

130° (dec.). The product was dried at 80° for four hours for analysis.

*Anal.* Calcd. for  $C_8H_{12}NS \cdot C_{10}H_7O_2S \cdot H_2O$ : C, 56.9; H, 5.5; N, 3.7; S, 16.9. Found: C, 56.9, 56.7; H, 5.6, 5.8; N, 3.6, 3.7; S, 16.7.

Further recrystallization did not raise the melting point, but seemed to cause deterioration. The salt was soluble in water, methanol, ethanol, and acetic acid, but was insoluble in ether, chloroform, and benzene. Aqueous base causes the salt to decompose with the formation of an orange color and water insoluble material.

**Test for Free Primary Aromatic Amino Group.**—Both the *p*-aminophenyldimethylsulfonium picrate and  $\beta$ -naphthalenesulfonate yielded a color characteristic of substances containing a primary aromatic amino group when treated with 4-pyridylpyridinium chloride hydrochloride.<sup>17</sup> On the other hand, the second picrate derived

(17) Feigl, "Qualitative Analysis by Means of Spot Tests," Nordemann Publishing Company, New York, N. Y., 1937, p. 283.

from the initial picrate by heating in methanol gave a completely negative test, indicating that the primary amino group had been destroyed.

### Summary

A new compound, *p*-aminophenyldimethylsulfonium  $\beta$ -naphthalenesulfonate, has been synthesized. The picrate of the sulfonium cation has also been prepared.

Microbiological tests showed that the sulfonium sulfonate has a low order of antibacterial activity which is slightly reversed by *p*-aminobenzoic acid.

The activity of the sulfonium salts has been related to the problem of the mode of action of sulfonamides.

MADISON, WISCONSIN

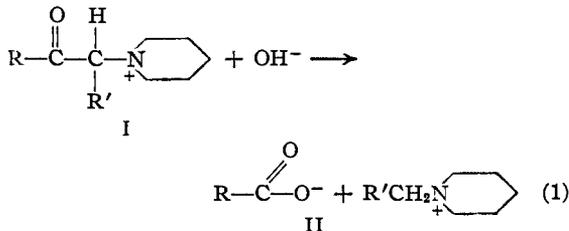
RECEIVED NOVEMBER 3, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

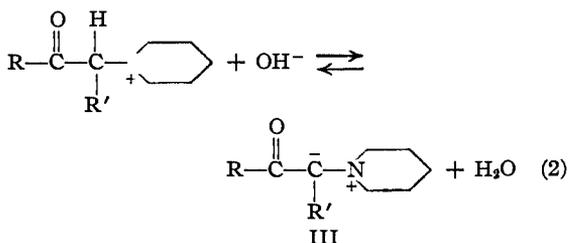
## Mechanism of the Alkaline Cleavage of $\beta$ -Ketoalkylpyridinium Salts<sup>1</sup>

BY RALPH G. PEARSON AND ROBERT L. DILLON

The alkaline hydrolysis of  $\beta$ -ketoalkylpyridinium salts to give the corresponding acid and a simpler alkylpyridinium salt<sup>2</sup> according to equation (1) was studied in some detail by Kröhnke.<sup>3</sup>



He showed by kinetic methods that in the presence of excess alkali the reaction was first order and that the stronger the acid, II, formed by the reaction, the greater the rate of hydrolysis. Furthermore, he showed<sup>4</sup> that the initial reaction of the cation, I, with alkali is a typical acid-base equilibrium in which the cation acts as an acid



He proposed the name "enol-betaine" for the isolable compound III, writing its structure with

(1) Based on the M.S. thesis of Robert L. Dillon.

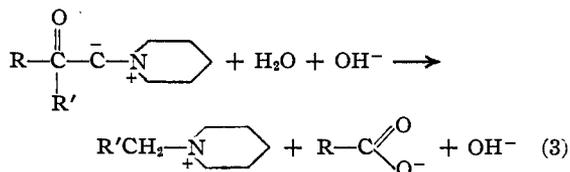
(2) (a) Bamberger, *Ber.*, **20**, 3344 (1887); (b) Babcock, Nakamura and Fuson, *This Journal*, **54**, 4407 (1932); (c) Babcock, and Fuson, *ibid.*, **55**, 2946 (1933).

(3) Kröhnke, *Ber.*, **70B**, 864 (1937).

(4) Kröhnke, *ibid.*, **66B**, 804 (1933); **68B**, 1177 (1935).

