Kinetics of the Formation of Triphenylimidazoles from Benzils

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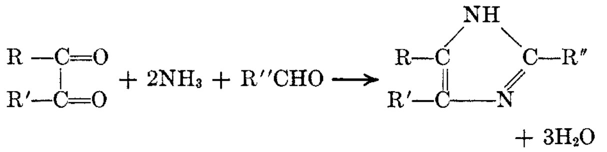
The formation of 2,4,5-triphenylimidazole by the condensation of benzil with benzaldehyde and ammonium acetate in glacial acetic acid at 110° has been kinetically studied by means of uv and visible spectrophotometry. The rate equation is $v = k[\text{benzil}][\text{AcONH}_4]^2$, where k varies slightly with varying initial concentration of benzaldehyde and the extent of variation of k depends on the substituent of benzaldehyde. The effect of substituents of benzil is small. These results suggest a mechanism involving the formation of benzil diimine (III) and the addition of III to benzaldehyde.

Radziszewski synthesis[1] for the preparation of imidazoles involves the condensation of α-dicarbonyl compounds with aldehydes and ammonia (eq 1). Although the mechanisms of this reaction have been postulated by some investigators,[2-4] no decisive evidence and no kinetic study is available. The present paper summarizes our data from the kinetic study on the formation of triarylimidazoles by the condensation of benzils with benzaldehydes and ammonium acetate in glacial acetic acid at 100°. The data involve the effects of substituent, solvent, and temperature on the rate, which imply the mechanism. Rates were measured by following the consumption of benzil and/or the formation of imidazole by spectrophotometry.



(1)

Results

When a mixture of benzil, ammonium acetate, and benzaldehyde in acetic acid was heated at 100°, 2,4,5-triphenylimidazole (lophine, V) was formed almost quantitatively (94%).

Rate Law.—The rate of the consumption of benzil was found to satisfy the third-order equation, as in eq 2. The stoichiometric concentration of ammonium acetate is represented by $[\text{AcONH}_4]$.

$$d[\text{lophine}]/dt = -d[\text{benzil}]/dt = k[\text{benzil}][\text{AcONH}_4]^2 \quad (2)$$

The rate of the formation of lophine (V) agrees with that of the consumption of benzil within experimental error. When the initial concentrations of benzil and ammonium acetate are kept constant, the third-order rate constant k increases only slightly with increasing initial concentration of benzaldehyde. The order with respect to benzaldehyde was virtually zero (Table I). However, the rates for substituted benzaldehydes are not independent of the concentration of benzaldehydes.

Effect of Substituent of Benzil on the Rate.—It is expected from the rate equation (2) that the substituents on benzil affect the rate, but the rates of monosubstituted benzils were almost independent of the *para* substituent (Table II). This result suggests that some compensation effect exists, as will be discussed below.

TABLE I

KINETIC DATA FOR THE REACTION OF BENZIL, AMMONIUM ACETATE, AND BENZALDEHYDE IN GLACIAL ACETIC ACID AT 98°

$[\text{Bz}_2]$, 10 M	[PhCHO], 10 M	$[\text{AcONH}_4]$, M	k,[a] 10^4 sec^{-1}	k,[b] 10^4 M^{-2} sec^{-1}
1.94	1.96	1.20	1.63	1.13
2.00	1.96	1.41	2.19	1.10
1.95	1.96	1.60	2.88	1.12
1.96	1.97	1.79	3.33	1.04
1.88	1.97	2.00	4.18	1.04
2.04	8.84	1.80	3.25	1.01
2.43	8.84	1.79	3.33	1.04
2.76	8.85	1.80	3.34	1.04
3.10	8.85	1.79	3.27	1.01
0.834	0.894	1.26	1.83	1.17
0.865	1.78	1.26	1.91	1.21
0.810	2.59	1.26	1.95	1.23
0.810	3.61	1.26	2.05	1.28

[a] Pseudo-first-order rate constant with regard to benzil. [b] Third-order rate constant calculated by mean of $k/[\text{AcONH}_4]^2$.

