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A Novel Synthesis of Alkyl Chloroformate in the Gas Phase by Palladium-Catalyzed Reaction Using XCl (X=H or NO), CO, and Alkyl Nitrite

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A novel synthesis of chloroformate was developed by palladium-catalyzed reaction of XCl (X=H or NO), CO, and alkyl nitrite in the gas phase. When $PdCl_2/\gamma$-Al_2O_3 or $PdCl_2/SiO_2$ was used as a catalyst, chloroformate was produced in good yield and with high selectivity. The reaction temperature had a strong influence on the formation rate of chloroformate, and its selectivity drastically depended on the nitrite/chloride ratio. When the nitrite/chloride ratio was less than 2, the selectivity of chloroformate was almost 100%. Dependence of the formation rate on the concentrations of CO and methyl nitrite was also examined.

Organic synthesis using the carbonylation reaction is receiving much attention and is used in many industrial processes. Especially, palladium-catalyzed reactions using alkyl nitrite, not only as a substrate but as a reoxidation reagent of palladium, have been widely explored and a variety of organic compounds are now produced by Ube Industries such as dimethyl carbonate,[1—3] dibutyl oxalate,[4] and 3,3-dimethoxypropionitrile,[5] a key intermediate of vitamin B_1 synthesis.[6]

Chloroformates are now produced by the reaction between alcohols and phosgene, which is formed by the reaction Cl_2 with CO over an active charcoal catalyst, according to Eqs. 1 and 2.[7]

$$CO + Cl_2 \rightarrow COCl_2 \tag{1}$$

$$COCl_2 + ROH \rightarrow ClCOOR + HCl \tag{2}$$

Because of the extremely high toxicity of phosgene, however, it is not a good method to produce chloroformate on an industrial scale. Furthermore, it is difficult to remove HCl completely from the product.

It has been reported that the reaction of $PdCl_2$ and LiCl with CO in ethanol gave ethyl chloroformate and two by-products.[8] Synthesis of perfluoroalkyl chloroformates by direct carbonylation of perfluoroalkyl hypochlorites has also been reported.[9] Recently, Giannoccaro have reported chloroformate synthesis by palladium bis(methoxycarbonyl) complex and $CuCl_2$.[10] But these methods could not be applied to the catalytic synthesis of the usual alkyl chloroformates.

Quite recently, we have reported the novel synthesis of alkyl chloroformates by a palladium-catalyzed reaction using Cl_2, CO, and alkyl nitrite.[11] During our research it was found that HCl and NOCl can be used in place of Cl_2. We report here a novel synthesis of alkyl chloroformates in the gas phase by a palladium-catalyzed reaction using XCl (X=H or NO), CO, and alkyl nitrite. This method is safe because it does not require highly toxic materials like phosgene. Moreover, the NO produced can be used to reproduce methyl nitrite by the reaction with methanol and oxygen according to Eq. 3.

$$4NO + O_2 + 4CH_3OH \rightarrow 4CH_3ONO + 2H_2O \tag{3}$$

Experimental

1. Materials. Methyl nitrite was prepared from controlled amounts of NO and O_2 by passing through methanol. Hydrogen chloride was purchased from Nippon Sanso Co., Ltd. as 1% or 10% standard gas (N_2 as the balance). Other gases are also purchased and used without further purification. One wt% $PdCl_2/\gamma$-Al_2O_3 catalyst was purchased from N. E. Chemcat. One wt% $PdCl_2/SiO_2$ catalyst was prepared using aqueous H_2PdCl_4 solution and silica gel purchased from Fuji Davison Co., Ltd.

2. Apparatus and Procedures. The apparatus for the experiment is shown in Fig. 1. A reaction tube (13 mmϕ) was filled with a required amount of catalyst, and fixed vertically. Then hot silicone oil was pumped through the jacket around the reaction tube to keep the catalyst at the required temperature. From the top of the reaction tube, reactant gas, which has been passed through a cold trap kept under 5 °C, was introduced at the required flow rate. After it passed through the catalyst at atmospheric pressure, the

