Kinetics and Mechanism of the Oxidation of Pyridine by Caro's Acid Catalyzed by Ketones

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The kinetics of the oxidation of pyridine by peroxomonosulfate ion catalyzed by acetone and cyclohexanone has been investigated. The oxidation product was identified as pyridine 1-oxide, and the yield was found to be pH dependent. The rate law for the pyridine oxidation was shown to be $-\mathrm{d[Py]}/\mathrm{d}t = K_1K_2k_1k_2[\mathrm{Py}][\mathrm{HOOSO_3^-}][\mathrm{OH^-}][\mathrm{ketone}]/(k_a[\mathrm{HOOSO_3^-}] + k_a'K_3[\mathrm{OH^-}][\mathrm{HOOSO_3^-}] + k_b[\mathrm{Py}])$. A mechanism involving a dioxirane intermediate which is consistent with the rate law has been postulated. Experiments leading to simplified forms of the rate law have been carried out. The ratios of rate constants k_b/k_a and k_a'/k_a were determined for both acetone and cyclohexanone. A side reaction, the Baeyer-Villiger process, is significant with cyclohexanone near pH 7.

The catalysis by ketones of reactions by peroxymonosulfate was reported by Montgomery.[1] He demonstrated that ketones catalyze the oxidation of chloride ion

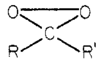
$$\mathrm{HSO_5^-} + \mathrm{Cl^-} \xrightarrow{\text{ketone}} \mathrm{OCl^-} + \mathrm{H^+} + \mathrm{SO_4^{2-}}$$

the self-decomposition of caroate

$$2\mathrm{HSO_5^-} \xrightarrow{\text{ketone}} \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{SO_4^{2-}}$$

and the bleaching of the dye Polar Brilliant Blue GAW.

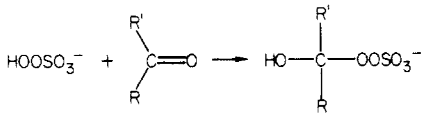
On the basis of Montgomery's data, the intermediate dioxirane (I) was suggested to be a likely intermediate.



I

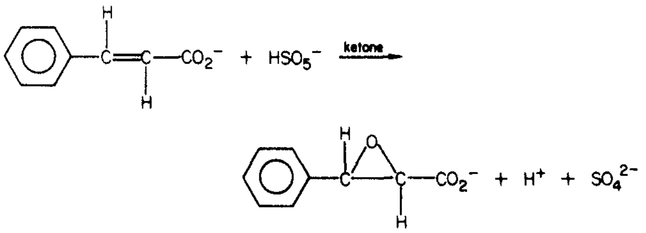
Some of the bases on which the ring structure was deduced and then substantiated are given elsewhere.[2,3] Many ketones where R and R′ vary considerably were found to act as catalysts.[1b]

For simplicity, we use the following terminology. The peroxymonosulfate (both $\mathrm{HSO_5^-}$ and $\mathrm{SO_5^{2-}}$) is termed caroate, the peroxide–ketone complex that is formed very rapidly and probably is in equilibrium with reactants is designated as the adduct, the dioxirane ring intermediate will be called dioxirane, and the oxidizing mixture (caroate, ketone, buffer, and solvent) will be termed the peroxone system. Pyridine and pyridine 1-oxide will be symbolized Py and PyO, respectively.



The oxidation of a variety of olefins by the peroxone system has been studied, primarily from the product yield viewpoint.[2,3] Dioxirane was considered to be the active oxidant in these reactions, and the data are consistent with this interpretation.