TABLE II

THE SUBSTITUENT EFFECT OF BENZIL ON THE RATE[a]

Substituent	10^4k M^{-2} sec^{-1}
p-NO$_2$	1.19
p-Cl	0.98
H	1.04
p-MeO	0.94
p-Me$_2$N	1.10

[a] Initial concentration: ArCOCOPh, 0.03–0.09 M; AcONH$_4$, 1.3–2.0 M; PhCHO, 0.03–0.09 M.

Substituent Effect of Benzaldehyde.—When the initial concentrations of benzil and ammonium acetate were kept constant, the rates of reactions with p-chloro- and p-methoxybenzaldehydes were measured at their various initial concentrations. The third-order rate constant, k in eq 2, increases with increasing initial concentration of aldehydes. The dependence of k on the initial concentration of aldehyde decreases in the order p-Cl > p-MeO > H, but in each case the order with respect to aldehyde is lower than unity, as shown in Figure 1.

The rates were measured in the presence of excess water, so that the change of water concentration as the reaction proceeded would be negligible. The addition of water caused a decrease in the rates. Plots of the third-order rate constant k against the initial concentration of aldehyde are shown in Figure 2.

When the initial concentrations of benzil, benzaldehyde (excess), and water (excess) were kept constant, k

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[1] K. Hofman, "Imidazole and its Derivatives," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1953, p 33.

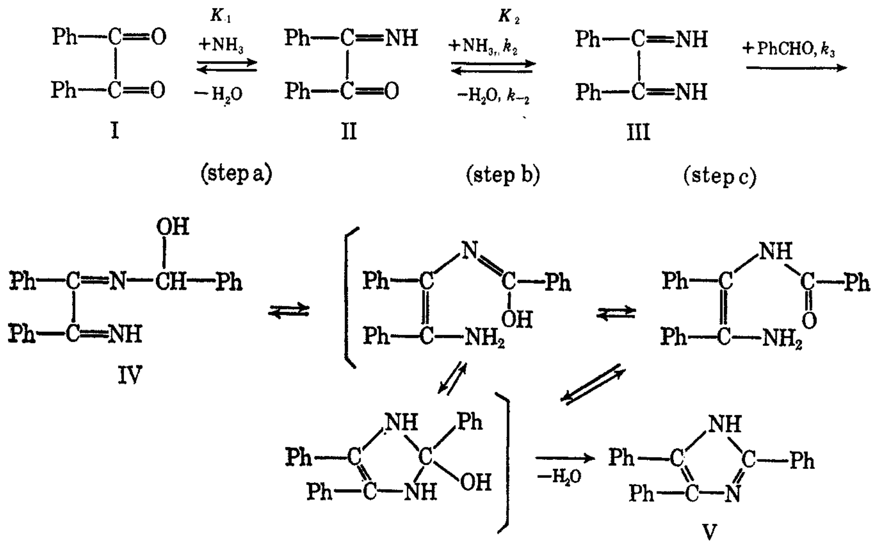
[2] E. C. Franklin and F. W. Bergstrom, *Chem. Rev.*, **16**, 311 (1935).

[3] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

[4] C. M. Selwitz and A. I. Kosak, *J. Amer. Chem. Soc.*, **77**, 5370 (1955).

Scheme I

$$AcONH_4 \overset{K_a}{\rightleftarrows} AcOH + NH_3 \qquad (3)$$



(4)

