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Kinetic Evidence for the Occurrence of the Oxydianionic Tetrahedral Intermediates in the Hydrolyses of Methyl Salicylate and Methyl *o*-Methoxybenzoate in a Highly Alkaline Medium

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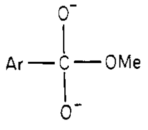
The kinetics of hydrolyses of methyl salicylate and methyl *o*-methoxybenzoate have been studied at various hydroxide ion concentrations ranging from 0.01 to 4.40 M for methyl salicylate and from 0.005 to 0.200 M for methyl *o*-methoxybenzoate at 35 °C. The observed rate constants are independent of $[OH^-]$ within the range 0.01–0.04 M and vary according to the equation $k_{obsd} = A + B[OH^-] + C[OH^-]^2$ within the range 0.04–3.60 M for hydrolysis of methyl salicylate where $A = k_3k_1[H_2O]/(k_{-1} + k_3)$, $B = k_2k_4/(k_{-2} + k_4)$, and $C = k_2k_5K/(k_{-2} + k_4)$. The observed rate constants for hydrolysis of methyl *o*-methoxybenzoate follow the equation $k_{obsd} = B^1[OH^-] + C^1[OH^-]^2$ where $B^1 = k_1'k_2'/(k_{-1}' + k_2')$ and $C^1 = k_1'k_3'K'/(k_{-1}' + k_2')$. The pH-independent observed rate constants are $\sim 10^4$ and $\sim 10^5$ times larger than the corresponding values for water-catalyzed cleavages of methyl benzoate and methyl *o*-methoxybenzoate, respectively. This rate enhancement has been attributed to the probable intramolecular general-base-catalyzed neutral hydrolysis of methyl salicylate. The ratios B/B^1 and C/C^1 have been found to be 0.0214 and 0.0004, respectively. The appearance of C and C^1 terms in the kinetic equations has been attributed to the existence of the oxydianionic tetrahedral intermediates in the reaction mechanisms. The temperature dependence of hydrolysis of methyl salicylate has also been studied at two different OH^- concentrations. The intramolecular general-base-catalyzed rate enhancement has been found to be due to a favorable ΔS^*. The hydrolytic cleavage of methyl salicylate has been found to be sensitive to the ionic strength. The probable mechanisms for hydrolyses of both esters are considered.

The mechanism of hydrolytic cleavage of the ester bond is of great importance because of its involvement in many biochemical reactions.[1] Bender et al.[2] have studied the hydrolytic cleavage of *p*-nitrophenyl salicylate and other related compounds, and the aim of their studies was to find out quantitatively the effect of the neighboring hydroxyl group on hydrolysis. Capon and Ghosh[3] have studied the neutral and alkaline hydrolysis of phenyl salicylates and its derivatives and have discussed the mechanism of these reactions. These studies, however, were carried out at rather low alkalinity where the existence of an oxydianionic tetrahedral intermediate could not be detected. Since the pioneering work of Biechler and Taft[4] on the kinetically detectable oxydianionic tetrahedral intermediate in the alkaline hydrolysis of anilide, a large number of papers have appeared to support the existence of such intermediates in the alkaline hydrolysis of various amides[5] and imides.[6] To the best of our knowledge, the oxydianionic tetrahedral intermediate has not been found in alkaline hydrolysis of any ester except ethyl oxamate.[7] In this paper we are, for the first time, reporting kinetic evidence for the existence of an oxydianiomic tetrahedral intermediate (1) in the alkaline hydrolysis of compounds containing only an ester group which could be hydrolytically cleaved. Methyl salicylate, in particular, has medicinal importance, and thus a detailed diagnosis of the mechanism of hydrolysis of this compound would help, to some extent, to provide a better understanding of its in vivo reactivity.



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Experimental Section

Materials. Methyl salicylate (2) was prepared from salicylic acid with a standard procedure in 83% yield. The spectral data as well as the boiling point (bp 224–225 °C) were in complete agreement with literature values.[8]

Methyl *o*-methoxybenzoate (3) was prepared from 2 with dimethyl sulfate as the alkylating agent.[9a] The boiling point (bp 229–230 °C) as well as the spectral data were in agreement with literature values[9b] (yield 52%).

All other chemicals used were of analytical grade. Deionized glass-distilled water was used throughout the kinetic studies.