Also a preliminary kinetic study was conducted on the oxidation of cinnamate ion by the peroxone system;[4] the reaction is



A mechanism involving the adduct, and its conjugate base (both rapidly formed), and dioxirane (formed in a slow step) was postulated. On the assumption of a steady state for dioxirane, the rate law is

$$\frac{-\mathrm{d[cinnamate]}}{\mathrm{d}t} = \frac{k'[\mathrm{HSO_5^-}][\mathrm{acetone}][\mathrm{cinnamate}][\mathrm{OH^-}]}{k_x[\mathrm{HSO_5^-}] + k_y[\mathrm{cinnamate}]}$$

where k' represents a collection of rate and equilibrium constants, for disappearance of cinnamate (rather than for disappearance of caroate). When the inequality $k_x[\mathrm{HSO_5^-}] \gg k_y[\mathrm{cinnamate}]$ holds, the rate law derived from the above mechanism reduces to $-\mathrm{d[cinnamate]}/\mathrm{d}t = k'_{\mathrm{obsd}}\cdot[\mathrm{acetone}][\mathrm{cinnamate}][\mathrm{OH^-}]$. This approximated the experimentally obtained rate law under some conditions.[4]

The present study was undertaken to check this rate law (particularly the inequality above), to expand the number of reductants oxidized by the system, and to find out if dioxirane is attacked by $\mathrm{HSO_5^-}$ or $\mathrm{SO_5^{2-}}$ in the competing peroxide decomposition. Pyridine, a water-soluble nitrogen nucleophile that is not readily oxidized by caroate alone, was chosen for study.

Results and Discussion

Stoichiometry. Pyridine 1-oxide was isolated and identified (eq 1), and amounts of PyO have been measured.

$$\mathrm{Py} + \mathrm{HSO_5^-} \xrightarrow[\text{buffer}]{\text{ketone}} \mathrm{PyO} \qquad (1)$$

The percent yields of this product as a function of pH are given in Table I and also are shown in Figure 1, along with the percent ketone remaining (when no reductant is present). In this experiment, cyclohexanone was the

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[1] (a) R. E. Montgomery, *J. Am. Chem. Soc.*, **96**, 7820 (1974); (b) R. E. Montgomery, U.S. Patent 3 822 114 (1974).

[2] R. H. Pater, Ph.D. Thesis, 1977, Brown University.

[3] (a) J. O. Edwards, R. H. Pater, R. Curci, and F. DiFuria, *Photochem. Photobiol.*, **30**, 63 (1979); (b) R. Curci, M. Fiorentino, L. Troisi, J. O. Edwards, and R. H. Pater, *J. Org. Chem.*, **45**, 4758 (1980).

[4] J. O. Edwards and K. M. Ibne-Rasa, unpublished data.

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Table I. Percent Yield of Pyridine 1-Oxide[a] and Percent Remaining of Cyclohexanone[b]

pH	% yield of PyO	% remaining of c-HxO
7.0	72	31
7.5	85	58
8.0	94	79
8.5	96	99
9.0	95	84
9.5	86	85

[a] For reaction 13 under the following conditions: $[Py]_0$ = [Caro's acid] = 2.93×10^{-4} M, 0.0198 M cyclohexanone, 0.15 M potassium phosphate buffer for pH 7.0–8.5, and sodium carbonate buffer at pH 9.0 and 9.5. [b] Under the following conditions: $[\text{cyclohexanone}]_0$ = 0.0198 M, $[\text{Caro's acid}]_0$ = 0.0150 M (no pyridine), 0.12 M potassium phosphate buffer for pH 7.0 to 8.5, and sodium carbonate buffer at pH 9.0–9.5.

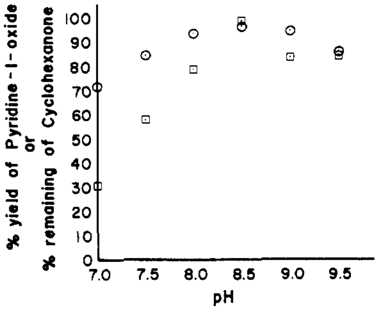

Figure 1. Percent yield of pyridine 1-oxide (⊙) with $[py]_0$ = $[HSO_5^-]_0$ = 2.93×10^{-4} M, 0.15 M buffer potassium phosphate for pH 7.0–8.5 and sodium carbonate for pH 9.0–9.5, and cyclohexanone catalysis; also, percent remaining cyclohexanone (▢) with $[\text{cyclohexanone}]_0$ = 0.0198 M and $[HSO_5^-]$ = 0.0150 M and the buffers as above, but no pyridine.