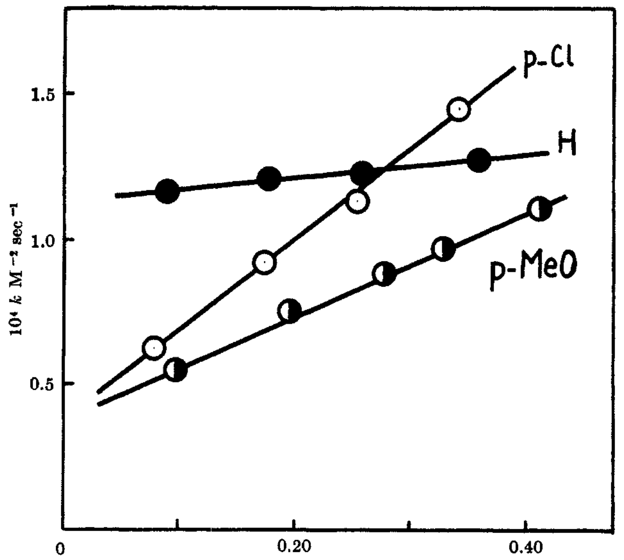


Figure 1.—The effects of substituent and initial concentration of benzaldehyde on the third-order rate constant for lophine formation at 98°.

was found to be independent of the concentration of ammonium acetate (Table III).

Table III
The Effect of the Concentration of Ammonium Acetate on the Rate, in the Presence of Benzil, Excess Benzaldehyde, and Excess Water[a]

[AcONH$_4$], M	0.900	1.00	1.27	1.41
10^4k, M^{-2} sec^{-1}	1.07	1.01	1.04	0.90

[a] Initial concentration: PhCOCOPh, 0.086 M; PhCHO, 0.40 M; H_2O, 3.0 M.

Enthalpy and Entropy of Activation.—The third-order rate constants (10^{-4} M^{-2} sec^{-1}) were 0.34 at 81.4°, 0.58 at 88.2°, 0.79 at 92°, and 1.71 at 103.0°, which afforded the enthalpy and entropy of activation as 18.3 kcal mol^{-1} and −9.2 eu, respectively.

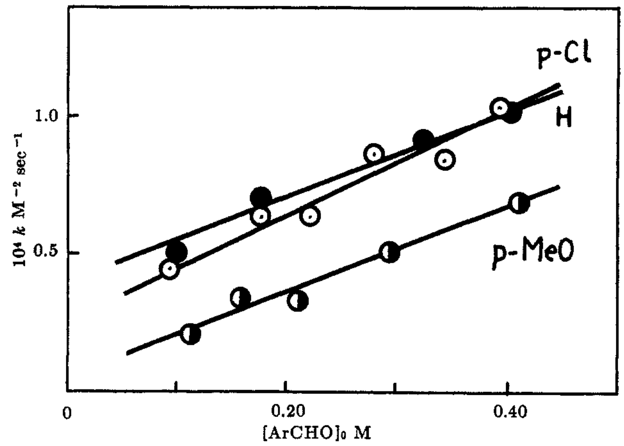


Figure 2.—The effects of substituent and initial concentration of benzaldehyde on the third-order rate constant for lophine formation in the presence of excess water at 98°.

Discussion

The rate equation for unsubstituted benzaldehyde is expressed as $d[\text{lophine}]/dt = k[\text{benzil}][AcONH_4]^2$. However, k increases slightly with increasing initial concentration of aldehyde.

The extent of dependence of k on the initial concentration of aldehyde varies with the kind of substituent on the aldehyde.

The effect of substituents on benzil is small.

Mechanism.—Since acetic acid has a fairly low dielectric constant, the concentration of completely dissociated ions, NH_4^+ and AcO^-, is negligible compared with that of the added salt, NH_4OAc.[5] Therefore, the concentration of free ammonia is approximately proportional to the stoichiometric concentration of ammonium acetate. Hence, the rate equation 2 suggests a mechanism such that two molecules of ammonia and one molecule of benzil are involved in the

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[5] S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 2974 (1956). Dissociation constants (pK) in acetic acid of sodium acetate, lithium acetate, and tribenzylamine hydrochloride have been reported to be 6.68, 6.79, and 6.71, respectively. Hence, that of ammonium acetate would be 7 or higher.

rate-determining steps, *i.e.*, the reversible condensations of benzil with ammonia to form monoimine II and then diimine III followed by the condensation of III with benzaldehyde. See Scheme I.

