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## Ketyl Radicals of Benzoylpyridines

by D. A. Nelson\*<sup>1</sup> and E. Hayon

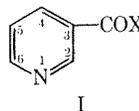
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*Publication costs assisted by the U. S. Army Natick Laboratories*

The absorption spectra, extinction coefficients, decay kinetics, and dissociation constants of the ketyl radicals and the radical anions of 2-, 3-, and 4-benzoylpyridines have been observed and determined. These radicals were produced from the reaction with hydrated electrons in aqueous 1.0 *M* *tert*-butyl alcohol, using the technique of pulse radiolysis. The ketyl radicals have high extinction coefficients and absorption bands in the visible and uv regions. The  $pK_a$ 's are  $12.3 \pm 0.2$ ,  $9.2 \pm 0.2$ , and  $12.0 \pm 0.2$  for 2-, 3-, and 4-benzoylpyridine, respectively. A second dissociation constant of the ketyl radicals for the corresponding benzoylpyridinium ions is observed with  $pK_a$ 's of  $3.1 \pm 0.1$ ,  $4.1 \pm 0.2$ , and  $4.2 \pm 0.2$ , respectively. Identical spectra were observed from the reaction of acetone ketyl radicals  $(CH_3)_2\dot{C}OH$  with these benzoylpyridines (BP), indicating a quantitative electron transfer to form the corresponding ketyl radicals. The rate constants of reactions of  $(CH_3)_2\dot{C}OH$  radicals with BP were found to be dependent on the  $pK_a$  of the BP. The ketyl radical and radical anions of 3-benzoyl-*N*-methylpyridinium ion were found to be distinctly different from those of 3-BP and a  $pK_a = 5.9 \pm 0.2$  was determined. The absorption spectra of the H atom adducts to benzoylpyridinium ions were also determined and are compared with those of the ketyl radicals. Analogies between the photochemistry and radiation chemistry of benzoylpyridines and benzophenone are discussed.

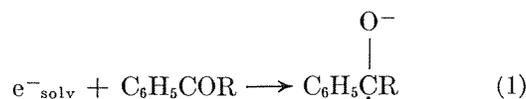
### Introduction

Relatively little work appears to have been carried out on the photochemistry of nicotinamide and its de-



rivatives. Studies on nicotinamide<sup>2,3</sup> ( $X = NH_2$ ) and nicotinic acid ( $X = OH$ ), on 3-acetylpyridine<sup>4a</sup> ( $X = CH_3$ ), and on dipyrindyl ketone<sup>4b</sup> have been performed. The mechanism leading to the observed photoproducts has not been established. Since a considerable amount of work has been done on the photochemistry of benzophenone, it seemed of interest to consider the photochemistry of benzoylpyridine ( $X = C_6H_5$ ). Work on both the flash photolysis<sup>5</sup> and steady-state photolysis<sup>6</sup> of benzoylpyridines is in progress. In the course of trying to identify the transient species observed<sup>5</sup> in the flash photolysis, it appeared necessary to produce by some independent method the ketyl radicals and radical anions of benzoylpyridines since these have not been

previously observed or reported. The reaction of solvated electrons with aromatic ketones has been found<sup>7</sup> to be a convenient way of generating ketyl radicals for the purpose of determining their absorption spectra, dissociation constants, and extinction coefficients.



(1) Permanent address: Chemistry Dept., University of Wyoming, Laramie, Wyoming.

(2) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Pergamon Press, New York, N. Y., 1964.

(3) S. Y. Wang, *Biochemistry*, **7**, 3740 (1968); F. Takenchi, *et al.*, *Bull. Chem. Soc. Jap.*, **43**, 3637 (1970).

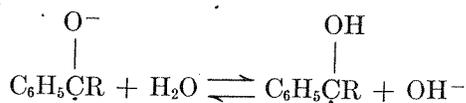
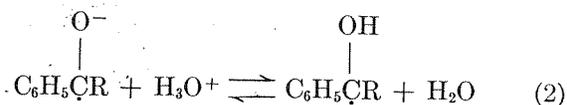
(4) (a) W. L. Benzze, C. A. Burckhardt, and W. L. Yost, *J. Org. Chem.*, **27**, 2865 (1962); (b) F. L. Minn, C. L. Trichilo, C. R. Hurt, and N. Filipescu, *J. Amer. Chem. Soc.*, **92**, 3600 (1970).

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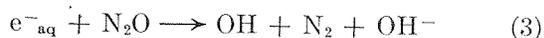
In this work, we report results on the absorption spectra, extinction coefficients, dissociation constants, and decay kinetics of the ketyl radicals and radical anions of 2-, 3-, and 4-benzoylpyridines, their corresponding pyridinium ions, and of *N*-methyl-3-benzoylpyridinium ion. The technique of pulse radiolysis was used to produce the solvated electrons. In addition, the rate constants of the reaction of acetone ketyl radicals,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , with these benzoylpyridines as a function of the  $\text{p}K_a$  of the benzoylpyridines and of the acetone ketyl radicals have been determined. For comparison with the absorption spectra of the ketyl radicals, the absorption spectra of the H-atom adducts to 2-, 3-, and 4-benzoylpyridines were obtained.