catalyst employed. (It is worthy of reiteration here that the oxidation of pyridine by caroate is negligible in the absence of ketone.) The yield of PyO reaches a maximum at approximately pH 8.5 and then slightly decreases on going to higher pH, presumably due to the increasing loss of caroate by self-decomposition[5] as one increases the pH toward the $pK_a(2)$ of Caro's acid; this pK_a value is about 9.4 in aqueous solution. The maximum rate of loss of caroate in the catalyzed decomposition occurs at a pH of about 10.[1]

It is seen in Figure 1 that the reaction is less efficient at pH 7 than at pH 8.5 or above. The reason for this loss of efficiency can be traced to competing Baeyer–Villiger reaction. Evidence for this is found in the facts that (1) there is a significant decrease in cyclohexanone concentration[4] at pH 7, (2) there is a lower yield of PyO, (3) there is a change in the apparent rate constant near pH 7 (first observed by Montgomery;[1] see his Figure 2), and (4) the lactone product has been isolated and identified.[2]

The Baeyer–Villiger side reaction can be quite serious, particularly at low pH (i.e., near pH 7 in our work). In one experiment at pH 7 with $[HSO_5^-]_0$ = 0.015 M and $[\text{cyclohexanone}]_0$ = 0.0198 M, 91% of the oxidizing power was lost by this lactone-forming reaction. It is clear that near pH 7 acetone is preferred as a catalyst for caroate reactions because the fraction of oxidizing power going to Bayer–Villiger is much less for the acyclic ketone (see below). On the other hand, the cyclic ketone is a better catalyst ratewise than acetone by about a factor of 10.[1,3,4]

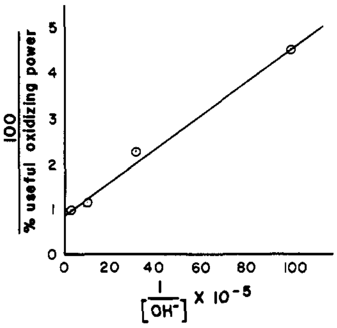

Figure 2. Plot of 100% useful oxidizing power against $(1/[OH^-]) \times 10^5$ under conditions of $[\text{cyclohexanone}]_0$ = 0.0198 M, $[HSO_5^-]_0$ = 0.0150 M, no pyridine, and potassium phosphate buffer (0.12 M) for pH 7.0–8.5. The y intercept is 0.85 and the slope is 0.037.

Because of the complexity of the several processes involved, a tentative rate law comparison of the two competing reactions is given here. (I) The individual rate laws are as follows: (A) for Baeyer–Villiger

$$-d[\text{peroxide}]/dt = k_{BV}[HSO_5^-][\text{ketone}] \qquad (2)$$

(B) for ketone-catalyzed decomposition

$$-d[\text{peroxide}]/dt = k_{KCD}[HSO_5^-][\text{ketone}][OH^-] \qquad (3)$$

(II) The combined rate laws are as follows: (A) for peroxide loss

$$-d[\text{peroxide}]/dt = k_{BV}[HSO_5^-][\text{ketone}] + k_{KCD}[HSO_5^-][\text{ketone}][OH^-] \qquad (4)$$

(B) for ketone loss

$$-d[\text{ketone}]/dt = k_{BV}[HSO_5^-][\text{ketone}] \qquad (5)$$

Hence it follows that

$$\frac{\%\text{UOP}}{100} = \frac{k_{KCD}[OH^-]}{k_{BV} + k_{KCD}[OH^-]} \qquad (6)$$

where UOP refers to useful oxidizing power, and therefore

$$\frac{100}{\%\text{UOP}} = \frac{k_{BV}}{k_{KCD}} \frac{1}{[OH^-]} + 1 \qquad (7)$$