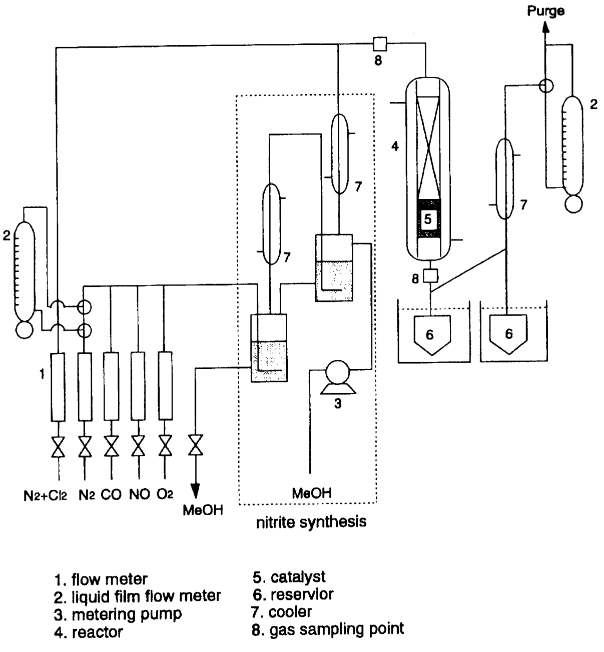

Fig. 1. Apparatus for the experiments.

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Table 1. Formation Rate of Methyl Chloroformate by Using HCl[a)]

Run	Reactant gas concentration (in) CO	MN[b)]	NO	MeOH	HCl	Formation rate MCF[b)]	By-products
	vol%					$mg\,h^{-1}$	
1	8.4	0.0	0.0	19.0	0.5	0	No reaction
2	6.1	6.6	2.3	8.1	0.5	600	DMC[b)] 330 $mg\,h^{-1}$
3	3.7	1.9	3.9	6.8	1.0	1225	DMC[b)] 7 $mg\,h^{-1}$

a) Reaction conditions 1% $PdCl_2/Al_2O_3$ 2 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$.
b) MN: Methyl nitrite, MCF: Methyl chloroformate, DMC: Dimethyl carbonate.

product gas was analyzed by gas chromatography. Typical reaction conditions are as follows.

Pressure: 1 atm; Gas flow rate: 30000 $cm^3\,h^{-1}$; Catalyst: 1% $PdCl_2/\gamma\text{-}Al_2O_3$ or 1% $PdCl_2/SiO_2$; Catalyst volume: 1—2 cm^3; Temperature: 30—130 °C; CO concentration: 4—10 vol%; XCl concentration: 0.5—1 vol%; Nitrite/Cl molar ratio: 2—10; Balance gas: N_2

3. Analysis. Analytical conditions of gas chromatography are as follows.

Methyl Nitrite: Column: Chromosorb 101 (60—80 mesh), 2 m; Column temperature: 50 °C; Carrier gas: He 1.2 $kg\,cm^{-2}$; Detector: FID.

CO and NO: Column: Chromosorb 101 0.3 m+ Molecular sieve 5A 1.7 m; Column temperature: 50 °C; Carrier gas: He 1.6 $kg\,cm^{-2}$; Detector: TCD.

Dimethyl Carbonate and Methyl Chloroformate: Column: 20% PEG-20M/Chromosorb WAW (80—100 mesh), 3 m; Column temperature: 60 °C; Carrier gas: He 0.4 $kg\,cm^{-2}$; Detector: FID.

Results and Discussion

Synthesis of Chloroformate Using HCl. By the reaction of HCl, CO, and methyl nitrite in the presence of palladium catalyst, methyl chloroformate (MCF) was found to be formed in good yield and highly selectively. In this reaction HCl can be converted to methyl chloroformate completely under the best reaction conditions as shown in Table 1 (Run 3, yield 100%, selectively 99.4%). Moreover, the NO produced can be used to reproduce methyl nitrite by the reaction with methanol and oxygen as Eq. 3.

On the other hand, methyl chloroformate was not formed by the reaction between HCl, CO, and methanol (Table 1, Run 1). This result shows that nitrite is indispensable for the formation of chloroformate.