### Experimental Section

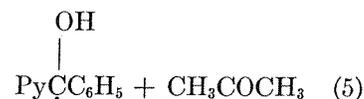
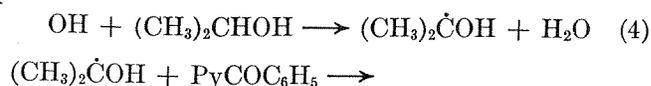
The pulse radiolysis set-up used has been described elsewhere.<sup>8</sup> Single pulses of 2.3-MeV electrons and  $\sim 30$  nsec duration were used. The 450-W xenon lamp monitoring light source was boosted for  $\sim 1$  msec thus increasing the total light output 25-fold. A double monochromator (two high-intensity Bausch & Lomb monochromators placed in series) was used to obtain better wavelength resolution and reduce the scattered light. Various solution and glass filters were positioned between the monitoring light and the solution containing the benzoylpyridines in order to minimize possible photochemical changes induced by the monitoring light. In addition, a synchronized shutter was used which opened for a total time duration of  $\leq 5$  msec.

The benzoylpyridines (Aldrich Chemical Co.) after purification by three recrystallizations from isopropyl alcohol-water and by two sublimations were kept in the dark.

Aqueous solutions containing 1–2 *M* *tert*-butyl alcohol or isopropyl alcohol were used to scavenge the OH radicals produced from the radiolysis of water. In argon-saturated aqueous *t*-BuOH solutions, the solvated electrons  $e^-_{\text{aq}}$  reacted with the benzoylpyridines according to reaction 1, and the *tert*-butyl alcohol radicals were found *not* to react with the benzoylpyridines (BP). This was established on saturation of the solution with nitrous oxide when the transient absorptions of the ketyl radicals disappeared, and no other transients could be observed above 300 nm. In  $\text{N}_2\text{O}$ -saturated solutions, all the  $e^-_{\text{aq}}$  ( $\geq 98\%$ ) produce OH radicals according to reaction 3



with  $k_3 = 6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  (ref 9). The acetone ketyl radical was found to react quantitatively with BP to produce exclusively the corresponding ketyl radicals.



The pH of the solutions was adjusted using perchloric acid, potassium hydroxide, and  $\sim 2$  mM phosphate and borate buffers.

Extinction coefficients were derived taking  $G(e^-_{\text{aq}}) = G(\text{OH}) = 2.8$  and  $G(\text{H}) = 0.6$ .

Products produced subsequent to the initial formation of the ketyl radicals were observed under some conditions. In neutral aqueous 2 *M* isopropyl alcohol solutions, a permanent product with  $\lambda_{\text{max}} \sim 355$  nm was observed with 3-BP. The 4-BP formed an intermediate ( $\tau_{1/2} \sim 30$  sec) with  $\lambda_{\text{max}} \sim 390$  nm. No intermediate was observed from 2-BP. Considerable care was taken to eliminate possible photochemical effects from the analyzing light. However, products with essentially the same characteristics were observed both in the flash and steady-state photolysis of 3- and 4-BP. Similar intermediates have been observed in the photochemistry of benzophenone<sup>10</sup> and di(4-pyridyl) ketone,<sup>4b</sup> and various structures have been suggested. Since it has been definitely determined that these intermediates are formed subsequent to the initial formation of ketyl radicals in the pulse radiolysis experiments, they are not of concern to the major conclusions of this work. The decay kinetics of the ketyl radicals, however, might be affected.

Hydrogen atoms were produced from the reaction  $e^-_{\text{aq}} + \text{H}^+ \rightarrow \text{H}$  in acid solutions at  $\text{pH} \leq 1$ , under conditions that all the  $e^-_{\text{aq}}$  formed H atoms. *tert*-Butyl alcohol was added to scavenge the OH radicals; its rate constant for reaction with H atoms is  $\sim 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ .

### Results

In order to determine the extinction coefficients of the ketyl radicals of the benzoylpyridines all the electrons must react quantitatively with the benzoylpyridines. It was necessary, therefore, to determine the rate constants of reaction 1. This was done by following the pseudo-first-order decay of  $e^-_{\text{aq}}$  at 700 nm. The rates of reaction for 2-, 3-, and 4-BP were found to

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(10) N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968), and references cited therein.