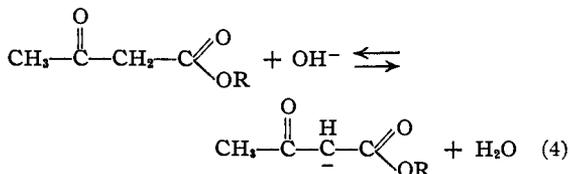
the double bond between the two carbon atoms. The enol-betaines in general are highly colored, soluble in organic solvents and not stable in air.

The mechanism that he assumed for the cleavage included the rapid establishment of equilibrium (2) and the subsequent rate-determining reaction of the enol-betaine with excess hydroxide ion and water. If reaction (2) goes well to the right then pseudo first order kinetics will be ob-

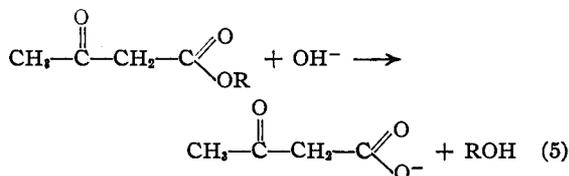


tained since hydroxide ion is not used up in (3). However, Kröhnke worked with only one set of concentrations for all of the compounds which he investigated and it can readily be shown that there are several other mechanisms which will turn out to be first order in excess alkali.

For example in the formally similar hydrolysis of acetoacetic ester by dilute alkali, Goldschmidt and Oslan<sup>5</sup> showed that the reaction was first order under a variety of conditions and the mechanism included an acid-base equilibrium and a rate-determining reaction between hydroxide ion and the unneutralized acetoacetic ester



(5) Goldschmidt and Oslan, *ibid.*, **32**, 3390 (1899); **33**, 1140 (1900).



Accordingly it seemed advisable to repeat part of Kröhnke's work and to vary the ratios of reactants in such a way as to establish a unique mechanism for the hydrolysis. At the same time the effect of temperature on the rates was investigated and the effect of substituents on the rate constants and the energies of activation determined. The salts selected for this work were phenacylpyridinium iodide and *p*-bromo- and *m*-nitrophenacylpyridinium iodides, all three of which Kröhnke had previously studied as the bromides. The solvent used was distilled water whereas Kröhnke used a mixture of alcohol and water to keep some of the enol-betaines in solution.

**Methods and Materials.**—The salts used were of high purity<sup>6</sup> and were recrystallized from water-alcohol just before use. The melting points were determined as follows: phenacylpyridinium iodide, 218–219°; *p*-bromophenacylpyridinium iodide, 233–235°; *m*-nitrophenacylpyridinium iodide, 202–203°. Stock solutions made up in distilled water were used within two or three days of preparation.

The extent of reaction was followed by titration of the excess alkali and unreacted enol-betaine. (The enol-betaine is strongly basic.) Selected volumes of solutions of the above salts and carbonate-free standard sodium hydroxide were mixed at the reaction temperature and the zero time recorded. Temperature was controlled to  $\pm 0.02^\circ$  over a range from 13 to 35°. From time to time samples were withdrawn, added to excess acid to stop the hydrolysis and back-titrated. Phenolphthalein indicator was used. A sample was titrated after the reaction was completed also and it was verified that one mole of alkali was used up as in (1). The completion of the reaction could be seen by the disappearance of the intense green-yellow color of the enol-betaine.

As a check on the above method of analysis the kinetics were followed in a few cases with a Beckman photoelectric

spectrophotometer. At a wave length of 4400 Å. the enol-betaines absorb strongly while the salts themselves and the products do not absorb at all. In this procedure samples were withdrawn from the thermostat into an absorption cell and the transmission measured within a few seconds after withdrawal. The amount of reaction occurring during measurement was negligible.

### Calculations and Results

It will be convenient to introduce a list of abbreviations at this point.

- PP<sup>+</sup> = the phenacylpyridinium (substituted or unsubstituted) cation  
 PP<sup>±</sup> = the corresponding enol-betaine  
*a* = concentration of limiting reactant  
*a* + *b* = concentration of reactant in excess  
*x* = concentration of products  
*k*' = experimental rate constant  
*k* = corrected rate constant  
*K*<sub>h</sub> = hydrolysis constant for reaction (2)  
*V*<sub>0</sub> = volume of base needed to back-titrate a sample at time *t* = 0  
*V* = volume of base needed to back-titrate a sample at time *t* = *t*  
*V*<sub>∞</sub> = volume of base needed to back-titrate a sample at time *t* = ∞

If the acid strength of PP<sup>+</sup> is great enough then (2) goes to completion and [PP<sup>±</sup>] = (*a* - *x*) and in solutions where alkali is in excess [OH<sup>-</sup>] = *b* and is constant. When PP<sup>+</sup> is in excess we must solve for [OH<sup>-</sup>] from the equilibrium *K*<sub>h</sub> = [PP<sup>+</sup>][OH<sup>-</sup>]/[PP<sup>±</sup>] so that [OH<sup>-</sup>] = *K*<sub>h</sub> (*a* - *x*)/*b*, putting in the values of [PP<sup>±</sup>] = (*a* - *x*) and [PP<sup>+</sup>] = *b*.

