EFFECTS OF SILVER ION ON THE CARBOXYLATE-CATALYZED SOLVOLYSIS

OF 2,4-DINITROPHENYL-3-BUTENOATE

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A metal ion-catalyzed hydrolysis of α-amino ester has been already reported[1]. This reaction has received considerable attention because the reaction process can serve as a model for the catalytic role of a metal in some enzymatic hydrolyses. Breslow, et al. have reported the hydrolysis of a coordinating substrate[2], and proposed a model for the reaction mechanism of carboxypeptidase A[3]. In that case, a metal ion catalyzes the reaction via a rather strong interaction with nitrogen atom of the substrate.
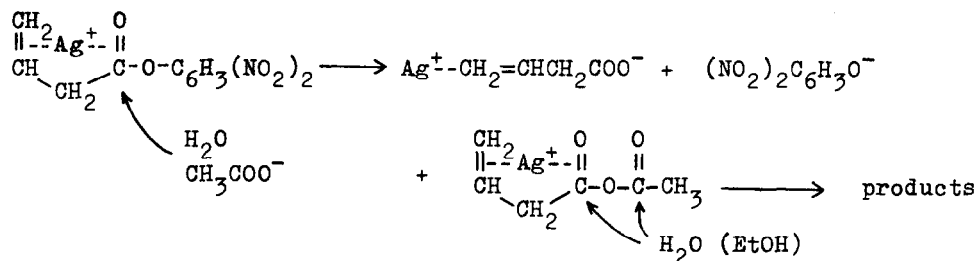
We found that the acetate ion-catalyzed 2,4-dinitrophenyl-3-butenoate (IV) solvolysis was enhanced by the presence of silver ion[4]. This observation might be the first case in which an esterolytic reaction was catalyzed by a metal via a weak interaction between the metal ion and C-C double bond of the ester. The reaction was followed spectrophotometrically, and the appearance of phenolate ion was found to follow the pseudo-first-order kinetics. The observed first-order rate constants (k_{obs}) were listed in Table I.

Table I. The observed rate constant (k_{obs}) for each esterolysis.

Ester	$k_{obs} \times 10^3$ (min^{-1})			
	$[Ag^+]=0$	(pH)	$[Ag^+]=0.01$ M	(pH)
$CH_3COO-DNP^*$ (I)	3.29	(5.29)	3.12	(5.26)
$CH_2=CHCOO-DNP$ (II)	1.38	(5.30)	1.38	(5.28)
$CH_3CH_2CH_2COO-DNP$ (III)	1.29	(5.29)	1.10	(5.27)
$CH_2=CHCH_2COO-DNP$ (IV)	12.30	(5.29)	45.80	(5.27)
$CH_2=CHCH_2CH_2COO-DNP$ (V)	2.96	(5.30)	2.99	(5.29)

DNP*= 2,4-dinitrophenyl-,   20 vol-% EtOH-water, $[CH_3COOK]$ = 0.15 M, $[AgNO_3]$ + $[KNO_3]$ = 0.05 M, $[CH_3COOH]$ = 0.02 M,   20°C.

A large k_{obs} of IV is due to an electron-withdrawing effect of vinyl group which exceeds the effect of steric hindrance.   Since other substrates are not affected at all by silver ion, it is clear that IV is not activated only by the interaction of the metal with the ester carbonyl.   It is well known that many olefinic compounds form complexes with silver ion. The mechanism of the acetate ion-catalyzed hydrolysis of 2,4-dinitrophenyl ester was investigated by using an isotopic tracer, which indicated the formation of anhydride intermediate[5]. Accordingly, we postulate the following reaction:

$$CH_2 \quad 0$$
$$\|\text{--}\overset{\cdot}{A}g^{+}\text{--}\| \quad \quad \quad \quad \quad$$
$$CH\diagdown_{CH_2}C\text{-}O\text{-}C_6H_3(NO_2)_2 \longrightarrow Ag^{+}\text{--}CH_2=CHCH_2COO^{-} + (NO_2)_2C_6H_3O^{-}$$

$$\searrow H_2O \quad \quad \quad \quad + \quad \quad CH_2 \atop \|\text{--}\overset{\cdot}{A}g^{\pm}\text{--}\| \quad \|$$
$$CH_3COO^{-} \quad \quad \quad \quad \quad CH\diagdown_{CH_2}C\text{-}O\text{-}C\text{-}CH_3 \longrightarrow products$$
$$\searrow H_2O \text{ (EtOH)}$$

where the carbonyl is activated by the coordination.   That the solvolysis of V was not enhanced by the silver ion could be explained as follows: the carbonyl can not participate in the coordination because of the hindrance effect of two methylene groups.   The reason why the silver ion has no effect for II is that the argentation constant of conjugated double bond is very small, for example, the first argentation constant of crotonic acid is 9×10^{-3} M^{-1} in water[6].