Kinetics. Reaction mixtures containing all the reaction components except substrate (either 2 or 3) were prepared in a total volume of either 49.2 or 48 mL of water as the solvent and were then placed in a thermostatic water bath for equilibration at 35 °C. After about 10–15 min of equilibration, the reaction was initiated by adding either 0.8 or 2 mL of concentrated stock solutions of either 2 or 3, respectively, to the equilibrated reaction mixture. The stock solutions of substrates were prepared in ethanol. This technique thus added 1.6% and 4% ethanol into the reaction mixtures for hydrolysis of 2 and 3, respectively. An aliquot of 2–3 mL was withdrawn from reaction mixture at different time intervals and placed in a 3-mL quartz cuvette which was then quickly placed into the cell compartment of the spectrophotometer. The decrease in optical density of the reaction mixture due to disappearance of substrate was recorded at fixed wavelengths of either 340 (for 2) or 310 nm (for 3) by using a Hitachi 100-50 double-beam UV–visible spectrophotometer.

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Table I. Effect of Ionic Strength on Hydrolytic Cleavage of 2[a]

ionic strength, M	$10^2 k_{obsd}$,[b] min^{-1}	E_{app},[b] M^{-1} cm^{-1}	A_∞[b]
0.4	2.05 ± 0.03	4130 ± 22	0.075 ± 0.005
1.2	2.24 ± 0.03	4068 ± 19	0.080 ± 0.004
2.0	2.41 ± 0.03	4150 ± 21	0.084 ± 0.004
2.8	2.63 ± 0.03	4020 ± 16	0.099 ± 0.004
3.9	2.88 ± 0.06	4060 ± 32	0.096 ± 0.007
4.4	3.13 ± 0.05	4032 ± 28	0.115 ± 0.006

[a] Conditions: 2.266 × 10^{-4} M methyl salicylate, 0.4 M NaOH, 35 °C. [b] Error limits are standard deviations.

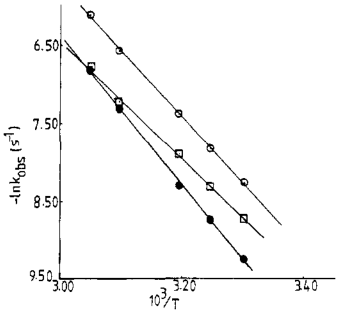

Figure 1. Plots showing the dependence of k_{obsd} on temperature for the k_3 step (●), the ($k_3 + k_4$) step (○), and the k_4 step (□). The solid lines are generated from eq 2 by using the respective values of ln A and E_a listed in Table II.

There was always a maximum lapse of ~30 s on the average between the time of removal of an aliquot and the time at which its optical density was recorded. During this period, the error due to the drop in the temperature of reaction mixture was considered to be negligible because the constant temperature (35 °C) for most of the kinetic runs was close to the ambient temperature (~29 °C). Almost all the kinetic runs were carried out at up to 5–8 half-lives with at least ten readings, and the absorbance changes were found to be ~0.8 and ~0.4 absorbance units for hydrolyses of 2 and 3, respectively. The sodium hydroxide concentrations were kept 2 × 10^2–2 × 10^4 and (2–6) × 10^2 times larger than the respective concentrations of 2 and 3. Under such conditions, the reaction kinetics were found to follow pseudo-first-order rate law. The observed pseudo-first-order rate constants, k_{obsd}, were calculated from eq 1 by using the nonlinear

$$A_{obsd} = E_{app}X_0e^{-k_{obsd}t} + A_\infty \qquad (1)$$

least-squares technique.[10] In eq 1, A_{obsd} and A_∞ are the absorbance values at any time t and at $t = \infty$, E_{app} is the apparent molar absorption coefficient, and X_0 is the initial concentration of substrate. With the nonlinear least-squares technique, k_{obsd}, E_{app}, and A_∞ were considered as three unknown parameters. The fittings of the observed data to eq 1 were found to be reasonably good for all kinetic runs. The percent deviations between observed and calculated values of absorbance were found to be less than 2% prior to 3–6 half-lives for most of the kinetic runs.

At the end of a few kinetic runs, the UV spectra of the reaction products were recorded and compared with those of authentic samples containing the expected products. Good agreement was always obtained.

Results

The ionic strength effect in the alkaline hydrolysis of 2 has been studied within the range of 0.4–4.3 M at 35 °C and at 0.4 M NaOH. The observed pseudo-first-order rate constants were found to increase with an increase in ionic strength (Table I).