Although little evidence is available at present, IV is perhaps converted into V *via* prototropy and cyclodehydration, since this pathway is the most common amine–carbonyl condensation. Selwitz's imidazole synthesis from aldehyde and 9,10-phenanthrenequinone diimine[4] presents a support for the conversion of III into V, but the rate measurement for the reaction of III with aldehyde failed because of the instability of III.

Application of the steady-state approximation to eq 3 and 4 leads to the following relationship for the third-order rate constant.

$$k = \frac{K_a^2K_1k_2k_3[\mathrm{ArCHO}]}{[\mathrm{H_2O}][\mathrm{AcOH}]^2(k_3[\mathrm{ArCHO}] + k_{-2}[\mathrm{H_2O}])} \qquad (5)$$

or

$$\frac{1}{k} = \frac{[\mathrm{H_2O}][\mathrm{AcOH}]^2}{K_a^2}\left(\frac{1}{K_1k_2} + \frac{[\mathrm{H_2O}]}{K_1K_2k_3[\mathrm{ArCHO}]}\right) \qquad (6)$$

Here, in eq 5 and 6, $[\mathrm{H_2O}]$ and $[\mathrm{AcOH}]$ are kept constant throughout a run. A plot of $1/k$ *vs.* $1/[\mathrm{ArCHO}]$ should be linear, which agrees with our observation (Figure 3).

If step b (II–III) is rate-determining, the dependence of the third-order rate constant k on the substituent of the aldehyde and on the initial concentration of aldehyde cannot be explained; hence step c (III–IV) may also be rate-determining. Water formed during the reaction may cause complications. In fact, excess water makes k begin to depend on the concentration of aldehyde, although the rate is not first order in aldehyde as shown in Figure 2.

While it is possible to write a reaction sequence which leads to the product and involves benzaldehyde and ammonia [or $(\mathrm{PhCH{=}N})_2\mathrm{CHPh}$] and no benzil,[6] or benzil and ammonia and no benzaldehyde,[3] neither of these possibilities can be correct, since lophine is actually formed only when both benzil and benzaldehyde are present.

Since the dicarbonyl system in benzil has a skew configuration[7] and the configuration of imine–carbonyl system in II and the configuration of diimine system in III are probably similar to that of benzil because of the steric hindrance between their phenyl groups, hydrogen bonding is difficult and steps a and b in eq 4 probably have comparable rate constants. Benzil has two reactive sites and monoimine II has one for the forward reaction, while monoimine II has one site and diimine III has two for the reverse reaction. Accordingly, the statistical relation of the two equilibrium constants is $K_1 = 4K_2$. Moreover, since the concentration of benzil is much higher than that of benzil monoimine II, the net rate of step b in eq 4 should be much slower than that of step a.

An alternative mechanism involving intermediate VI[3], VII, or VIII[2] is inconsistent with the observed rate law; *i.e.*, VI is not conceivable, since the observed rate equation is not first order in aldehyde, VII is not appropriate, because the derived steady-state rate equation is inconsistent with the observed one, and VIII

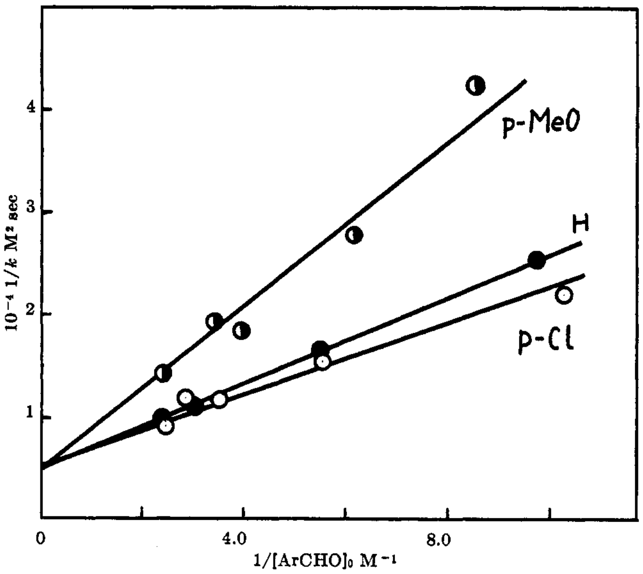
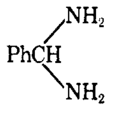
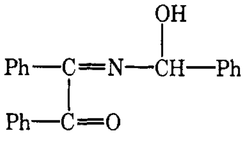


Figure 3.—The relation between reciprocal of initial concentration of benzaldehydes and reciprocal of third-order rate constant for lophine formation in the presence of excess water at 98°.