The simplest scheme for incurtion of the charge-transfer complex is

$$S \xrightarrow{k_0} products$$
$$S + Ag^{+} \underset{k_2}{\overset{K}{\rightleftharpoons}} SAg^{+} \xrightarrow{k_1} products$$
$$S + C \xrightarrow{k_2} products + C$$
$$SAg^{+} + C \xrightarrow{k_3} products + C$$
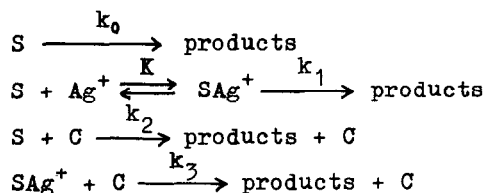
where S, C and SAg^{+} is a substrate, carboxylate ion and the complex, respectively.   In the case of $[Ag^{+}]_f \gg [S]_f$, where the subscript f denotes a feed concentration, the rate is

$$k_{obs} = \frac{k_0 + k_1 K [Ag^+]_f + k_2 [C] + k_3 K C [Ag^+]_f}{1 + K [Ag^+]_f}$$

where k_{obs} is first-order in the carboxylate ion as shown in Figure 1. Furthermore, Figure 2 shows a linear relationship between k_{obs} and $[Ag^+]_f$ under a limitted condition, $K [Ag^+]_f \ll 1$.
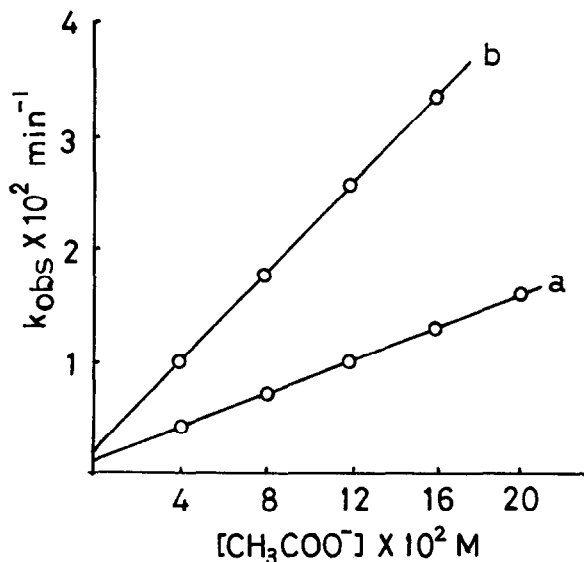

Figure 1. Acetate ion-catalyzed solvolysis of 2,4-dinitrophenyl 3-butenoate: 20 vol % EtOH-water, $[CH_3COOK] : [CH_3COOH] = 1:8$, $[CH_3COOK] + [KNO_3] = 0.20$ M, $20°C$. a: $[Ag^+] = 0$, pH 5.50-5.54. b: $[Ag^+] = 0.005$ M, pH 5.51-5.56.
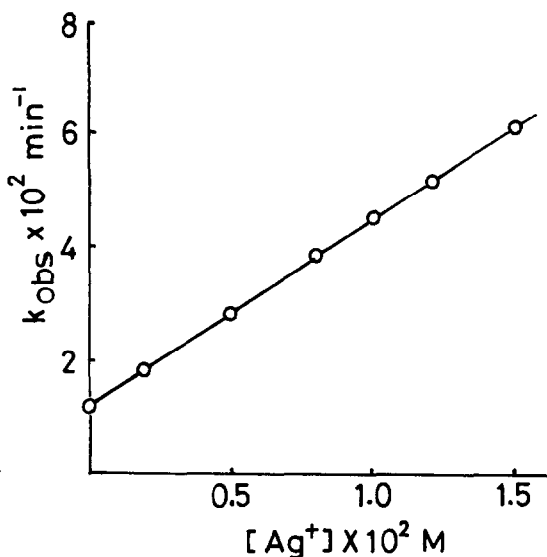
Figure 2. The effects of silver ion in the acetate ion-catalyzed solvolysis of 2,4-dinitrophenyl 3-butenoate: 20 vol % EtOH-water, $[CH_3COOK] = 0.15$ M, $CH_3COOH = 0.02$ M, $[AgNO_3] + [KNO_3] = 0.05$ M, $20°C$, pH 5.26-5.29.

Since the argentation constants of oxygen-containing olefines in water are usually small $(0.19 - 12.0 \text{ M}^{-1})$[6], the downward deviation from this linearity is calculated as 10% when $K = 10 \text{ M}^{-1}$, and 1% for $K = 1.0 \text{ M}^{-1}$ at $[Ag^+] = 0.01$ M. With the latter constant one can obtain a linearity within an experimental error Therefore, the linear relationship shown in Figure 2 suggests that the latter constant is fit for this case, i.e. $K \lesssim 1.0$. An attempt to see a downward cur-

vature at higher $[Ag^+]$ was unsuccessful because of low solubility of the silver acetate.

From the slopes and intercepts in Figure 1, each rate constant was calculated: $k_0 = 1.2 \times 10^{-3}$ min^{-1}, $k_1 = 0.16$ min^{-1}, $k_2 = 7.7 \times 10^{-2}$ M$^{-1} \cdot$min^{-1}, $k_3 = 25.7$ M$^{-1} \cdot$ min^{-1} for $K = 1.0$ M^{-1}. From these rate constants, it can be said that the coordinating substrate is 330 times as reactive as the free one for the acetate ion-catalyzed reaction. If the argentation constant is smaller than unity, the observed rate constants would originate from much larger reactivity of the metal complex.

Other metal ion such as Cu^{++}, Co^{++}, Ni^{++}, Zn^{++} and Cd^{++} did not affect the acetate ion-catalyzed solvolysis of olefinic ester because no complexation occurrs[6].

References and Notes

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