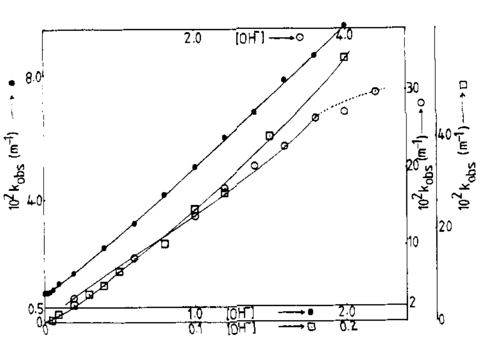

Figure 2. Plots showing the dependence of k_{obsd} on hydroxide ion concentration at 35 °C for hydrolysis of methyl salicylate (○, ●) and methyl o-methoxybenzoate (□). The solid lines are generated by using eq 4 with the constants A, B, and C listed in Table III for methyl salicylate and eq 5 with the constants B^1 and C^1 listed in Table III for methyl o-methoxybenzoate.

The effect of temperature on alkaline hydrolysis of 2 has been studied within the temperature range of 30–55 °C at two different OH⁻ concentrations. The observed data are shown graphically in Figure 1 and were found to reasonably fit the Arrhenius and Eyring equations (eq 2 and 3, respectively). The various activation parameters were

$$\ln k_{obsd} = \ln A - E_a/RT \qquad (2)$$

$$k_{obsd} = (k_BT/h)e^{-(\Delta H^* - T\Delta S^*)/RT} \qquad (3)$$

calculated from eq 2 and 3 by using linear[10] and nonlinear[10] least-squares techniques and are summarized in Table II.

The hydrolyses of 2 and 3 have been studied at various $[OH^-]$ ranging from 0.01 to 2.0 M and 0.005 to 0.200 M, respectively, at a 2.0 M ionic strength and 35 °C. The observed pseudo-first-order rate constants as shown in Figure 2 were found to follow an empirical equation (eq 4) within an OH⁻ concentration range of 0.04–2.00 M for

$$k_{obsd} = A + B[OH^-] + C[OH^-]^2 \qquad (4)$$

hydrolysis of 2 and of 0.005–0.200 M for hydrolysis of 3. The empirical parameters A–C were calculated by using linear least-squares techniques, and the results obtained are summarized in Table III. The relative numerical values of B and C (Table III) reveal that the C term contributes ~9% to k_{obsd} at 2.0 M NaOH for hydrolysis of 2 whereas for hydrolysis of 3 it contributes ~34% to k_{obsd} at 0.2 M NaOH. Although ~9% contribution is not enough to validate the use of C terms, the standard deviation of constant C (Table III) does not render it statistically insignificant. The hydrolysis of 2 appeared to be insensitive to $[OH^-]$ within the range of 0.01–0.04 M. In order to check further the validity of this term in eq 4 for hydrolysis of 2, we also carried out the reaction kinetics at a constant ionic strength of 4.4 M within the $[OH^-]$ range of 0.4–4.4 M. The data are shown graphically in Figure 2. These data were also found to follow eq 4 within the $[OH^-]$ range of 0.4–3.6 M, and the empirical parameters calculated from eq 4 are also shown in Table III. A least-squares treatment resulted a negative value for constant A with a standard deviation of more than 1300% for hydrolysis of 3. This shows that A is statistically insignificant compared with the other terms in eq 4. The observed pseudo-first-order rate constants obtained for hydrolyses of phenyl o-methoxybenzoate[3] (1.8 × 10^{-4} min^{-1} at pH 7.2 and 59.2 °C) and p-nitrophenyl o-methoxybenzoate[2] (1.47 × 10^{-5} min^{-1} at pH 8.0 and 25 °C) reveal that the contribution due to water-catalyzed hydrolytic cleavage of 3 compared with hydroxide ion catalyzed cleavage would be expected to be insignificant even at the lowest $[OH^-]$ attained in the present study. When the

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[10] The linear and nonlinear least-squares computer programs in BASIC were developed, and all computations were carried out on a Commodore Professional 3016 computer.