VI



$$\mathrm{Ph{-}C(=N{-}CH(OH){-}Ph){-}C(=O){-}Ph}$$

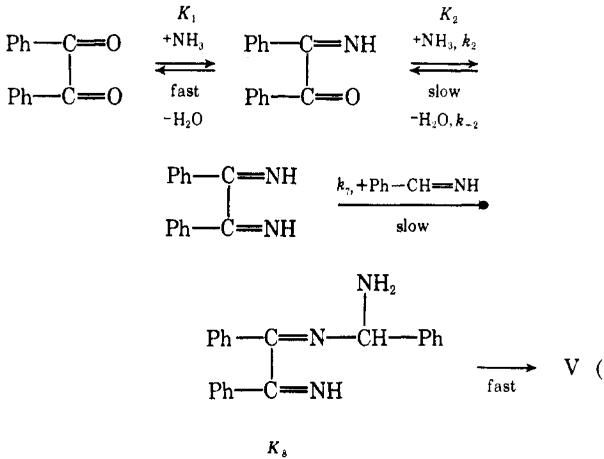
VII

$\mathrm{Ph{-}CH{=}NH}$

VIII

is not probable, because it demands an incorrect rate dependence on the ammonium acetate concentration (Table III).

For example, the third mechanism (eq 7 and 8), which has been proposed for a similar reaction,[2] can be discarded, since it does not fit the observed rate law.



(7)

$$\mathrm{PhCHO} + \mathrm{NH_3} \overset{K_8}{\rightleftharpoons} \mathrm{PhCH{=}NH} + \mathrm{H_2O} \qquad (8)$$

This mechanism leads to the following third-order rate constant k by means of a steady-state approximation.

$$k = \frac{K_a^3K_1k_2k_7K_8[\mathrm{PhCHO}][\mathrm{AcONH_4}]}{[\mathrm{H_2O}][\mathrm{AcOH}]^2(k_7K_8K_a[\mathrm{PhCHO}][\mathrm{AcONH_4}] + k_{-2}[\mathrm{H_2O}]^2[\mathrm{AcOH}])} \qquad (9)$$

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(6) Y. Ogata, A. Kawasaki, and N. Okumura, *J. Org. Chem.*, **29**, 1985 (1964).

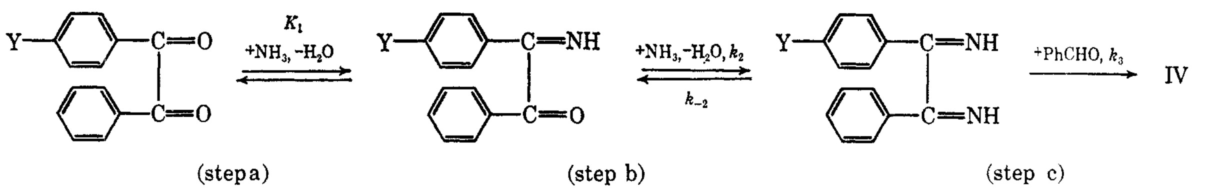
(7) I. E. Knaggs and K. Lonsdale, *Nature*, **143**, 1023 (1939).

or

$$\frac{1}{k} = \frac{[H_2O][AcOH]^2}{K_a^2}\left(\frac{1}{K_1k_2} + \frac{[AcOH]}{K_aK_1K_2k_7K_8[PhCHO][AcONH_4]}\right) \quad (10)$$

Here, in eq 9 and 10, k's and K's are the rate and equilibrium constants of the subscripted equations, respectively. When the initial concentrations of benzil, excess benzaldehyde, and excess water are kept constant, k is independent of the concentration of ammonium acetate and is nearly constant (Table III). The results show that diimine III does not attack on benzaldimine but on benzaldehyde (eq 4).