Synthesis of Chloroformate Using NOCl. It is well known that HCl and methyl nitrite reach an equilibrium between NOCl and methanol.[12)]

$$HCl + CH_3ONO \longleftrightarrow CH_3OH + NOCl \qquad (4)$$

The equilibrium is established instantly to increase the concentration of NOCl at high temperature. For this reason, it can be considered that chloroformate can be formed as the following equation.

$$NOCl + CO + CH_3ONO \rightarrow ClCOOCH_3 + 2NO \qquad (5)$$

When NOCl was used instead of HCl, similar results were obtained (Table 2, Runs 2 and 3). This supports that consideration. Moreover, the reaction between NOCl, CO and methanol also gave methyl chloroformate (Table 2, Run 1). It seems that methyl nitrite, which is formed from NOCl and methanol, reacts with CO and NOCl.

Verification of Reaction Path. As described above, it was found that methyl chloroformate is formed from HCl, CO, and methyl nitrite in good yield. First, the chlorine balance was measured to verify the reaction path. When HCl was introduced at a rate of 9.8 $mmol\,h^{-1}$ to 2 cm^3 of the catalyst (1% $PdCl_2/\gamma\text{-}Al_2O_3$) under the reaction conditions of gas flow rate 30000 $cm^3\,h^{-1}$, temperature 60 °C, methyl nitrite 3.3 vol%, CO 4.2 vol%, methanol 7.8 vol%, and NO 1.9 vol%, methyl chloroformate was found to be formed at a rate of 8.8 $mmol\,h^{-1}$. We concluded from this result that the molar ratio of chloroformate produced to HCl introduced is 1. Secondly, the mass balance of the reactants and the products was measured. The results are shown in Table 3. Though the mass balance was not very good, chloroformate was formed at about the same amount as the consumed nitrite. From these results, the reaction seems to proceed according to Eqs. 4 and 5.

Temperature Dependence. It was found that the reaction is very much influenced by the reaction temperature. The results are shown in Fig. 2. The formation rate of chloroformate is highest around 60 °C, and decreases as the temperature becomes higher. Chloroformate decomposes to chloromethane and CO_2 at high temperatures on Al_2O_3 (Eq. 6)

Table 2. Formation Rate of Chloroformate by Using NOCl[a)]

Run	Reactant gas flow rate (in) CO	MN[b)]	NOCl	Product flow rate MCF[b)]
	$mmol\,h^{-1}$			$mmol\,h^{-1}$
1	41.8	5.1[c)]	21.3	4.4
2	40.2	30.3[d)]	2.0	1.7
3	48.8	24.4[d)]	7.6	7.5

a) Reaction conditions 1% $PdCl_2/Al_2O_3$ 2 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$, MeOH 7—12 vol%.
b) MN: Methyl nitrite, MCF: Methyl chloroformate.
c) MN was formed by the reaction between NOCl and MeOH. d) MN was added.

Table 3. Mass Balance of Reactants and Products[a)]

Reactant gas flow rate (in/out(consumed amount)) CO	MN	Product flow rate (in/out(produced amount)) NO	MCF
$\mathrm{mmol\,h^{-1}}$		$\mathrm{mmol\,h^{-1}}$	
36.1/23.3 (12.8)	27.6/19.1 (8.5)	25.7/40.7 (15.0)	0.0/9.3 (9.3)

a) Reaction conditions 1% $PdCl_2/Al_2O_3$ 2 $\mathrm{cm^3}$, 60 °C, gas flow rate 30000 $\mathrm{cm^3\,h^{-1}}$, HCl: 0.8 vol% (9.8 $\mathrm{mmol\,h^{-1}}$), MeOH: 7.3 vol% (89.0 $\mathrm{mmol\,h^{-1}}$).