Table II. Activation Parameters of Hydrolytic Cleavage of 2[a]

reaction step	ΔF^*,[b] kcal/mol	ΔH^*,[e] kcal/mol	$-\Delta S^*$,[e] cal deg^{-1} mol^{-1}	ln A,[e] s^{-1}	E_a,[e] kcal/mol	max dev,[c] %
k_3[d]	23.44	19.10 ± 0.28	14.1 ± 0.8	22.52 ± 0.48	19.14 ± 0.48	7.6
$k_3 + k_4$[f]	22.87	16.76 ± 0.52	19.8 ± 1.6	19.74 ± 0.36	16.87 ± 0.22	5.5
k_4[g]	23.18	14.84 ± 0.70	27.0 ± 2.2	16.40 ± 0.58	15.13 ± 0.36	4.8

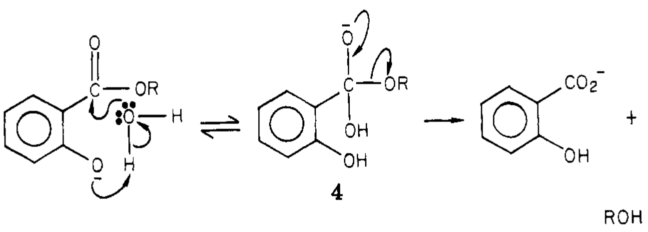
[a] Conditions: 2.266 × 10^{-4} M methyl salicylate; $\mu = 2.0$ M. [b] ΔF^* was calculated from the relationship $k_{obsd} = (K_BT/h) \exp(-\Delta F^*/RT)$ at 35 °C. [c] Maximum deviation between observed and calculated values of rate constants. [d] At 0.02 M NaOH. [e] Error limits are standard.deviations. [f] At 0.4 M NaOH. [g] k_4 (s^{-1}) was calculated from the relationship $k_4 = k_{obsd}$ (at 0.4 M NaOH) − k_{obsd} (at 0.02 M NaOH) where k_4 = B.

Table III. Empirical Parameters Obtained from Eq 4 and 4 for Hydrolytic Cleavages of 2 and 3

ester	ionic strength, M	10^3A,[c] min^{-1}	$10^2B(B^1)$,[c] M^{-1} min^{-1}	$10^2C(C^1)$,[c] M^{-2} min^{-1}	10^6R_{ms},[a] min^{-1}
2[b]	2.0	8.33 ± 0.32	3.99 ± 0.09	0.200 ± 0.004	3.119
	4.4	5.24 ± 4.01q	6.31 ± 0.45	0.230 ± 0.110	32.65[d]
3[e]	2.0	−0.372 ± 5.383	187 ± 15	493 ± 74	551.8
	2.0		186 ± 8	497 ± 51	552.1[f]

[a] $R_{ms} = (\sum_{j=1}^{N} (k_{obsd}{}^i - k_{calcd}{}^i)^2/(N-p))^{1/2}$, where p is the number of unknown parameters. [b] Conditions: 2.266 × 10^{-4} M methyl salicylate, 35 °C. [c] Error limits are standard deviations. [d] Sodium hydroxide concentration range is 0.4–3.6 M. [e] Conditions: 8.69 × 10^{-4} M methyl *o*-methoxybenzoate, 35 °C. [f] Calculated from eq 5.

Scheme I



observed data were subjected to eq 5, the resulting values of B^1 and C^1 (Table III) were changed only by 0.5% and 0.8%, respectively.

$$k_{obsd} = B^1[OH^-] + C^1[OH^-]^2 \quad (5)$$

Discussion

The pH–rate constant profiles (Figure 2) for hydrolyses of both esters 2 and 3 indicate that there is a change in rate determining steps with change in [OH^-]. This conclusion is based on many earlier studies carried out on related reactions.[11] In extensive studies of the alkaline hydrolysis of esters[12] and amides[13] carried out under considerably low alkaline medium conditions, the existence of an oxydianionic tetrahedral intermediate was not observed, but at higher pH it was observed in many reactions[14] involving amide and imide bond cleavage. From these studies as well as from the one carried out on hydrolysis of formamide[15] we concluded that the existence of an oxydianionic tetrahedral intermediate is not an implicit function of either the alkalinity of the reaction medium or the structural features of the substrate but is rather a composite function of both effects.

The enhanced reactivity of phenyl salicylate[3] and salicylamide[16] in comparison to that of phenyl *o*-methoxybenzoate and *o*-methoxybenzamide, respectively, in the plateau regions of pH–rate profiles have been attributed to the participation of the neighboring hydroxyl group acting as either a general-base or general-acid catalyst. Although the mechanism has not been unambiguously sloved, the preferred mechanism may be shown as in Scheme I.