A plot of (100/%UOP) vs. $1/[OH^-]$ should yield a straight line with a slope equal to k_{BV}/k_{KCD} and a y intercept equal to 1. A typical plot is shown in Figure 2 for cyclohexanone as the ketone. Similar experiments were performed with p-nitroacetophenone and acetone. In the case of the aromatic ketone, one would expect a lower amount of Baeyer–Villiger reaction, and our experiments showed that ketone oxidation in this case did not occur in the pH range 7.0–9.5. Unfortunately, this ketone has a significant ultraviolet absorption that interferes with our analytical techniques, so it could not be used for the kinetic experiments. With acetone, experiments were run from pH 7.0–8.5. The Baeyer–Villiger reaction occurred to a much lesser extent than with cyclohexanone. A plot similar to that of Figure 2 was made with acetone; the results from the two figures are given in Table II, from which it is apparent that the ratio of rate constants k_{BV}/k_{KCD} is about a factor of 20 lower for acetone than for cyclohexanone. The y intercepts are roughly what one would expect from eq 7. It is from these data that our conclusion above concerning the choice of ketone as catalyst was derived.

The oxidation of Py by the peroxone system occurs under suitable and mild conditions (25 °C for about 3–4

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[5] (a) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, 78, 1125 (1956). (b) J. F. Goodman and P. Robson, *J. Chem. Soc.*, 2781 (1963). (c) E. Koubek, G. Levey and J. O. Edwards, *Inorg. Chem.*, 3, 1331 (1964). (d) For general reviews see: S. B. Brown, P. Jones, and A. Suggett, *Prog. Inorg. Chem.*, 13 (1970); (e) R. Curci and J. O. Edwards, "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, 1970, p 199.

Table II. Intercept Values and Rate Constant Ratios for Two Processes Related to Caroate Loss[a]

ketone	y intercept	slope (k_{BV}/k_{KCD})
acetone	0.98 ± 0.03	0.0020 ± 0.0001
cyclohexanone	0.89 ± 0.08	0.040 ± 0.004

[a] For cyclohexanone the conditions were [cyclohexanone]$_0$ = 0.0198 M, $[HSO_5^-]_0$ = 0.0150 M, 0.12 M potassium phosphate buffer for pH 7.0–8.5, no pyridine, and 25 °C. For acetone the conditions were [acetone]$_0$ = 0.0180 M, $[HSO_5^-]_0$ = 0.0165 M, 0.12 M potassium phosphate buffer for pH 7.0–8.5, no pyridine, and 25 °C.

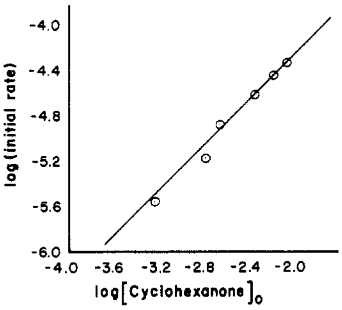


Figure 3. Plot of log (initial rate) against log [cyclohexanone]$_0$ with 0.10 M potassium phosphate for pH 7.90, $[HSO_5^-]_0$ = 8.7 × 10^{-4} M, and $[Py]_0$ = 1.60 × 10^{-4} M at 25 °C. The slope is 0.98.

h), and good yields of PyO can be obtained. For comparison purposes, it should be mentioned that an accepted method for preparing PyO involves rather drastic conditions (i.e., 35% hydrogen peroxide with Py in acetic acid solvent for 12 h at 80 °C).[6] It is worthy of note here that the synthetic usefulness of the peroxone system is not limited to nitrogen nucleophiles; the results that have been obtained in the oxidations of olefins indicate that excellent yields of unstable and/or water-insoluble epoxides may be obtained under mild conditions, including in some cases phase-transfer catalysis.[2-4]

