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Hydrolysis of p-Nitrophenylacetate in Micellar Solution by N,N'-Dichloroisocyanuric Acid Sodium Salts (DCI)

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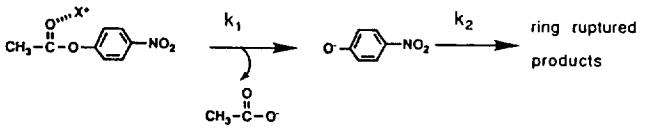
As a mimic system of enzyme reaction and as a model system of destruction of nerve agents, the hydrolysis reaction of p-nitrophenylacetate (PNPA) or p-nitrophenyl-diphenylphosphate (PNPDPP) in micellar or microemulsion system has been extensively investigated.[1]

However, the hydrolysis of PNPA catalyzed by a N-chloro compound has not yet been investigated. We now report some interesting results in the hydrolysis reactions of PNPA by N,N'-dichloroisocyanuric acid sodium salts (DCI) in micellar phase (Table 1). In the nonmicellar phase, DCI gave a 240-fold rate enhancement for the hydrolysis of PNPA over the system without DCI, which means that DCI itself catalyzes the hydrolysis reaction. The degree of the catalyzing effect of DCI was even larger than that of CTABr or 16-OH micellar system. In the micellar system without DCI, 16-OH showed a slightly higher reactivity than CTABr. This result was due to the hydroxy functional group of 16-OH.[2]

Table 1. Rate Constants for the Hydrolysis Reaction of PNPA with N,N'-Dichloroisocyanuric Acid Sodium Salts (DCI)[a]

Surfactant	Catalyst	k_1 (s^{-1})	k_2 (s^{-1})	k_1^{cat} (1, s^{-1}, mol^{-1})	k_1/k_0
CTABr[b]	DCI	5.1×10^{-2}	1.1×10^{-2}	42.5	2040
16-OH[b]	DCI	1.1×10^{-2}	2.2×10^{-3}	9.2	440
CTACl	DCI	7.6×10^{-3}		6.3	300
none	DCI	6.1×10^{-3}		5.1	240
16-OH	none	6.7×10^{-4}			27
CTABr	none	1.0×10^{-4}			4
none	none	2.5×10^{-5}			1

[a] Condition : 0.05 M phosphate buffer, pH 8.0, 25± 0.1℃, [DCI]= 1.2×10^{-3} M, [PNPA]=4×10^{-5} M, [Surfactant]=4×10^{-3} M. Calculated by pseudo first-order kinetics for the release of p-nitrophenolate ion, monitored at 400 nm. Reproducibilities of the rate constrants are <± 5%. [b] Calculated by series first-order kinetics equation.[2]



X^+: Halogen species

Scheme 1.

However, when DCI was used in the micellar system CTABr revealed superior results in the hydrolysis of PNPA than 16-OH did. In CTABr and 16-OH micellar system, the hydrolysis product, p-nitrophenolate was rapidly transformed to other unknown compounds which did not have λ_{max} at 400 nm. It was supposed that the series of decomposition reactions of p-nitrophenolate would occur very rapidly.[4,5] As a result, the hydrolysis reaction of PNPA in CTABr and 16-OH micellar solution showed a typical series first-order kinetics (Scheme 1).

On the other hand, the same reaction condition in CTACl micellar solution did not give typical series first-order kinetics, but simple first-order kinetics. The decay rate of p-nitrophenolate was almost ignorable within 20 min. Moreover, the rate for the hydrolysis reaction of PNPA was 6.7 times slower than in CTABr and even comparable with that of nonmicellar DCI. This means that the counter ions should play an important role in the hydrolysis of PNPA as well as in the breakdown of p-nitrophenolate. As far as we know, this will be the first report that demonstrates the importance of the counter ion of surfactant in catalytic reactions of micellar system.