In Scheme I, the nature of the rate-determining step has not been discussed by earlier workers. However, it has been well established in various acyl-transfer reactions[17] that in a stepwise mechanism, the rate-determining step depends upon the relative acidity of leaving group and nucleophiles. Thus in hydrolytic cleavages of phenyl salicylate and *p*-nitrophenyl salicylate, the nucleophilic water attack (assisted by a neighboring ionized hydroxyl group) should be the rate-determining step because the leaving groups are much more acidic compared with the hydroxyl group in 4. The enhanced reactivity due to the neighboring hydroxyl group could possibly be detected only in those reactions where nucleophilic attack would be the rate-determining step. This conclusion is based on the observed enhanced hydrolytic cleavage of *p*-nitrophenyl acetate[18] in presence of *o*-[(dimethylamino)methyl]benzyl alcohol (ODMBA) while no such enhanced reactivity was observed for the hydrolytic cleavages of methyl formate[19] and acetylcholine[19] in the presence of ODMBA. The nonappearance of an enhanced reactivity in the hydrolysis of ethyl salicylate,[2] where the leaving group is less acidic than a hydroxyl group,[20] supports the conclusion of the dependence of enhanced reactivity on the nature of the rate-determining step. Similarly, Fife et al.[21] have observed a value of k_{OH} nearly 10^3 times larger for cleavage of trifluoroethyl *o*-(2-imidazoyl)benzoate than the corresponding value for the cleavage of methyl *o*-(2-imidazoyl)benzoate.

On recaptitulating the observations of earlier and present studies we are led to the mechanisms shown in Schemes II and III for alkaline hydrolysis of 2 and 3, respectively.

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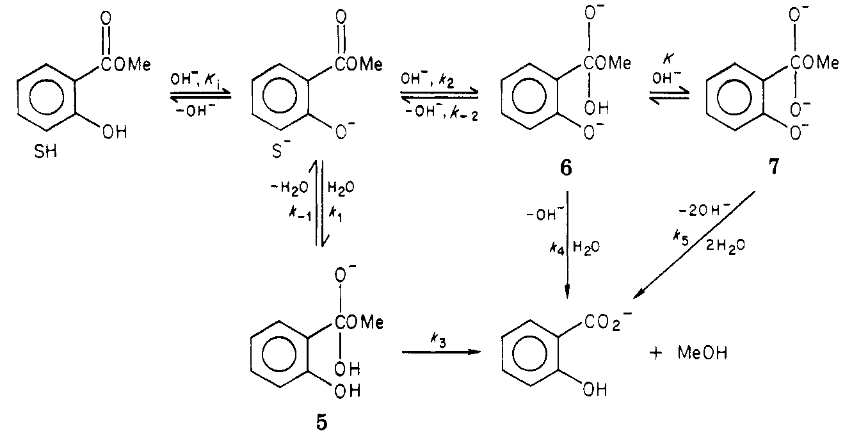
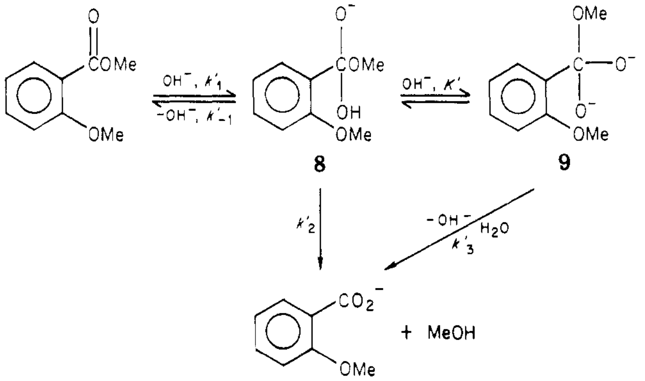
Scheme II



Scheme III



In Schemes II and III, structures **5**–**9** were considered to be transient intermediates, and hence application of the steady-state approximation yields the kinetic equations 6 and 7 for hydrolysis of **2** and **3**, respectively, where K_i^1

$$k_{\text{obsd}} = \frac{k_3k_4K_i^1[\text{OH}^-][\text{H}_2\text{O}]}{(k_{-1} + k_3)(1 + K_i^1[\text{OH}^-])} + \frac{k_2K_i^1[\text{OH}^-]^2(k_4 + k_5K[\text{OH}^-])}{(1 + K_i^1[\text{OH}^-])(k_{-2} + k_4 + k_5K[\text{OH}^-])} \quad (6)$$

$$k_{\text{obsd}} = \frac{k_1'[\text{OH}^-](k_2' + k_3'K'[\text{OH}^-])}{(k_{-1}' + k_2' + k_3'K'[\text{OH}^-])} \quad (7)$$