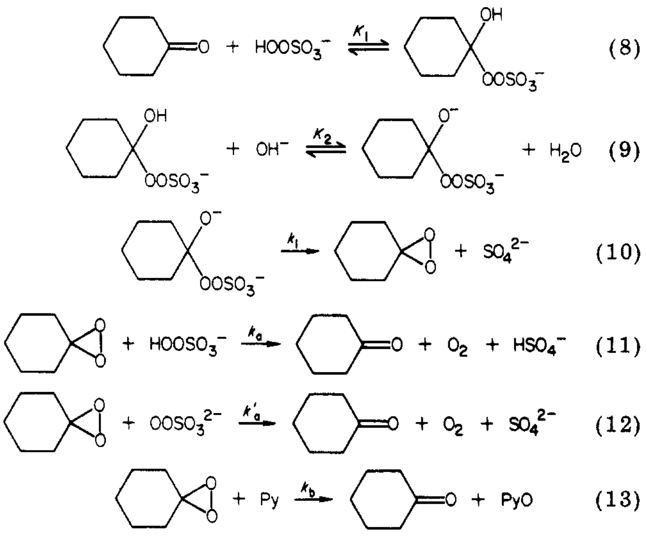
Kinetics. The method of initial rates was employed to obtain rate data. Pyridine and cyclohexanone concentrations and pH were varied one at a time.

To obtain the order in cyclohexanone, we varied its concentration over a factor of 16. A plot of the logarithm of initial rate against the logarithm of the concentration was made (see Figure 3) from which a slope of 0.98 was obtained. Thus the reaction is first order in ketone catalyst.

Because the Py competes with caroate for the dioxirane intermediate, a simple integral order in Py was not expected. When the amine concentration was varied by a factor of 5 (at constant ketone and caroate concentrations), the rate changed by a factor of 2.6. From the mechanism and derivation below, it was predicted that a plot of $[Py]_0$/initial rate vs. $[Py]_0/[HOOSO_3^-]_0$ would be linear. As may be seen in Figure 4, this is the case. Some of the data employed to construct the figures of this type are listed in Table III.

Variation of pH. Groups of rate experiments were carried out at diverse pH values from 7.5 to 8.3, which is a factor of 6.3 for change in $[OH^-]$. The type of linear plots as seen in Figure 4 were obtained, with the slopes and intercepts varying according to a rate law to be given below. Some results are listed in Table IV.

Mechanism. Our results are consistent with the mechanism shown in eq 8–13. It is to be remembered at this point that the second ionization of caroate (eq 14) and the Baeyer–Villiger reaction can be important under some circumstances.



$$HOOSO_3^- + OH^- \overset{K_3}{\rightleftharpoons} OOSO_3^{2-} + H_2O \tag{14}$$

Using the steady-state approximation for the dioxirane intermediate, one arrives at the following rate law (eq 15),

$$\frac{-d[Py]}{dt} = \frac{k_b k_1 K_1 K_2 [Py][OH^-][ketone][HOOSO_3^-]}{k_a[HOOSO_3^-] + k_a' K_3 [OH^-][HOOSO_3^-] + k_b[Py]} \tag{15}$$

which can be converted algebraically to eq 16 which in turn

$$\frac{-d[Py]}{dt} = \frac{\dfrac{k_b k_1 K_1 K_2}{k_a}[Py][OH^-][ketone]}{1 + \dfrac{k_a' K_3 [OH^-]}{k_a} + \dfrac{k_b[Py]}{k_a[HOOSO_3^-]}} \tag{16}$$

can be represented as eq 17, where k_{obsd} and k_2 are as

$$rate = \frac{k_{obsd}[Py]}{k_2 + \dfrac{k''[Py]}{[HOOSO_3^-]}} \tag{17}$$

shown in eq 18 and 19, respectively, and k'' as is shown

$$k_{obsd} = \frac{k_b k_1 K_1 K_2}{k_a}[OH^-][ketone] \tag{18}$$

$$k_2 = 1 + \frac{k_a' K_3}{k_a}[OH^-] \tag{19}$$

in eq 20.