In terms of experimental quantities, the volumes of base needed to back-titrate given samples, *a* is proportional to (*V*<sub>∞</sub> - *V*<sub>0</sub>) and (*a* - *x*) is proportional to (*V*<sub>∞</sub> - *V*). Accordingly plots of log (*V*<sub>∞</sub> - *V*) against the time were made and straight lines were obtained as shown in Fig. 1 with slopes equal to *k*'/2.303. As Table I brings out the experimental rate constant *k*' varies with the excess hydroxyl ion concentration so that *k*'/*b* is essentially constant.

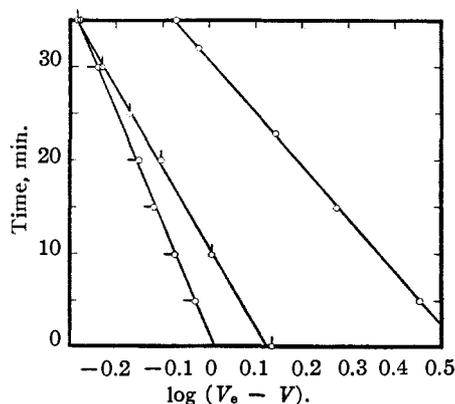


Fig. 1.—O, plot of 0.00714 *M* *p*-bromophenacyl- and 0.01013 *M* NaOH 25.2°; O, 0.00380 *M* *m*-nitrophenacyl- and 0.00482 *M* NaOH 20.0°; O, 0.00714 *M* phenacyl- and 0.01015 *M* NaOH 25.2°.

(6) Kindly supplied by Dr. L. C. King and prepared by the methods described by him, THIS JOURNAL, 66, 894 (1944), *et seq.*

TABLE I

PHENACYL-PYRIDINIUM IODIDE + EXCESS NaOH AT 31.5°

Excess [OH <sup>-</sup> ] mole/liter	Slope	(Slope) (2.3/[OH <sup>-</sup> ])	<i>k</i> liters/mole- min.
0.00384	0.01790	10.70	12.2
.00258	.01130	10.00	12.0
.00201	.00840	9.60	12.1
.00062*	.00201	7.46	13.8

\* Spectrophotometric.

In solutions where the salt was in excess 1/(*V*<sub>∞</sub> - *V*) was plotted against the time and the results showed a change to second order kinetics in these solutions. Figure 2 presents the type of curves

TABLE II

Salt	Temp., °C.	(Slope) ( <i>V</i> <sub>∞</sub> - <i>V</i> <sub>0</sub> )( <i>b</i> / <i>a</i> )	<i>K</i> <sub>h</sub>
Phenacyl-	31.5	5.40 × 10 <sup>-3</sup>	5.40 × 10 <sup>-4</sup>
<i>m</i> -Nitrophenacyl-	25.5	1.68 × 10 <sup>-3</sup>	2.83 × 10 <sup>-3</sup>
<i>p</i> -Bromophenacyl-	25.2	2.46 × 10 <sup>-3</sup>	1.87 × 10 <sup>-4</sup>

that were obtained. Furthermore, the slopes multiplied by  $(V_e - V_0)(b/a)$  were constant for a given salt at constant temperature. Table II summarizes the results for solutions where  $PP^+$  was in excess.

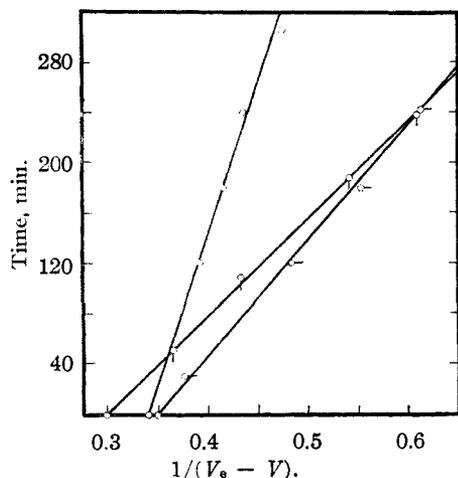


Fig. 2.—O, 0.00882 *M* *m*-nitrophenacyl- and 0.00373 *M* NaOH 25.5°; □, 0.00833 *M* *p*-bromophenacyl- and 0.00529 *M* NaOH 25.2°; ○, 0.00882 *M* phenacyl- and 0.00373 *M* NaOH 31.5°.