$= K_i/[\text{H}_2\text{O}] = K_a/K_w$ with $K_a = a_\text{H}[\text{S}^-]/[\text{SH}]$. Under the experimental conditions, $1 \ll K_i^1[\text{OH}^-]$, and also $k_{-2} + k_4 \gg k_5K[\text{OH}^-]$ and $k_{-1}' + k_2' \gg k_3'K'[\text{OH}^-]$, as discussed in earlier studies.[6] Applying these assumptions, the eq 6 and 7 are reduced to eq 8 and 9, respectively. Equations 8 and

$$k_{\text{obsd}} = \frac{k_3k_1[\text{H}_2\text{O}]}{(k_{-1} + k_3)} + \frac{k_2[\text{OH}^-](k_4 + k_5K[\text{OH}^-])}{(k_{-2} + k_4)} \quad (8)$$

$$k_{\text{obsd}} = \frac{k_1'[\text{OH}^-](k_2' + k_3'K'[\text{OH}^-])}{(k_{-1}' + k_2')} \quad (9)$$

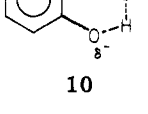
9 are similar to the empirically observed eq 4 and 5, respectively, with $A = k_3k_1[\text{H}_2\text{O}]/(k_{-1} + k_3)$, $B = k_2k_4/(k_{-2} + k_4)$, $C = k_2k_5K/(k_{-2} + k_4)$, $B^1 = k_1'k_2'/(k_{-1}' + k_2')$, and $C^1 = k_1'k_3'K'/(k_{-1}' + k_2')$. The value of B^1 is nearly 10^3 times smaller than the corresponding value obtained at 59.2 °C in the hydrolysis of phenyl *o*-methoxybenzoate[3] and nearly 4 times smaller than that of methyl benzoate.[22]

The pH-independent rate of hydrolysis of **2** (Figure 2) indicates that within the [OH⁻] range of 0.01–0.04 M, the k_4 and k_5 paths are insignificant in comparison to k_3 path. Thus, under such conditions, the eq 8 is reduced to eq 10.

$$k_{\text{obsd}} = k_3k_1[\text{H}_2\text{O}]/(k_{-1} + k_3) \quad (10)$$

The average value of k_{obsd}, in the region of the pH–rate constant profile where eq 10 is strictly true, was found to be $(9.60 \pm 0.05) \times 10^{-3}$ min^{-1}. It can be shown that this value is nearly 10^4, 10^5, and 10^2 times larger than the rate constants for water-catalyzed cleavage of methyl benzoate,[23] methyl *o*-methoxybenzoate,[23] and methyl *o*-(2-imidazoyl)benzoate,[21] respectively. The rate enhancement due to a neighboring hydroxy group is significantly larger than the one obtained in *p*-nitrophenyl salicylate.[2]

A further increase in [OH⁻] beyond 0.04 M causes an increase in k_{obsd}. This indicates that, under such conditions, the inequality $k_3k_1[\text{H}_2\text{O}]/(k_{-1} + k_3) \gg k_2[\text{OH}^-](k_4 + k_5K[\text{OH}^-])$ is no longer true, and the observed rate constants vary according to eq 8. The calculated values of B and C are 45 and 2.5×10^3 times smaller than B^1 and C^1, respectively. This difference of reactivity could be attributed to (i) a significantly stronger electron-donating power of the *o*-O⁻ group compared with the *o*-OMe group and to (ii) an intramolecular electrostatic repulsion between two negatively charged groups (*o*-O⁻ and (–O⁻) in **7**.[25] A possible stabilization due to intramolecular hydrogen bonding in **6** as shown in **10** will partially offset the rate-retarding electron-donating effect of *o*-O⁻. The ratios B/C (~20 M) and B^1/C^1 (~0.38 M) clearly display the probable existence of intramolecular hydrogen bonding in **6**. The observed points at 4.0 and 4.4 M NaOH were found to be negatively deviated from the plot (Figure 2) which could be due to the failure of the assumption that k_{-2} +



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(23) Estimated from the corresponding values of phenyl benzoate[24] and phenyl *o*-methoxybenzoate[3] with temperature correction and a 100-fold change due to the difference in the acidity of the leaving groups.