$$k'' = k_b/k_a \tag{20}$$

On consideration of eq 15, it can be seen that if the pH and the concentrations of caroate and pyridine are held constant, one should observe simple first-order kinetics with cyclohexanone as catalyst. This is what is observed. Equation 17 can be rearranged into eq 21, from which it

$$\frac{[Py]}{rate} = \frac{k''[Py]}{k_{obsd}[HOOSO_3^-]} + \frac{k_2}{k_{obsd}} \tag{21}$$

is apparent that a plot of $[Py]_0$/initial rate vs. $[Py]_0/[HOOSO_3^-]_0$ should give a straight line, with the slope and y intercept varying according to the concentrations of

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[6] E. Ochiai, *J. Org. Chem.*, 18, 534 (1953).

Table III. Variation of Initial Rate with Pyridine Concentration

run[a]	$[\text{pyridine}]_0$, M	10^5(initial rate), M min^{-1}	$[\text{pyridine}]_0$/ initial rate	$[\text{pyridine}]_0/[HSO_5^-]_0$
1	3.10×10^{-4}	2.61	11.9	3.75×10^{-1}
2	3.10×10^{-4}	2.56	12.1	3.75×10^{-1}
3	2.63×10^{-4}	2.41	10.9	3.18×10^{-1}
4	2.63×10^{-4}	2.38	11.0	3.18×10^{-1}
5	2.17×10^{-4}	2.20	9.86	2.63×10^{-1}
6	2.17×10^{-4}	2.20	9.86	2.63×10^{-1}
7	1.55×10^{-4}	1.94	7.99	1.88×10^{-1}
8	1.55×10^{-4}	1.91	8.12	1.88×10^{-1}
9	1.08×10^{-4}	1.51	7.15	1.31×10^{-1}
10	1.08×10^{-4}	1.50	7.20	1.31×10^{-1}
11	6.19×10^{-5}	1.00	6.19	7.49×10^{-2}
12	6.19×10^{-5}	1.00	6.19	7.49×10^{-2}

[a] $[\text{Cyclohexanone}]_0 = 6.13 \times 10^{-3}$ M, $[HSO_5^-]_0 = 8.26 \times 10^{-4}$ M, pH = 7.90, 0.10 M potassium phosphate buffer, 245 nm, and 25 °C.

Table IV. Parameters Derived from Linear Plots[a]

pH	$(\text{concn})_0$, M	slope	intercept	γ[b]
		Cyclohexanone		
7.50	6.13×10^{-3}	40.2	7.35	5.47
7.90	3.07×10^{-3}	42.7	9.55	4.47
7.90	6.13×10^{-3}	19.9	4.63	4.30
8.30	2.06×10^{-3}	23.8	8.05	2.96
		Acetone		
7.50	5.66×10^{-2}	52.5	15.5	3.39
7.90	3.88×10^{-2}	33.0	15.1	2.19
8.30	2.00×10^{-2}	18.7	14.4	1.30

[a] At 25 °C, $[HOOSO_3^-]_0 = 8.3 \times 10^{-4}$ M, and $[\text{pyridine}]_0 = 6.19 \times 10^{-5}$ to 3.10×10^{-4} M, values are plus or minus approximately 3-4%. [b] γ = slope/y intercept of the type show in Figure 4.

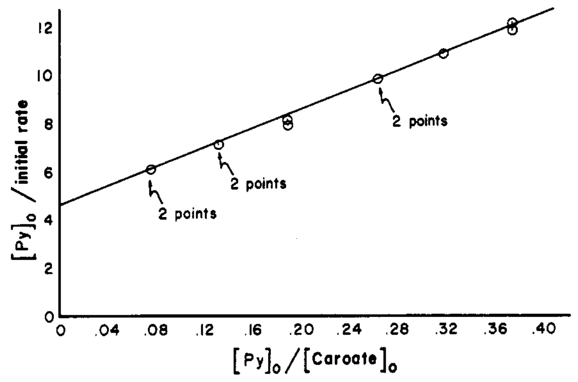

Figure 4. Typical plot of $[Py]_0$/initial rate against $[Py]_0/[HSO_5^-]_0$: $[\text{cyclohexanone}]_0 = 6.13 \times 10^{-3}$ M, $[HSO_5^-]_0 = 8.26 \times 10^{-4}$ M, $[Py]_0$ from 6.19×10^{-5} to 3.10×10^{-4} M, and pH 7.90 with 0.1 M potassium phosphate buffer at 25 °C. The slope is 19.9, and the intercept is 4.63.