The use of the spectrophotometer has been referred to as a means of following the rate. Here the optical density,  $D$ , is proportional to  $(a - x)$ , the concentration of unreacted enol-betaine. So a plot of  $\log D$  versus the time should be linear with a slope of  $k'/2.3$ . Figure 3 shows the results obtained.

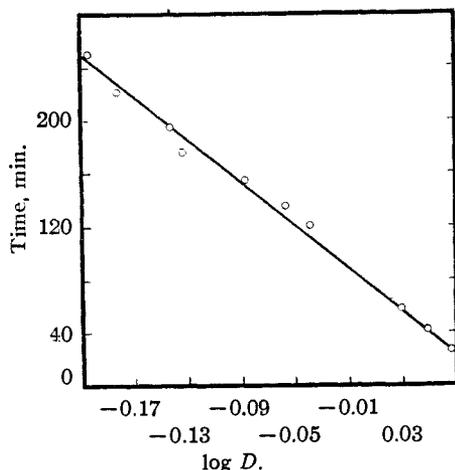


Fig. 3.—0.00080 *M* phenacylpyridinium iodide and 0.00142 *M* NaOH at 25.2°.

Runs were made at least in duplicate at three different temperatures for all three salts. The plot of  $\log k$  against the reciprocal of the absolute temperature gave good straight lines from which the Arrhenius activation energy was computed. Table III gives this information for the three salts.

TABLE III

Salt <sup>a</sup>	Temp., °C.	$k, b$ liters/mole-min.	$E_{Arr}$ kcal.
Phenacyl-	31.5	12.0	13.2
	25.2	7.22	
	20.0	5.00	
<i>m</i> -Nitrophenacyl-	34.0	155	19.7
	25.5	61.2	
	20.0	26.7	
<i>p</i> -Bromophenacyl	34.0	30.1	15.8
	25.2	14.7	
	20.0	8.28	

<sup>a</sup> The salt concentrations were 0.005 to 0.008 *M*; the excess alkali 0.001 to 0.003 *M*. Similar concentrations were used for the same salt at different temperatures. <sup>b</sup> A single value of the hydrolysis constant was used to correct  $k$  at all three temperatures. While the hydrolysis constant probably changes with temperature, it is used to make only a minor correction and the error introduced is not large.

### Discussion

There are two mechanisms consistent with the experimental results. The first is Kröhnke's as shown in (2) and (3) which gives as a rate expression

$$dx/dt = k_1[OH^-][PP^+] \quad (6)$$

$$= k_1 b(a - x) \text{ excess alkali}$$

$$= \frac{k_1 K_b}{b} (a - x)^2 \text{ excess salt} \quad (7)$$

The second is a reaction of the phenacylpyridinium ion with two hydroxyl ions<sup>7</sup> so that

$$dx/dt = k_2[OH^-]^2[PP^+] \quad (8)$$

$$= k_2 K_b b(a - x) \text{ excess alkali}$$

$$= \frac{k_2 (K_b)^2}{b} (a - x)^2 \text{ excess salt} \quad (9)$$

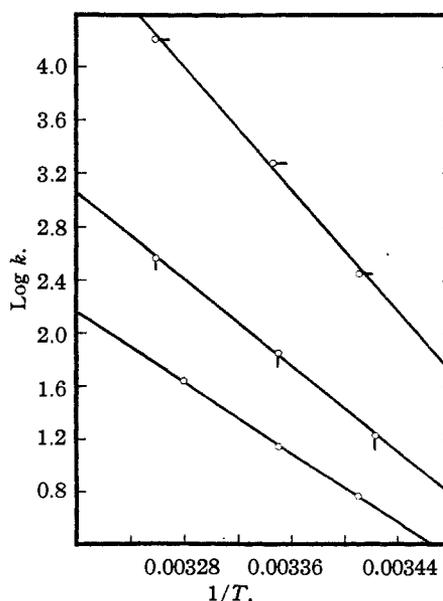


Fig. 4.—O, Phenacyl; □, *p*-bromophenacyl; ○, *m*-nitrophenacyl.

(7) The authors are indebted to one of the referees for pointing out this possibility of explaining the kinetic data.

Both of these predict correctly pseudo-first order kinetics in excess alkali with a slope varying with the excess alkali and a change to second order kinetics in solutions containing excess salt.