**Table II:** Absorption Maxima, Extinction Coefficients, and Dissociation Constants of the Ketyl Radicals and Radical Anions of Benzoylpyridines

System	Radical	pK	$\gamma_{\max}$ , nm	$\epsilon_{\max}$ , $M^{-1} \text{ cm}^{-1}$ <sup>a</sup>
2-Benzoylpyridine	2-Py $\dot{C}(O^-)C_6H_5$	12.3 $\pm$ 0.2	560, 328	$4.8 \times 10^3$ , $2.3 \times 10^4$
	$\Downarrow$			
	2-Py $\dot{C}(OH)C_6H_5$		495, 338	$3.0 \times 10^3$ , $2.0 \times 10^4$
3-Benzoylpyridine	2-PyH $^+\dot{C}(OH)C_6H_5$	3.1 $\pm$ 0.1	540, 350	$2.3 \times 10^3$ , $3.7 \times 10^4$
	3-Py $\dot{C}(O^-)C_6H_5$	9.2 $\pm$ 0.2	605, 336	$5.6 \times 10^3$ , $2.5 \times 10^4$
	$\Downarrow$			
	3-Py $\dot{C}(OH)C_6H_5$		530, 330	$3.4 \times 10^3$ , $3.2 \times 10^4$
3-PyH $^+\dot{C}(OH)C_6H_5$	4.1 $\pm$ 0.2	695, 503, 375, 331	$1.2 \times 10^3$ , $3.4 \times 10^3$ , $2.8 \times 10^3$ , $3.1 \times 10^4$	
4-Benzoylpyridine	4-Py $\dot{C}(O^-)C_6H_5$	12.0 $\pm$ 0.2	575, 325	$5.9 \times 10^3$ , $2.0 \times 10^4$
	$\Downarrow$			
	4-Py $\dot{C}(OH)C_6H_5$		500, 325	$5.6 \times 10^3$ , $1.8 \times 10^4$
	4-PyH $^+\dot{C}(OH)C_6H_5$	4.2 $\pm$ 0.2	510, 395, 322	$5.8 \times 10^3$ , $1.5 \times 10^4$ , $1.7 \times 10^4$
3-Benzoyl- <i>N</i> -methylpyridinium	3-PyCH $_3^+\dot{C}(O^-)C_6H_5$	5.9 $\pm$ 0.2	555, 395, 318	$5.2 \times 10^3$ , $2.0 \times 10^3$ , $1.9 \times 10^4$
	$\Downarrow$			
	3-PyCH $_3^+\dot{C}(OH)C_6H_5$		520, 385, 332	$3.2 \times 10^3$ , $3.2 \times 10^3$ , $2.0 \times 10^4$

<sup>a</sup> Values to  $\pm 10\%$ .**Table III:** Decay Kinetics of Ketyl Radicals of Benzoylpyridines in Aqueous Solution

System	pH	Radical	$\lambda$ , nm	$2k$ , $M^{-1} \text{ sec}^{-1}$ <sup>a</sup>
2-Benzoylpyridine	5.9	2-Py $\dot{C}(OH)C_6H_5$	500	$1.8 \times 10^8$ , $1.2 \times 10^8$
	13.3	2-Py $\dot{C}(O^-)C_6H_5$	550	$1.6 \times 10^8$ , $1.2 \times 10^8$
	1.1	2-PyH $^+\dot{C}(OH)C_6H_5$	550	$7.9 \times 10^8$
3-Benzoylpyridine			350	$7.1 \times 10^8$
	5.1	3-Py $\dot{C}(OH)C_6H_5$	530	$5.1 \times 10^8$ , $7.6 \times 10^8$
	13.0	3-Py $\dot{C}(O^-)C_6H_5$	605	$5.3 \times 10^7$
	0.9	3-PyH $^+\dot{C}(OH)C_6H_5$	505	$6.2 \times 10^8$ , $7.8 \times 10^8$
4-Benzoylpyridine	5.2	4-Py $\dot{C}(OH)C_6H_5$	500	$9.6 \times 10^7$
	13.2	4-Py $\dot{C}(O^-)C_6H_5$	575	$1.6 \times 10^8$ , $1.7 \times 10^8$
	0.8	4-PyH $^+\dot{C}(OH)C_6H_5$	505	$1.1 \times 10^9$
			390	$1.2 \times 10^9$
			340	$1.1 \times 10^9$
3-Benzoyl- <i>N</i> -methylpyridinium ion	4.7	3-PyCH $_3^+\dot{C}(OH)C_6H_5$	530	$1.1 \times 10^9$ , $1.2 \times 10^9$
			332	$1.2 \times 10^9$
	10.1	3-PyCH $_3^+\dot{C}(O^-)C_6H_5$	555	$1.2 \times 10^9$
			318	$1.3 \times 10^9$

<sup>a</sup> Rate values determined in aqueous 1.0 *M* *tert*-butyl alcohol and 2.0 *M* isopropyl alcohol, respectively. <sup>b</sup> Measured at pH 3.1.

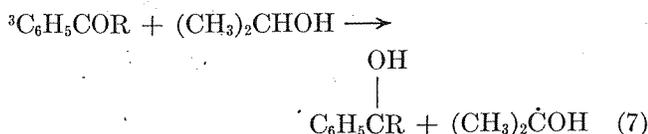
maxima of the ketyl radicals and radical anions of the three benzoylpyridines.

The decay kinetics of the ketyl radicals are presented in Table III.