hydroxide and ketone. This also is what is observed in Figure 4, and numerical results are given in Table IV.

Further, using eq 19 and the fact that the slope/y intercept for eq 21 is equal to k'/k_2', one arrives at eq 22,

$$\frac{1}{\gamma} = \frac{k_a' K_3/k_a}{k''}[OH^-] + \frac{1}{k''} \qquad (22)$$

where γ is defined as the slope/y intercept. By plotting $1/\gamma$ vs. $[OH^-]$, one can evaluate k'' and $k_a'K_3/k_a$. Using the data from Table IV, one arrives at the results in Table V. The plot for cyclohexanone is shown in Figure 5. The value of K_3 was estimated as 4.0×10^4 by using pK_a(2) for caroate as 9.4.

The ratio of k_b/k_a is generally consistent with the yields of PyO at pH 8.0 where only a very small amount of Baeyer–Villiger is occurring and where essentially all of the caroate exists as HSO_5^-, in which case the decomposition is not near the maximum rate. A moderately large ratio of k_a'/k_a is consistent with the pH dependence of yield in the oxidation of cinnamate ion.[2] Since the ketone-catalyzed decomposition involves nucleophilic attack of caroate on dioxirane (eq 11 and 12), it would seem reasonable for the k_a'/k_a to be moderately greater than 1 since SO_5^{2-} is presumably a better nucleophile than HSO_5^-.

Table V. Results from Linear Plots as Shown in Figure 4

ketone	k_b/k_a	k_a'/k_a
acetone	5.3 ± 0.6	39 ± 7
cyclohexanone	6.4 ± 0.4	15 ± 1

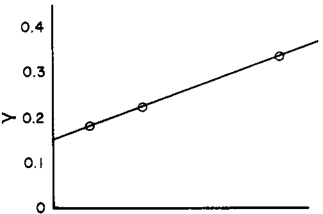

Figure 5. Typical plot of $1/\gamma$ vs. $[OH^-]$ for γ = slope/y intercept from plots such as Figure 4: $[\text{cyclohexanone}]_0 = 3.07 \times 10^{-3}$ and 6.13×10^{-3} M at pH values 7.50, 7.90, and 8.30. The slope is 9.19×10^4, and intercept is 0.155.

Experimental Section

Oxone (potassium salt of Caro's acid, manufactured by Du Pont) was analyzed by standard iodometric techniques. Aqueous solutions were prepared with demineralized water from a Barnstead column with a mixed-bed cartridge. Cyclohexanone was a reagent grade Mallinckrodt product and was distilled. Pyridine was reagent grade [Baker and Adamson (B and A)] and was purified by being refluxed and distilled over barium oxide (Fisher). The chemicals used to make buffers were KH_2PO_4 (MCB) and $NaHCO_3$ (Fisher) (both reagent grade). Sodium hydroxide was reagent grade (B and A). Pyridine 1-oxide was practical grade (Eastman), was recrystallized from toluene (B and A), and was stored under vaccum over P_2O_5.

The reaction product PyO was identified by a Varian A-60A NMR spectrometer. Kinetic and yield measurements were made by using a Cary 15 recording spectrophotometer with a constant-temperature bath connected to the cell holder. Measurements of pH were made on a pH Radiometer (Copenhagen, Type TTT1b).