Substituent Effect.—The fact that the substituent of benzil has little effect on the rate is unexpected from the rate law, but it is explicable by the mechanism shown below (eq 11). In step a, the benzoyl group with electron-withdrawing substituent Y is more reactive than the unsubstituted benzoyl group with nucleophilic ammonia. The rate of the second step, b, which is one of the slow steps, is little affected by Y. In the third step, c, which is another slow step, benzaldehyde reacts more easily with the nitrogen atom of unsubstituted benzilideneimine, because it is a stronger nucleophile. Therefore, the substituent effect on the overall rates tends to be cancelled. In contrast, a benzoyl group with an electron-releasing group is less reactive than that of an unsubstituted one. In this case, the second step is retarded by an electron-releasing group while the third step is accelerated, and the substituent effect is also cancelled. An explanation similar to that offered by Anderson[8] is improbable, since benzil has two reactive sites.



(11)

Equation 11 requires that the substituent, X, of benzaldehyde should affect k_3 alone in eq 6. In agreement with this expectation, the observed slope, $[AcOH]^2[H_2O]^2/K_a^2K_1K_2k_3$, depends on X, while the intercept, $[AcOH]^2[H_2O]/K_a^2K_1k_2$, is independent of X, as is apparent from Figure 3. The rate constant k_3 decreases in the order MeO < H $\lesssim$ Cl. It is interesting to note that the reactivity of *p*-chlorobenzaldehyde is not very different from that of benzaldehyde. Cook has reported the failure of this synthesis with α,β-unsaturated aldehydes such as acraldehyde and crotonaldehyde because of the delocalization of partial positive charge of the carbonyl.[9]

Finally, parallel reactions of third- and fourth-order, *i.e.*, the reaction of II with ammonia and that of VI with I, are not applicable to the present reaction, because they demand a plot of the third-order rate constant *vs.* benzaldehyde concentration having an intercept independent of the substituent of the aldehyde, which is inconsistent with the observed plot (Figure 2).

Enthalpy and entropy of activation are higher than those of ordinary carbonyl-amine reactions such as the reaction of aromatic aldehyde with ammonia or *n*-butylamine (7-10 kcal mol^{-1} and -30 to -45 eu),[6,10] which reflects the requirement of higher reaction temperature and involvement of many complicated steps.

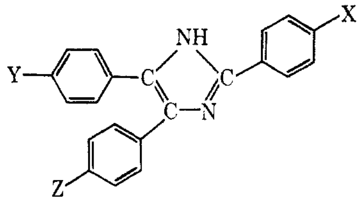
Experimental Section

Materials.—Ammonium acetate was dried in a desiccator over H_2SO_4. Glacial acetic acid was purified by rectification, bp 116.8–118° (lit.[11] 118°). Benzaldehyde and anisaldehyde were washed with 2% aqueous Na_2CO_3, dried with $MgSO_4 \cdot H_2O$, and rectified under nitrogen, bp 92.5° (46 mm) and 111–112° (9 mm), respectively. *p*-Chlorobenzaldehyde was recrystallized from water and had mp 46.1–46.8° (lit.[12] 47°). Benzil was prepared by oxidation of benzoin formed by the benzoin condensation of benzaldehyde, mp 94.8–95.2° (lit.[13] 95°), *p*-methoxybenzil, mp 52.0–54.0° (lit.[14] 52.0–53.0°), and *p*-dimethylaminobenzil, mp 101.0–102.4° (lit.[14] 101–102°). *p*-Methoxybenzoin obtained by the mixed benzoin condensation should be freed from benzoin by repeated recrystallization before oxidation into *p*-methoxybenzil to avoid contamination with benzil. *p*-Nitrobenzil, mp 136–136.7° (lit.[15] 142°), and *p*-chlorobenzil, mp 69.6–70.6° (lit.[16] 70°), were prepared according to the literature.