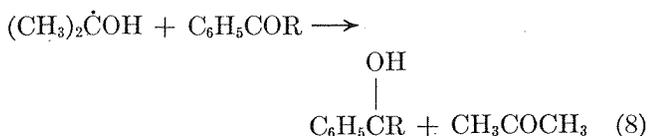
*Reaction of Acetone Ketyl Radicals with Benzoylpyridines.* In the photochemistry of aromatic ketones,

the triplet excited state has been shown to abstract an H atom efficiently from isopropyl alcohol (for review see ref 11).

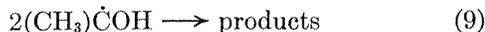
(11) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 366.



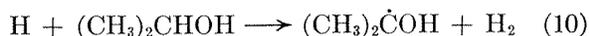
The subsequent reactions of the  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radical have been disputed. While reaction 8 has been sug-



gested to occur in most cases, leading to a doubling of the quantum yield of primary decomposition of the ketone, a range of quantum yields have been obtained for the same aromatic ketones by various workers. In only a few cases has the rate of reaction 8 been determined, and it is suggested that the discrepancy in the quantum yields could be due to incomplete scavenging of the  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals since a range of ketone concentrations was used by the different investigators. For complete scavenging  $k_8[\text{C}_6\text{H}_5\dot{\text{C}}\text{OR}] \geq 50k_9[(\text{CH}_3)_2\dot{\text{C}}\text{OH}]$

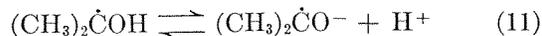


where  $k_9 = 1.4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  (ref 8a). In order to interpret certain aspects of the photochemistry of the benzoylpyridines in isopropyl alcohol, it was necessary to know the rate of reaction 5. These were determined by pulse radiolysis in 2.0 M aqueous isopropyl alcohol solutions saturated with nitrous oxide. Under these conditions all the  $e_{\text{aq}}^-$  are converted to OH radicals (reaction 3) and all the OH radicals and H atoms are converted to  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals *via* reactions 4 and 10. By monitoring the ketyl radicals formed *via* reac-

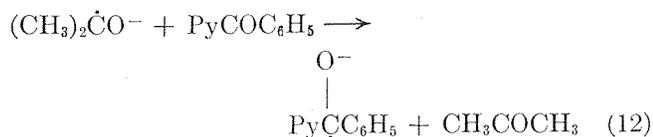


tion 5 at the wavelengths of maximum absorption,  $k_5$  was determined from the pseudo-first-order rate of formation of the ketyl radical. These rate constant values are given in Table IV. In neutral solutions, the values for  $k_5$  are  $\sim 1\text{--}2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for 2-, 3-, and 4-benzoylpyridines.

In alkaline solutions, beyond the  $\text{p}K_a = 12.2^{12}$  of



the acetone ketyl radical, the rate of electron transfer from the  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  radical to BP was found to be higher by about a factor of 10–20 (see Table IV),



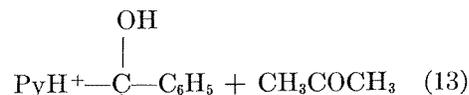
compared to  $k_5$ . This increase in  $k_{12}$  compared to  $k_5$  is to be expected, since an electron transfer process from a radical anion should be more favorable.

**Table IV:** Reaction Rate Constants of the Acetone Ketyl Radicals,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  and  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  with Benzoylpyridines in 2.0 M Aqueous Isopropyl Alcohol Solutions

System	pH	$\lambda$ (monitored), nm	$k$ , $\text{M}^{-1} \text{ sec}^{-1}$ <sup>a</sup>
2-Benzoylpyridine	5.9	500	$1.5 \pm 0.2 \times 10^8$
	13.2	550	$2.3 \pm 0.2 \times 10^9$
	1.0	500	$3.0 \pm 0.3 \times 10^9$
	1.0	330	$3.0 \pm 0.3 \times 10^9$
3-Benzoylpyridine	5.1	530	$1.0 \pm 0.2 \times 10^8$
	13.0	605	$2.0 \pm 0.2 \times 10^9$
	13.0	341	$2.0 \pm 0.2 \times 10^9$
	0.9	500	$1.7 \pm 0.2 \times 10^9$
	0.5	330	$2.3 \pm 0.3 \times 10^9$
4-Benzoylpyridine	7.7	500	$2.4 \pm 0.4 \times 10^8$
	13.2	575	$2.5 \pm 0.2 \times 10^9$
	0.7	510	$2.5 \pm 0.2 \times 10^9$
3-Benzoyl- <i>N</i> -methylpyridinium ion	5.0	530	$2.3 \pm 0.3 \times 10^9$
	1.0	530	$2.3 \pm 0.3 \times 10^9$
Benzophenone	13.1	605	$1.6 \pm 0.2 \times 10^9$

<sup>a</sup> In alkaline solution, radical is dissociated,  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ .

