

not significantly reduced upon replacing CH₄ with CD₄ in the feed mixture, indicating that breaking of the C-H bond of CH₄ molecule is a fast step over these catalysts. This means that the reaction between surface carbon species and the oxidant species (surface oxygen or surface carbonates) would be a rate-determining step over these catalysts.

Consequently, this study demonstrates that metallic Ni sites have strong reactivity on methane, while alkaline metal promoters on carbon dioxide. The retardation of coke deposition on KNiCa/ZSI catalyst is attributed to the abundantly adsorbed CO₂ species. Over the Ni/ZSI catalyst, the surface without potassium and calcium oxides is more reactive with methane. On the other hand, the surface having such promoters is more eligible toward the adsorption and the dissociation of carbon dioxide. Since coke deposition is mainly caused by methane decomposition, the catalyst surface covered with the adsorbed CO₂ or the reactive oxygen species from the dissociation of CO₂ can prevent from coke deposition. The addition of alkaline metal promoters also seems to greatly suppress the activity of supported Ni catalyst for the direct decomposition of methane. In the dry reforming, each dissociation of CO₂ and CH₄ is the initial step to produce CO and H₂, respectively. However, the surface reactions between the adsorbed carbon (Ni-C(s)) and the oxygen (Ni-O(s)) species into carbon monoxide is plausibly proposed as a rate-determining step in this reaction. This step leads to producing the stoichiometric ratio of H₂/CO as an unity in dry reforming and consequently metallic nickel species can be regenerated through the elimination of surface carbon species. Especially, the oxidation step of surface carbon with surface oxygen or sur-

face carbonates over KNiCa/ZSI catalyst is proved to be helpful to eliminate surface carbon species effectively.

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Chloroformyloxylation of Cinnamic Acid and Cinnamitrile Derivatives by Using the HCl/DMF/Potassium Peroxymonosulfate (Oxone) System

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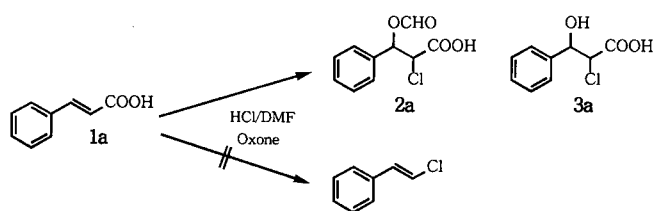
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Halofunctionalization of olefins toward synthetically useful substrates such as halohydrins, β -haloethers, and β -haloesters has received much attention.¹ These compounds were generally prepared from the combination of positive halogen source and appropriate nucleophile sources such as water, alcohols, or carboxylic acids.² The chloroformyloxylation achieved by the attack of *N,N*-dimethylformamide and 1,2-acetoxychlorination by *N,N*-dimethylacetamide as a nucleophile has been studied.³

In the course of our recent studies on the reaction of various kinds of organic substrates with HCl/DMF/Oxone (or *m*-CPBA) system,^{3a-d,4} we presumed to examine the reaction of α,β -unsaturated carboxylic acids or nitriles. In the reactions our interest was focused on whether chloroformyloxylation

derivatives were formed as in the case of α,β -unsaturated esters⁴ or β -chlorostyrene derivatives could be generated via the Hunsdiecker type reaction mechanism⁵ as exemplified in Scheme 1. Thus, we examined the reaction with some cinnamic acid and cinnamitrile derivatives, and describe the preliminary results in this report.

The reaction of cinnamic acid (**1a**) with this reagent system afforded a mixture of chloroformyloxylation derivative (**2a**, 40%) and chlorohydrin derivative (**3a**, 25%). In the reaction mixtures, we could not observe β -chlorostyrene, the Hunsdiecker reaction product. In the cases of 4-chlorocinnamic acid (**1b**) and 4-methylcinnamic acid (**1c**) the corresponding chloroformyloxylation derivatives were obtained as the major product, and we could observe trace amounts



Scheme 1

Table 1. The reaction of cinnamic acid and cinnamitrile derivatives with HCl/DMF/Oxone system

Starting material	Products (% yield)
	complex mixtures
	+ 1f (35%)
	+ 1g (52%)

of chlorohydrins on tlc. Interestingly in the case of 3-nitrocinnamic acid (**1d**), chlorohydrin derivative **3d** was obtained as the sole isolable product, presumably generated *via* hydrolysis of the formate. With cinnamitrile (**1f**) the reactivity was reduced, and the starting material remained even after 24 h at room temperature. However, we could obtain the desired chloroformylated derivative **2f** in low yield (26%) together with some α -chloro cinnamitrile (18%).⁴ When the α -position is substituted with phenyl group as in **1e** and **1g**, the reaction was not completed and many products were obtained to make separation impossible.

The mechanism of the reaction can be explained by the same way as that in the previous reports.^{3b-c} According to the reaction mechanism, the products from the chloroformyloxylated must have trans configurations.^{3e-f}

General procedure of chloroformyloxylated is as follows: To a stirred solution of **1a-g** (10 mmol) in HCl/DMF solution (10 mL, 3 M solution, 30 mmol of HCl) was added Oxone (9.2 g, 30 mmol) at room temperature and the reaction mixture was stirred for 3 h. The reaction mixture was poured into cold water (100 mL) and extracted with ether (2 \times 100 mL). The organic layer was washed with water (100 mL) and brine (100 mL), dried with MgSO₄, evaporated to afford a crude product mixture. Column chromatography on silica gel (hexane followed by hexane/ether, 19:1) afforded pure **2-5**. They were characterized by their ¹H NMR, ¹³C NMR, and/or mass spectra.

As discussed in this report α,β -unsaturated carboxylic acids could be converted to the corresponding chloroformyloxylated derivatives and/or their hydrolyzed chlorohydrin derivatives depending on the substrate. In the case of cinnamitrile derivatives the reaction was sluggish and gave mixtures of products. In the aforementioned reaction conditions the Hunsdiecker reaction product was not obtained. The study on the reaction mechanism and further applications to other C=C double bond systems such as vinyl sulfones are underway.

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