had a melting point 149.8–150.3°. In hot, concentrated solution of this acid in the more dilute PPA, a minor side reaction was indicated by the faint odor of hydrogen chloride. This reaction was not a problem in the kinetic experiments.

2-Chloroanthraquinone was prepared by the cyclization of *o*-(*p*-chlorobenzoyl)-benzoic acid in PPA at 80°. Recrystallization from ethanol gave crystals melting at 209.6–210.2°.

***o*-(*p*-Toluyl)-benzoic acid** was prepared by the Friedel-Crafts reaction of phthalic anhydride and toluene. After purification the crystals melted at 138.7–139.6°. Although high concentrations of *o*-(*p*-toluyl)benzoic acid are known to polymerize in PPA,[20] low concentration, as needed for the kinetic runs, did not result in detectable polymerization during the first four half-lives of the main reaction.

2-Methylanthraquinone.—Matheson, Coleman and Bell practical grade material was recrystallized from ethanol and then sublimed to give crystals melting at 176–177°.

***o*-Phenoxybenzoic Acid and Xanthone.**—The acid had a melting point of 112.8–113.8° after numerous recrystallizations. Xanthone, recrystallized twice from ethanol, had a melting point of 175.6–176.4°.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, R. I.]

The Mechanism of Nitrosodecarboxylation of 3,5-Dibromo-4-hydroxybenzoic Acid and Nitrosodeprotonation of 2,6-Dibromophenol

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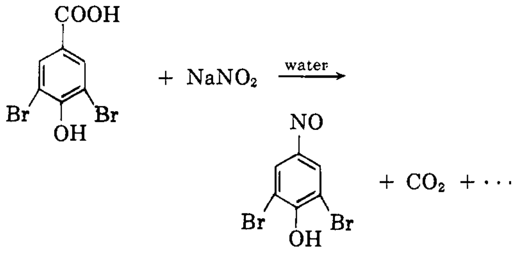
The kinetics of the nitrosodecarboxylation reaction of sodium nitrite with 3,5-dibromo-4-hydroxybenzoic acid has been studied at 30° in aqueous medium. The observed rate law is given in equation 6 of the text. The rates of the nitrosation reaction of sodium nitrite with 2,6-dibromophenol and with 2,6-dibromophenol-4-d_1 have also been measured. A significant kinetic hydrogen-isotope effect (k_H/k_D = 3.6) has been observed. The reaction of the dibromophenol is general base catalyzed while that of the dibromohydroxy acid is not. The observed rate of nitrosodecarboxylation is about 13 times as fast as that of nitrosodeprotonation under identical conditions of acidity and NO_2^- concentration. *p*-Hydroxybenzoic acid reacts at least 300 times more rapidly than does *p*-methoxybenzoic acid. The observed rates of the present reactions are considerably slower than the rate of aniline nitrosation under comparable conditions. These facts are explained on the basis of the reversible formation of a quinonoid intermediate upon the electrophilic attack of the species $H_2O{\cdot}NO^+$ or $NO_2{\cdot}NO$ on the phenolate ion form of the substrate; the subsequent rate-determining loss of CO_2 or H^+ from the quinonoid intermediate leads to the nitrosated product.

Introduction

The reaction of 3,5-dibromo-4-hydroxybenzoic acid with $NaNO_2$ in aqueous or aqueous ethanolic medium (eq. 1) gives 2,6-dibromo-4-nitrosophenol



(1)

with evolution of CO_2.[1] Salicylic acid,[2] *p*-hydroxybenzoic acid and 3-, 4- and 5-methylsalicylic acids also undergo this reaction, but 3-nitrosalicylic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid and 3,5-dinitro-4-hydroxybenzoic acid do not.[1] The reaction thus appears to be an electrophilic aromatic substitution involving the attack of an NO^+ carrier on the carbon atom bearing the carboxylic group and has been termed nitrosodecarboxylation[1] by analogy with bromodecarboxylation[3] and bromodesulfonation.[4]

The present investigations were undertaken to find out the nature of the nitrosation carrier and to determine whether the over-all mechanism is indeed analogous to that of bromodecarboxylation and bromodesulfonation. A comparison with N-nitrosation of anilines[5-7] on the one hand and with the corresponding brominations[3,4] on the other would be interesting and instructive.

Results

Symbols.—The reactants and the product of the reaction under investigation are acid–base systems. In the following discussion, I will symbolize totally the mixture of the neutral molecule 3,5-dibromo-4-hydroxybenzoic acid and its anionic forms, and II the mixture of 2,6-dibromo-4-nitrosophenol, its tautomer 3,5-dibromo-*p*-quinonemonoxime and their anion; [I], [II] and $[NO_2^-]$ will represent the stoichiometric concentrations, *i.e.*, a total of the concentrations of all the acidic and basic forms of the species enclosed within the brackets.

For a kinetic study of the nitrosodecarboxylation reaction, compound I was chosen as the substrate. Preliminary spectrophotometric studies showed that the reaction of I with aqueous $NaNO_2$ (eq. 1) was uncomplicated by side reactions and that the reaction kinetics could be conveniently measured by following the rate of appearance of the product II in the visible region at 420 mμ, where II has an intense absorption band.[8] The 2,6-dibromo-4-nitrosophenol was prepared according to the method

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[8] Although the absorption maximum is at 420 mμ, the wave length 425 mμ was monitored for most of the kinetic measurements to avoid any interference by absorption due to nitrous acid at the lower wave length.