The dissociation constants of benzoylpyridines have been measured, and  $\text{p}K_a$  of 3.18 and 3.35 for 3-BP and 4-BP, respectively, have been reported.<sup>13</sup> The  $\text{p}K_a$  of 2-BP has apparently not been determined. The



rate constant for reaction 13 in acidic solution was determined and values of  $\sim 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  were obtained, for 2-, 3-, and 4-benzoylpyridines, almost identical with the values of  $k_{12}$ . This high value for  $k_{13}$  (see Table IV) would appear to support an electron transfer mechanism to the benzoylpyridinium ion, followed by rapid protonation at pH values lower than the  $\text{p}K_a$  of the BP ketyl radicals.

In order to ascertain that the observed values of  $k_{13}$  were indeed associated with the protonated forms of benzoylpyridines, these rate constants were determined as a function of pH, and are presented in Figure 4. It can be seen that these rates decrease with increase in pH, and from the curves in Figure 4 one can derive  $\text{p}K_a$  values of  $2.6 \pm 0.2$ ,  $3.3 \pm 0.2$ , and  $3.8 \pm 0.2$  for 2-, 3-, and 4-benzoylpyridines, respectively. The  $\text{p}K_a$  for 3-BP is in good agreement with the literature value<sup>13</sup> of 3.18. The  $\text{p}K_a$  of 4-BP was redetermined

(12) K. D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **70**, 756 (1966).

(13) A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964).

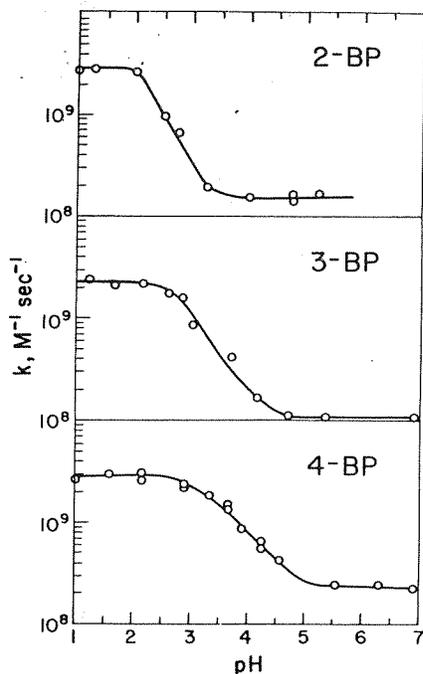
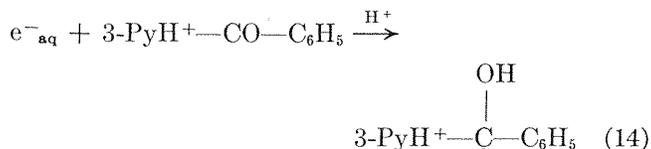


Figure 4. pH dependence of the rate constant of reaction of the acetone ketyl radical,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , with benzoylpyridines in 1–2 *M* aqueous isopropyl alcohol solutions.

(spectrophotometrically by following the change in absorbance with pH at 250 nm) and a value of  $3.6 \pm 0.1$  was obtained, compared to 3.35.<sup>13</sup> The  $\text{p}K_a$  of 2-BP was determined for the first time (by following  $\Delta\text{OD}$  at both 250 and 320 nm) and a value of  $2.15 \pm 0.1$  was derived. In view of the larger experimental error involved in determining the value of  $k_{13}$ , the results shown in Figure 4 are considered to be in reasonably good agreement with the  $\text{p}K_a$ 's of the parent molecules.

Concomitant with the change in the rate constant for reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  with  $\text{PyH}^+\text{COC}_6\text{H}_5$ , different optical absorption bands of the corresponding ketyl radicals were observed, see Figures 5 and 6 and Table II. For 3- $\text{PyH}^+\text{COC}_6\text{H}_5$ , the absorption spectrum of the ketyl radical has maxima at 695, 503, 375, and 331 nm (Figure 5). In order to demonstrate that the intermediate produced *via* reaction 13 is the ketyl radical, 3- $\text{PyH}^+\text{COC}_6\text{H}_5$  was allowed to react with  $e^-_{\text{aq}}$  in presence of 2.0 *M* *t*-BuOH



An identical spectrum and extinction coefficient were obtained (see Figure 5), indicating a quantitative formation of the ketyl radical *via* reaction 13. Furthermore, the flash photolysis of 3-BP in 2.0 *M* aqueous isopropyl alcohol at pH 1.6 produced a similar spectrum, which has been normalized with the pulse radiolysis results, see Figure 5.

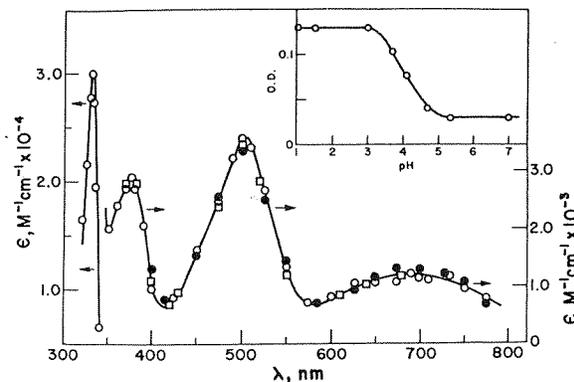


Figure 5. Optical absorption spectrum of the ketyl radical of 3-benzoylpyridinium ion produced from (a) the reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals at pH 0.88 in aqueous 2 *M* isopropyl alcohol (○), and (b) the reaction of  $e^-_{\text{aq}}$  at pH 3.1 in  $1 \times 10^{-2}$  *M* 3-BP, 2.2 *M* *tert*-butyl alcohol, and  $\text{N}_2\text{O}$  (1 atm) (□). The spectrum of the ketyl radical of 3-benzoylpyridinium ion ( $10^{-4}$  *M*) produced by flash photolysis at pH 1.6 in 2.0 *M* aqueous isopropyl alcohol is also shown (●).