Products.—2,4,5-Triarylimidazoles were prepared by the reaction of benzil, substituted benzaldehydes, and ammonium acetate in glacial acetic acid at 100°; their melting points and λ_{max} are summarized in Table IV.

TABLE IV

SUBSTITUTED LOPHINES



Registry no.	Substituent X	Y (or Z)	Z (or Y)	Mp, °C	λ_{max}, mμ	Log ϵ, max	Ref
	H	H	H	269.0–271.5	301	4.43	*a*
	Cl	H	H	268.0–270.0	310	4.43	*b*
	MeO	H	H	226.2–227.0	300	4.43	*b*
	H	NO_2	H	235.9–236.3	373	4.07	*c*
21690-78-8	H	Cl	H	255.1–256.3	302	4.45	*d*
21690-79-9	H	MeO	H	210.0–212.0	299	4.38	*d*
21748-38-9	H	Me_2N	H	102.0–103.7	312	4.36	*d*

[a] Reference 3. [b] G. E. Philbrook, M. A. Maxwell, R. E. Taylor, and J. R. Tatler, *Photochem. Photobiol.*, **4** (6), 1175 (1966). [c] Reference 9. [d] This paper.

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(8) B. M. Anderson and W. P. Jencks, *J. Amer. Chem. Soc.*, **82**, 1773 (1960).

(9) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

(10) G. M. Santerre, C. J. Hansrote, Jr., and T. I. Crowell, *J. Amer. Chem. Soc.*, **80**, 1254 (1958); R. K. McLeod and T. I. Crowell, *J. Org. Chem.*, **26**, 1094 (1961).

(11) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955, p 145.

(12) W. L. McEwen, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 133.

(13) H. T. Clarke and E. E. Dreger, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 87.

(14) H. Kwart and M. M. Baevsky, *J. Amer. Chem. Soc.*, **80**, 580 (1958).

(15) E. B. Womack, N. Campbell, and G. B. Dodds, *J. Chem. Soc.*, 1402 (1938).

(16) K. Lempert, M. Lempert-Streiter, J. Breuer, I. Pataky, and K. A. Pfeifer, *Chem. Ber.*, **95**, 2885 (1962).

Rate Measurements.—Benzil has an absorption maximum in methanol at 380 mμ (ε 73.3), where benzaldehyde, triphenylimidazole, and ammonium acetate have little absorption. The data with various imidazoles are shown in Table IV. All of the compounds satisfy the Lambert–Beer law and the concentration of the above compounds can be estimated by spectrophotometry.

A typical measurement was made in the following manner. An acetic acid solution of ammonium acetate and a mixture of benzil, benzaldehyde, and acetic acid were mixed in a flask fitted with a reflux condenser and thermometer after reaching thermal equilibrium (100 ± 0.5°). Aliquots (each 1 ml) were taken out at regular intervals of time and diluted with methanol, and the absorbances at 380 mμ for benzil and for imidazole were measured. The first-order rate coefficient with benzil was calculated from the ordinary integrated equation.

Acknowledgment.—The authors wish to thank the referees for their helpful suggestions.

Registry No.—Benzil, 134-81-6; ammonium acetate, 1066-32-6; benzaldehyde, 100-52-7.

Kinetics of the Baeyer–Villiger Reaction of Benzaldehydes with Perbenzoic Acid in Aquoorganic Solvents

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The Baeyer–Villiger reaction of benzaldehydes with perbenzoic acid to give ultimately phenols and/or benzoic acids has been studied kinetically in aquoorganic solvents at various pH's. The rate in acidic media increases with increasing pH and exhibits general base catalysis but not acid catalysis. The rate at pH > 10 is independent of pH with some kind of aldehydes, while the rate for others decreases with increasing pH. The effect of substituent in benzaldehydes on hydride shift affording benzoic acids gives a ρ value of 1.1–1.8. These results, together with solvent and temperature effects, are discussed in terms of a mechanism containing formation, ionization, and rearrangement of an addition intermediate between the carbonyl group and peracid.