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(25) We thank to one of the referees of *J. Am. Chem. Soc.* for pointing our attention toward it.

$k_4 \gg k_5K[OH^-]$ as discussed earlier in other reactions.[7]

There appears to be different opinions about assigning the factors which control the rate enhancement of intramolecular reactions.[26] The observed values of activation parameters at 0.02 M NaOH (Table II), where contribution of the k_3 step is nearly 100%, are comparable with those of various intramolecular nucleophilic reactions.[25,27] The comparison of these values with those obtained recently in neutral hydrolysis of phenyl benzoate[24] indicates that the entire rate acceleration in the pH-independent hydrolytic cleavage of **2** comes from a favorable ΔS^* value while the ΔH^* value is actually unfavorable compared with that of phenyl benzoate. The activation parameters obtained at 0.4 M NaOH, where the contributions due to the k_3 and k_4 steps constitute ~40% and ~60% of the rate, respectively, indicates that an increase in the contribution of the k_4 step to the total rate decreases the values of both ΔH^* and ΔS^*. Significantly low values of ΔH^* ΔS^* were obtained for the k_4 step (Table II) which are comparable with those obtained in alkaline hydrolysis of monomethyl phthalate[28] and di-*n*-butyl phthalate.[29] The similarity of activation parameters obtained for hydrolytic cleavages of phenyl salicylate[30] and methyl salicylate under comparable conditions indicates the involvement of an almost similar reaction mechanism. In the hydrolysis of phenyl salicylate, the nucleophilic attack could be considered as the rate-determining step because of the considerably high acidity of the leaving group compared with the nucleophile. However, in the hydrolysis of **2**, both the leaving group and nucleophile have almost similar acidities[20] in **5** and **6**. But the probable intramolecular hydrogen bonding in **10** will make the expulsion of the leaving group more facile than that of nucleophile. Under such circumstances, we propose that nucleophilic attack is more likely to be the rate-determining step in the hydrolytic cleavage of **2**.

A kinetically indistinguishable additional step in Scheme II as shown in eq 11 may be ruled out on the basis of the

$$5 \xrightleftharpoons{K^{11},\, OH^-} 6 + H_2O \qquad (11)$$

observed values of ΔS^* obtained for both the k_3 and k_4 steps. A significant role for eq 11 should result in approximately similar values of ΔS^* for both the k_3 and k_4 steps provided nucleophilic attack is the rate-determining step.

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Thermolysis of Vinyldiazomethanes as a Method for the Generation of Vinylcarbenes and a Comparison with Cyclopropene Photochemistry

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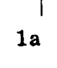
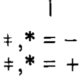
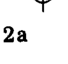
The pyrolysis of the vinyldiazomethanes **6** (X = H), **8**, **9**, and **10** gives mixtures of 3*H*-pyrazoles and cyclopropenes. The kinetics and product distribution for each case lead to a determination of the rate of vinylcarbene formation and, therefore, a direct determination of the relative carbene stabilities. The conclusion is that carbene **14** is more stable than **15**. These results are then used as a basis for a discussion of the carbenes generated from the singlet photochemistry of unsymmetrical cyclopropenes, **11**.

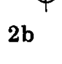
Introduction

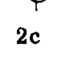
Vinvylcarbenes have attracted considerable interest recently as probable intermediates in a variety of related reactions. Examples include the pyrolysis of cyclopropenes,[1] the singlet photochemistry of cyclopropenes,[2] and the pyrolysis[3] and photolysis[4-6] of vinyldiazomethanes. As is well recognized, there are a variety of electronic states possible for vinylcarbenes: a nonplanar singlet and triplet corresponding to **1a** (the singlet could, depending on the substituents present, have ionic character **1b** or **1c**), planar singlets of the type **2b** (2π or σ^2)[7,8] and **2c** (4π or p^2), and both singlet and triplet corresponding to **2a** (3π or σp). Both molecular orbital calculations[7-9] and ESR results[6,10] indicate that triplet **2a** is the most stable of the states, but


1a


1b, ‡,* = −,+
c, ‡,* = +,−


2a


2b


2c

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