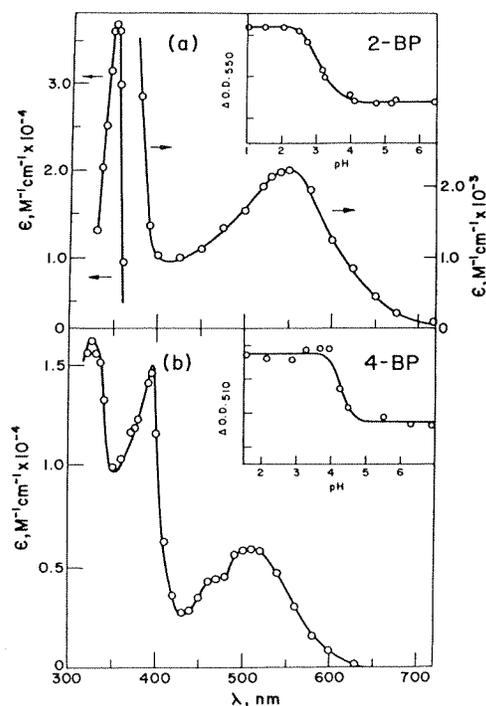


Figure 6. Optical absorption spectrum of the ketyl radical of benzoylpyridinium ion produced in aqueous 2.0 *M* isopropyl alcohol from the reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals with (a) 2-benzoylpyridine at pH 1.2 and (b) 4-benzoylpyridine at pH 0.8. Inserts show the absorbances of ketyl radicals of benzoylpyridinium ions *vs.* pH.

The dissociation constants of the ketyl radicals of benzoylpyridinium ions were found to be different from the  $\text{p}K_a$ 's of the corresponding parent compounds. From the inserts in Figures 5 and 6, the  $\text{p}K_a$ 's of the ketyl radicals were determined to be  $3.1 \pm 0.1$ ,  $4.1 \pm 0.2$ , and  $4.2 \pm 0.2$  for the 2-, 3-, and 4-benzoylpyri-

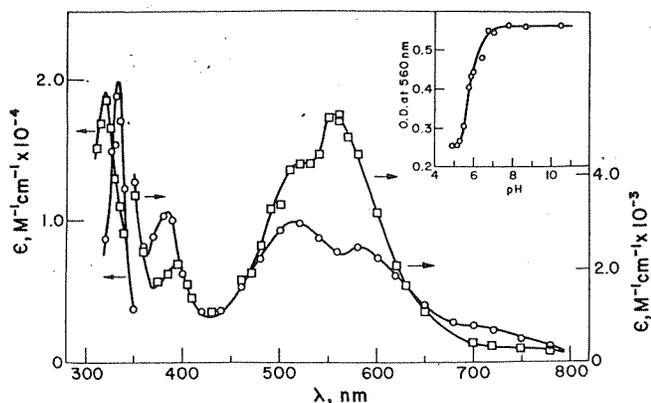


Figure 7. Optical absorption spectrum of the ketyl radical (O, pH 5.0) and radical anion (□, pH 10.1) of 3-benzoyl-*N*-methylpyridinium chloride in 1.0 *M* aqueous *tert*-butyl alcohol. Insert shows the absorbance of ketyl radical at 560 nm vs. pH.

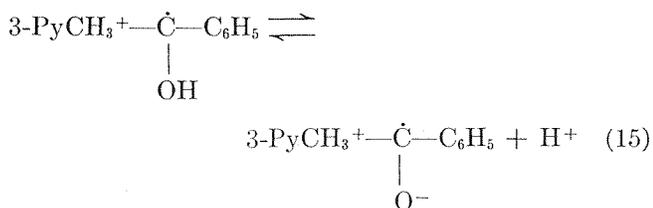
dinium ions, respectively. It is to be noted that in all these cases, the  $pK_a$  of the ketyl radical is higher than that of the parent compounds.

The decay rates of the ketyl radicals of benzoylpyridinium ions are given in Table III.