Heterolytic 1,2 rearrangements of organic peroxides have been studied extensively and they are recognized as intramolecular nucleophilic substitution on peroxide oxygen.[1] For example, highly negative ρ values were observed with heterolysis of substituted cumene hydroperoxide esters ($\rho = -5.1$)[2] and with acid-catalyzed rearrangement of cumene hydroperoxides ($\rho = -4.6$ for σ^+).[3] A similar but smaller ρ value (−1.1 to −1.4) was obtained for the Baeyer-Villiger reaction of acetophenones with trifluoroperacetic acid,[4] although most others afforded smaller and less straightforward effects of substituents, which deviates from the Hammett equation.[5]

The Baeyer–Villiger reaction in alkaline media, especially in aqueous media, has been disclosed less than that in acidic media. A typical alkaline reaction is the Dakin reaction.[6] The oxidation of ketones with alkaline hydrogen peroxide[7a] or with alkaline *t*-butyl hydroperoxide[7b] has been reported to give fission products by way of an ionic mechanism, but a homolysis could not be included.[1] Kinetics of the alkaline oxidation of *o*-sulfobenzaldehyde with substituted perbenzoate ion has been reported.[8]

The present study is an attempt at the elucidation of the mechanism of the Baeyer–Villiger reaction of benzaldehydes on the basis of migratory aptitude together with the effects of substituents, pH, solvent, and temperature.

Results

Migratory Aptitude.—Migrating groups in the Baeyer–Villiger rearrangement of benzaldehydes are either hydride or aryl anion (eq 1).

$$\mathrm{ArCHO} \xrightarrow{\mathrm{PhCO_3H}} \mathrm{ArCO_2H} + \mathrm{ArOH} \tag{1}$$

Migrating ratios of Ar/H differ largely, not only by ring substituents in the aldehydes, but also by the acidity of media, as shown in Table I. The aryl shift occurs exclusively with *p*- and *o*-hydroxybenzaldehydes. On the other hand, unsubstituted benzaldehyde and those with electron-attracting groups (*p*-Cl, *m*- and *p*-NO_2) gave solely the corresponding acids by a hydride shift regardless of the acidity of media. The oxidation of anisaldehydes is in a border line; *i.e.*, the hydride

TABLE I

MIGRATORY APTITUDE FOR THE BAEYER–VILLIGER REACTION OF BENZALDEHYDES BY PERBENZOIC ACID IN 80% METHANOL AT 2–5° FOR 24 HR[a]

		Products, %[b]					
		Alkaline[c]		Neutral[d]		Acidic[e]	
Registry no.	Substituent	$ArCO_2H$	ArOH	$ArCO_2H$	ArOH	$ArCO_2H$	ArOH
123-08-0	*p*-OH	0	94	0	92	0	91
90-02-8	*o*-OH	0	99	0	95	0	98
100-83-4	*m*-OH	65	2.1				
123-11-5	*p*-OMe	69	4.7	17	40	19	73
135-02-4	*o*-OMe	39	37	1	68		
100-52-7	H	100	0	90	0	90	0
104-88-1	*p*-Cl	93	0	97	0		
555-16-8	*p*-NO_2	100	0	98	0		
99-61-6	*m*-NO_2	98	0				

[a] Initial concentration: [ArCHO] ∼ 0.10 *M* and [$PhCO_3H$] ∼ 0.13 *M*. Reaction in nitrogen atmosphere. [b] Per cent yield based on a charged aldehyde. Material balance is above 95%. [c] [NaOH] ∼ 0.60 *M*. [d] Weakly acidic conditions caused by the presence of perbenzoic and produced benzoic acids. [e] [H_2SO_4] ∼ 0.30 *M*.

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(1) A. G. Davies, "Organic Peroxides," Butterworth and Co. Ltd., London, 1961, p 143.

(2) K. Nelson, quoted by S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958).

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