The method of initial rates was used to collect kinetic data (usually at 240 or 245 nm) by following the appearance of PyO accompanied by the decrease in Py. A solution of Caro's acid and buffer was thermostated in the cell compartment, and then solutions of Py and cyclohexanone were added to the cell by way of syringes. The resulting solution was mixed thoroughly and put into the spectrometer. Determination of the extinction coefficients of Py and PyO permitted one to evaluate rates. The precision of rate determinations was usually ±2–4%.

Product yields were determined by running the reaction in vials ($[\text{pyridine}]_0 \simeq [\text{Caro's acid}]_0$) and allowing enough time to elapse such that all the Caro's acid reacted. The reaction mixture was then scanned (after dilution) in the UV. Absorbance readings were taken at 250 and 270 nm, and two simultaneous equations were solved to find the concentration of PyO.

The percent remaining of cyclohexanone (used to determine the percent of Baeyer–Villiger reaction) was evaluated by running the reaction in vials ($[\text{cyclohexanone}]_0 \simeq [\text{Caro's acid}]_0$, no pyridine) and allowing enough time to elapse such that all the Caro's acid reacted. An absorbance reading at 280 nm as compared with the initial absorbance due to cyclohexanone alone allows one to calculate the percent remaining. Similar procedures were followed for acetone and *p*-nitroacetophenone.

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Registry No. HSO_5^-, 12188-01-1; Py, 110-86-1; PyO, 694-59-7; c-HxO, 108-94-1; acetone, 67-64-1.

Electrocyclic Ring Opening of the 6b,7a-Dihydro-7*H*-cycloprop[*a*]acenaphthylene Radical Anion

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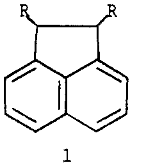
The Na–K alloy and electrochemical reduction of the naphthocyclopropane **6** were investigated. The radical anion of **6** was found to be very labile and could not be observed spectroscopically. In the Na–K reduction of **6**, the phenalenyl radical (**9**) was detected as an intermediate in the reduction, and the phenalenyl anion (**10**) and perinaphthane (**8**) were found to be the products of the reduction. Evidence was obtained from polarographic and cyclic voltammetric studies that **8–10** are also formed in the electrochemical reduction of **6**. A mechanism is proposed for this reduction which involves an initial electrocyclic ring opening of the cyclopropane ring in the radical anion of **6** which is followed by a 1,2-shift of hydrogen to yield the radical anion of phenalene (**11**). The radical anion of **11** is then further transformed into **8** and **10**; the latter transformation has previously been reported.

There has been increasing interest in recent years in the pericyclic reactions of radical anions[2] and, to a lesser extent, radical cations.[3] These reactions make interesting comparisons with the thermal and photochemical reactions of the corresponding neutral molecules, where the predictions of the Woodward–Hoffmann rules are easily made and usually verified experimentally. Ambiguities abound when one attempts to apply these simple rules to species which possess an odd number of electrons. In the electrocyclic ring opening of the benzocyclobutene radical anion, for example, the use of correlation diagrams yields a different prediction than the frontier orbital approach. Other examples of these ambiguities for the electrocyclic reactions of radicals and radical anions have recently been cited by Bauld and Cessac.[4] The electrocyclic reactions of radical cations, on the other hand, are almost always predicted to be forbidden by both orbital correlation diagrams and state symmetry, although the barriers to reactions are predicted to be low and the mode of ring opening is predicted to be identical with the thermal reaction of the neutral molecule.[4,5]

Acenaphthene (**1a**) is a particularly interesting molecule in this regard. Ring opening of the CH_2–CH_2 σ bond yields the 1,8-naphthoquinodimethane biradical (**2a**). The biradical **2a** possesses a degenerate set of nonbonding π molecular orbitals (MO's), one of which is symmetric and one of which is antisymmetric to a plane bisecting the molecule through the middle of the naphthalene ring.[6] In the neutral species these degenerate MO's will contain two electrons, which gives rise to not only singlet states but



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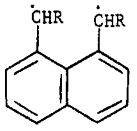

2

a)R=H, b)R=Ph, c)R=p-Ph-Ph-

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