#### Ketyl Radicals of Benzoyl-*N*-methylpyridinium Ions.

The optical absorption spectrum of the ketyl radical of 3-benzoyl-*N*-methylpyridinium chloride ( $3\text{-PyCH}_3^+\text{CO-C}_6\text{H}_5$ ) in 1.0 *M* aqueous *t*-BuOH can be seen to be distinctly different from that of the corresponding radical of 3-benzoylpyridine, compare Figure 7 with Figures 1 and 5. The spectrum is more structured, and an additional band is observed at  $\sim 385$  nm. In the wavelength region 350–420 nm, and subsequent to the initial formation of the ketyl radical at pH 4.7, the "build-in" of a new absorbing species can be seen with a rate of formation of  $\sim 4.0 \times 10^4 \text{ sec}^{-1}$ . This new species has an absorption maximum in this region and appears to be a permanent product (no decay could be seen in oxygen-free solutions after 5 min). A similar effect was observed for the corresponding band at pH 10.1.

In alkaline solutions, the absorption spectrum of the ketyl radical anions undergoes similar changes to those observed for the benzoylpyridines, and from the change in absorbance with pH at 560 nm, a  $pK_a = 5.9 \pm 0.2$  was determined for the equilibrium



This acid dissociation constant compares with the  $pK_a = 9.2 \pm 0.2$  for the ketyl radical of 3-benzoylpyridine. The strong inductive effect of the *N*-methylpyridinium ion can be seen to influence the acid-base properties of

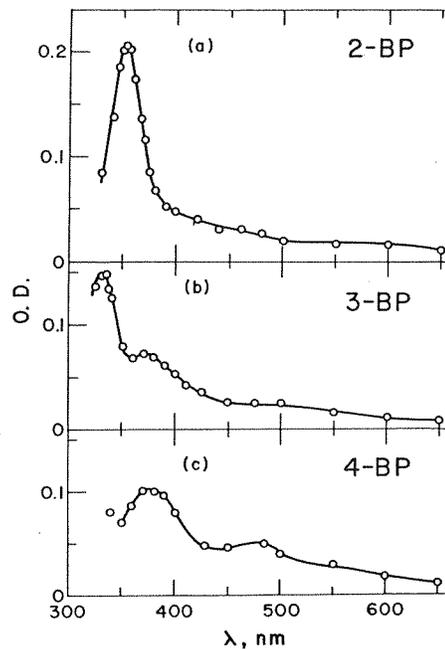
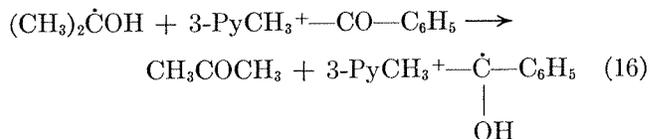


Figure 8. Absorption spectra of the H atom adducts of 2-, 3-, and 4-benzoylpyridinium ions obtained at pH 0.8–1.0 in 1.0 *M* aqueous *tert*-butyl alcohol.

the ketyl radical of the 3-substituted benzoyl derivative.

Similar spectra were produced from the reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals with  $3\text{-PyCH}_3^+\text{CO-C}_6\text{H}_5$  at pH 4.7 and 10.1. At pH 1.0, the spectrum was found to be unchanged from that observed at pH 4.7. It is interesting to note (see Table IV) that  $k_{16} = 2.3 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  at pH 5.0 and 1.0, and that it is the same



as the rate constant of reaction 13. This indicates that it is the pyridinium ion which enhances the rate of reaction with the acetone ketyl radical, indicating that the reaction presumably takes place *via* an electron transfer from  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , followed by rapid protonation.

The extinction coefficients and decay kinetics of these radicals are given in Tables II and III.

*Hydrogen Atom Adducts to Benzoylpyridines.* The reactions of hydrogen atoms with aromatic carbonyl compounds are quite different from the reactions of electrons with the same ketones. The reaction rate constants, the site(s) of addition, and the transient optical absorption spectra of the resulting intermediates all attest to this difference. Recent work<sup>7</sup> has demonstrated quite clearly that the solvated electrons add to aromatic ketones, quinones, and  $\beta$  diketones to produce exclusively the ketyl radicals and radical

anions of the corresponding carbonyl compounds. Interaction of the odd electron with the aromatic and pyridine rings gives rise to various resonating structures. The H atoms, however, are much less selective and add to the aromatic ring at presumably more than one position on the ring.<sup>7</sup>

Similar effects and observations are found for the reactions of H atoms with benzoylpyridinium ions. The rate constants of the reaction (Table I) are  $\sim 3 \times 10^9 M^{-1} \text{sec}^{-1}$ , similar to the rate constants found<sup>7</sup> for other aromatic ketones. Figure 8 shows the absorption spectra of the H atom adducts to 2-, 3-, and 4-benzoylpyridinium ions. These were obtained at pH 0.8–1.0 in presence of 1.0 *M* *tert*-butyl alcohol to scavenge all the OH radicals. The decay rates of these adducts and their extinction coefficients are given in Table V. The difference in the spectra of the H atom adducts compared to the spectra of the ketyl radicals supports the conclusion reached above that the reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals with benzoylpyridines produces radicals which are identical with those formed directly from the reaction of  $e^-_{\text{aq}}$  with BP.