Since for both mechanisms the rate constants in excess alkali and in excess salt differ by a factor of  $K_h$  it is possible to evaluate the hydrolysis constant of reaction (2) by dividing  $(\text{Slope})(V_e - V_0)(b/a)$  in Table II by  $k'/b$  obtained from alkaline solutions at the same temperature. These values are listed in Table II also and it is possible to check the original assumption that  $[\text{PP}^*] = (a - x)$ . Actually it can be shown that  $[\text{PP}^*] = (a - x)[\text{OH}^-]/(K_h + [\text{OH}^-])$  which reduces to the assumed form when  $[\text{OH}^-] \gg K_h$ . The rate constants can be corrected for the small amount of hydrolysis by multiplying them by  $(K_h + [\text{OH}^-])/[\text{OH}^-]$ . This has been done for all of the rate constants finally recorded. The magnitude of the effect is seen in Table I where the column  $(\text{slope})(2.3)/[\text{OH}^-]$  gives the uncorrected rate constant and the last column gives the corrected value. This rate constant  $k$  is equal to either  $k_1$  or  $k_2K_h$  depending upon which mechanism is correct.

It is interesting to compute the values of  $K_a$ ,

the acid ionization constant of the quaternary ammonium cation, from the values of  $K_h$ , the hydrolysis constant. Dividing into the ionization product of water at the temperatures indicated we obtain  $K_a$  equal to  $3.08 \times 10^{-11}$ ,  $5.94 \times 10^{-11}$ , and  $39.6 \times 10^{-11}$  for the phenacylpyridinium, *p*-bromophenacylpyridinium and *m*-nitrophenacylpyridinium cations, respectively. These values are in the same relative order as the corresponding acidities of the substituted benzoic acids.

### Summary

1. The alkaline cleavage of enolizable  $\beta$ -keto-alkylpyridinium salts is shown to be pseudo-first order in excess alkali and second order in the presence of excess salt.

2. The mechanism involves either the reaction of a hydroxyl ion with the enol-betaine or the reaction of two hydroxyl ions with the quaternary cation.

3. The rate constants have been determined for the *m*-nitro-, *p*-bromo- and unsubstituted phenacylpyridinium iodides at several temperatures and the activation energies computed.

EVANSTON, ILLINOIS

RECEIVED DECEMBER 22, 1947

[CONTRIBUTION NO. 646 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

## The Reaction of Metallic Copper with Titanium(IV) Chloride

BY DONALD E. KOONTZ AND DOUGLAS G. NICHOLSON

During the course of an investigation of the nature of the reaction(s) taking place in the decolorization of commercial titanium(IV) chloride by metallic copper,<sup>1</sup> it was observed that clean dry metallic copper would react with chemically pure titanium(IV) chloride at room temperature. Accordingly, a detailed study was conducted on the interaction of these substances.

Loose rolls of copper foil made from sheets approximately  $4 \times 6 \times 0.0127$  cm. were heated to remove carbonaceous matter, cooled, rinsed in dilute hydrochloric acid, then water, and dried. They were then inserted in Pyrex test-tubes containing 5-8 ml. of titanium(IV) chloride, which were tightly closed with lead foil-covered corks.

The purplish-black scale which became evident after two or three hours could be shaken or jarred off, but on continued exposure the bright copper surface again became coated with the scale. After three to five weeks of exposure, the titanium(IV) chloride had entirely disappeared, and an appreciable residue of dry, purplish-black material and flakes of unreacted copper remained. Using dry powdered (150 mesh) copper, the process was complete in twenty to thirty hours, but the residue

tended to form a hard cake which, because of its expansion, sometimes cracked the tubes.

The rate of scale formation was not appreciably increased by heating the reaction tubes to approximately 100°, unless the metal surface was re-exposed. It appeared that the scale tended to protect the metal surface from further action.

Small samples of the dry scale, with adhering flakes of metallic copper, were subjected to the tests and analyses described below.

(a) Exposure to atmospheric oxygen showed a gradual color change, becoming progressively gray, tan, and greenish-blue. The material was hygroscopic.

(b) Treatment with distilled water produced an immediate white turbidity which gradually (five to ten minutes) became reddish-brown in color. The interior surface of the retaining vessel became coated with a very thin mirror-like copper-colored deposit. This coating was insoluble in dilute hydrochloric acid, but was readily soluble in nitric acid or ammonia water-hydrogen peroxide mixture, yielding solutions which gave positive tests for copper(II) ion but negative tests for titanium(IV). The initial water solution gave a positive test for titanium(III) ions.

(c) Treatment with 6*N* hydrochloric acid produced a clear purplish-pink solution containing

(1) From a thesis submitted to the Graduate School of the University of Pittsburgh by Donald E. Koontz in partial fulfillment of the requirements for the Master of Science degree, January, 1948.