When DCI was added in CTABr micellar solution, strong absorbance appeared at 264 nm, which was supposed to be the absorbance of Br_3^- ion (λ_{max}, lit[6] 266 nm, ε, 35000 M^{-1} cm^{-1}). The formation of Br_3^- ion[7] can be easily conjectured if the reaction between DCI and bromide ion yielded BrCl (Scheme 2), which are equilibrated with various bromine species according to the following equations.[8] The bromine species such as BrCl or Br_3^- ion were known to be more reactive than N-chloro compounds in various oxidation reac-

	Eqilibrium constants
$BrCl+H_2O \rightleftharpoons HOBr+H^+ +Cl^-$	2.95×10^{-5}
$HOBr \rightleftharpoons OBr^- +H^+$	2.00×10^{-9}
$HOBr+H^+ +Br^- \rightleftharpoons Br^2+H_2O$	2.27×10^{8}
$Br_2+Br^- \rightleftharpoons Br_3^-$	17

Scheme 2.

tions.[9] Hydrolysis reaction was accelerated by these bromine species which might act as a Lewis acid catalyst on the carbonyl group in the hydrolysis of PNPA.

However, in CTACl micellar solution the same reaction between N-chloro compound and ion yielded chlorine and various chlorine species, which were less reactive than bromine species[9]. The low reactivity of DCI in 16-OH micellar system was expected as the result. It may be due to the side reaction between the hydroxy group of 16-OH and DCI which might yield alkylhypochlorite. Its relative reactivity might be less than that of bromine species. This side reaction may even decrease the amount of active bromine species. In conclusion, the difference in reactivity of the catalytic hydrolysis of PNPA by DCI in various cationic micellar system was derived from the formation of different halogen species during the hydrolysis reactions. Similar studies of the effect of this halogen species on other organic reactions will be followed soon.

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4. The decomposition of p-nitrophenolate was also accelerated in CTABr micellar solution with the same amount of DCI. In separate experiments, when 2.5 eq of DCI was reacted with 72 mM of p-nitrophenolate in 4×10^{-3} M CTABr solution, only negligible amount of 2,6-dibromo-4-nitrophenol was able to be isolated.
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The Reaction of Carbenes Formed by Decomposition of the Diazo Group in β- or γ-Position in 4-Alkylthioazetidin-2-one Derivatives

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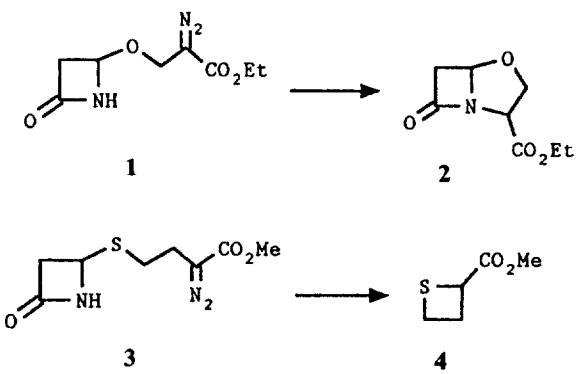
Oxonium,[1] ammonium[2] or sulfonium[3] ylide intermediates were presumed in carbene reactions and these intermediates should be very useful for the construction of organic compounds. Usually the empty orbital of carbenes interacts with the unshared electron pair of heteroatoms to form ylides. These reactive intermediates may abstract a nearby proton to induce sigmatropic rearrangements and may be transformed to stabilized products. The oxonium[1] and the ammonium[2] ylides were used for sigmatropic rearrangements and for the formation of carbapenems. The carbenes formed at the γ-position on the side chain at C-4 of azetidin-2-ones react easily with the nitrogen atoms of the β-lactam rings to give ammonium ylides which are converted to carbapenems through the rearrangement of the proton on the nitrogen atom.[2] Similarly the sulfur atom readily reacts with various carbenes to form sulfonium ylides.[4] The intermediates were adapted in the formation of new C-glycoside bonds.[3] The carbene-metal complexes, carbenoids, can be easily produced at low temperature when diazo compounds are reacted with metal powder or metal salts, and they are very selective in reactions.[5] During the course of our study on the synthesis of penem antibiotics, we have examined the reaction of carbenes formed by different ways and wish to report the result in this communication.

4-(2-Diazo-2-ethoxycarbonylethoxy)azetidin-2-one (**1**) was obtained from 4-acetoxyazetidin-2-one by reacting with 2-diazo-3-hydroxy propionate which was prepared from L-serine. 4-(2-Diazo-2-methoxycarbonylpropylthio)azetidin-2-one (**3**), and 4-(2-diazo-2-ethoxycarbonylethylthio)azetidin-2-one (**5**) were obtained by diazotization,[6] with isoamyl nitrite, of the amino compounds produced from 4-acetoxyazetidin-2-one by reaction with DL-homocysteine methyl ester hydrochloride[7] and L-cysteine ethyl ester hydrochloride, respectively.



Scheme 1.