**Table V:** Absorption Maxima, Extinction Coefficients, and Decay Kinetics of the Hydrogen Atom Adducts of Benzoylpyridines Determined at pH  $\sim 1.0$  in 1–1.5 *M* Aqueous *tert*-Butyl Alcohol

System	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$ , $M^{-1} \text{cm}^{-1}$	$2k$ , $M^{-1} \text{sec}^{-1}$
2-Benzoylpyridine	350	$7.0 \times 10^3$	$3.0 \pm 0.4 \times 10^8$
3-Benzoylpyridine	395	$4.8 \times 10^3$	$3.2 \pm 0.5 \times 10^8$
	332	$7.9 \times 10^3$	
4-Benzoylpyridine	375	$3.6 \times 10^3$	$2.9 \pm 0.4 \times 10^8$
	335	$2.9 \times 10^3$	

## Discussion

The results and mechanism presented above indicate that in some respects the chemistry of benzoylpyridines is similar to that of benzophenone, *e.g.*, even though the pyridine ring has a greater electron affinity than the benzene ring, all the solvated electrons appear to lead to the formation of the corresponding ketyl radical anions. The odd electron on the carbonyl carbon atom subsequently interacts with both benzene and pyridine rings. Furthermore, the  $pK_a$  of the ketyl radical of 3-BP,  $pK_a = 9.2 \pm 0.2$ , is the same as that of benzophenone,  $9.25 \pm 0.1$ .<sup>7</sup> However, the  $pK_a$  of the ketyl radicals of 2-BP and 4-BP are distinctly higher,  $12.3 \pm 0.2$  and  $12.0 \pm 0.2$ , respectively. These results indicate that the electronegative nitrogen atom on the ring

plays an important role in determining the acid–base properties of these ketyl radicals. It would appear that its effect is strongest for substituents at positions 2 and 4.

The pyridine ring also influences the rate constant for reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals with benzoylpyridines. These rates are  $\sim 1\text{--}2 \times 10^8 M^{-1} \text{sec}^{-1}$  for 2-, 3-, 4-benzoylpyridines and  $2.3 \times 10^9 M^{-1} \text{sec}^{-1}$  for 3-benzoyl-*N*-methylpyridinium ion, while the rate of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals with benzophenone at pH 6.0 is  $< 10^7 M^{-1} \text{sec}^{-1}$ . At pH 1.0, the  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals react much faster with the corresponding benzoylpyridinium ions (see Table IV), but the rate constant with benzophenone is still  $< 10^7 M^{-1} \text{sec}^{-1}$ . In alkaline solutions, the rate of reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  radicals with benzophenone becomes similar to those for the benzoylpyridines (see Table IV),  $k \sim 2.0 \times 10^9 M^{-1} \text{sec}^{-1}$ .

A very interesting observation in this work is that the  $pK_a$  of the ketyl radical of 3-benzoyl-*N*-methylpyridinium ion is about three units lower than that of 3-benzoylpyridine,  $5.9 \pm 0.2$  and  $9.2 \pm 0.2$ , respectively. This can be attributed to an inductive effect of the pyridinium ring. Methylation of the nitrogen considerably affects the electron distributions of the ketyl radical, making it a stronger acid. Furthermore, protonation, like alkylation, produces a hyperchromic effect, *i.e.*, an increase in absorbance particularly at longer wavelengths. This result is potentially of considerable interest in the understanding of electron transfer processes in NAD–NADH reactions. Work on nicotinamide,  $\text{NAD}^+$ , and NADH is in progress.

The decay kinetics of the ketyl radicals presented in Table III all follow second-order processes, and show certain general similarities. The  $\text{PyH}^+\dot{\text{C}}\text{OHC}_6\text{H}_5$  radicals of 2-, 3-, and 4-BP decay with  $2k \sim 7\text{--}12 \times 10^8 M^{-1} \text{sec}^{-1}$ . The decay rates of the  $\text{Py}\dot{\text{C}}(\text{OH})\text{C}_6\text{H}_5$  radical of 2- and 4-BP are  $\sim 10^8 M^{-1} \text{sec}^{-1}$ , while the corresponding 3-BP radical decays faster with  $2k \sim 7 \times 10^8 M^{-1} \text{sec}^{-1}$ . The decay kinetics of the ketyl radical anions ( $\text{P}\cdot^-$ ) were all determined at pH  $\sim 13$ . For 3-BP, the decay rate was found to be lower by a factor of about 10,  $2k \sim 5 \times 10^7 M^{-1} \text{sec}^{-1}$ , presumably due to the slower termination of two negatively charged radicals,  $\text{P}\cdot^-$ . In the cases of 2-BP and 4-BP, the observed decay rates of the corresponding  $\text{P}\cdot^-$  are not significantly different from those of  $\text{PH}\cdot$  radicals. Since the  $pK_a$  of the ketyl radicals is 12.3 and 12.0, respectively, at the pH used to determine these rates some 10% or more of the radicals are present as  $\text{PH}\cdot$ , and the observed rates are therefore probably due to  $\text{P}\cdot^- + \text{PH}\cdot$  reactions, as well as to  $\text{P}\cdot^- + \text{P}\cdot^-$  reactions.