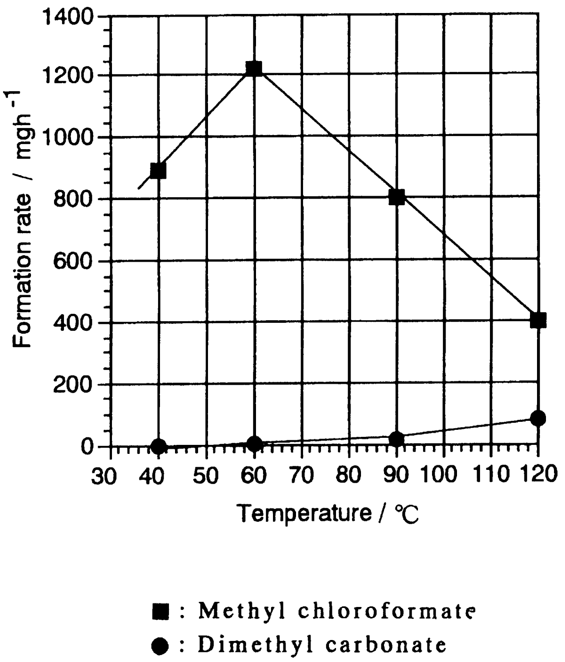


Fig. 2. Formation rate of products vs. reaction temperature. Reaction conditions: Pressure: 1 atm; Gas flow rate: 30000 $\mathrm{cm^3\,h^{-1}}$; Catalyst: 1% $PdCl_2/Al_2O_3$; Catalyst volume: 2 $\mathrm{cm^3}$; CO: 3.5—4.0 vol%; HCl: 1 vol%; methyl nitrite: 1.5—2 vol%; NO: 2—3 vol%; MeOH: 5—8 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

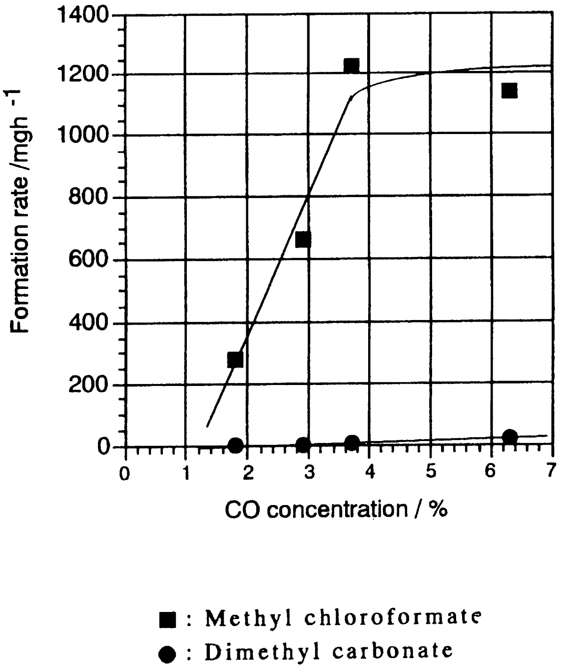


Fig. 3. Formation rate of products vs. CO concentration. Reaction conditions: Pressure: 1 atm; Temperature: 60 °C; Gas flow rate: 30000 $\mathrm{cm^3\,h^{-1}}$; Catalyst: 1% $PdCl_2/Al_2O_3$; Catalyst volume: 2 $\mathrm{cm^3}$; HCl: 1 vol%; methyl nitrite: 1—2 vol%; NO: 2—4 vol%; MeOH: 4—8 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

$$ClCOOCH_3 \rightarrow CH_3Cl + CO_2 \qquad (6)$$

At temperatures higher than 60 °C, dimethyl carbonate (DMC) begins to form. As already reported, similar behavior has been observed when Cl_2 was used.[11)]

Effects of Reactant Concentrations. The concentrations of CO and methyl nitrite also influenced the formation rate of products. The results are shown in Figs. 3 and 4, respectively. The formation rate of chloroformate depends on the concentration of CO almost by first order. When the concentration of nitrite is lower than twice of HCl concentration, the formation rate depends on the concentration of methyl nitrite also by first order.

Effects of Nitrite/Chloride Molar Ratio. It was also found that the nitrite/chloride ratio influences the selectivity of methyl chloroformate very drastically as shown in Fig. 5. Selectivity was defined as Eq. 7.

$$\text{MCF selectivity (\%)} = \frac{\text{MCF }(\mathrm{mmol\,h^{-1}}) \times 100}{\text{MCF }(\mathrm{mmol\,h^{-1}}) + \text{DMC }(\mathrm{mmol\,h^{-1}})} \qquad (7)$$

Interestingly, when the nitrite/Cl molar ratio is less than 2, selectivity is almost 100%. As the concentration of nitrite increases relative to HCl concentration, selectivity decreases because of the formation of carbonate. As already reported,[11)] almost the same results were obtained when Cl_2 was used.

Mechanism. A mechanism accounting for the formation of chloroformate is proposed in Scheme 1. $PdCl_2$ reacts with CO and methyl nitrite to form a methoxycarbonyl complex $[Pd^{IV}Cl_2(COOCH_3)(NO)]$. A similar type of complex has been isolated by Bréchot as a phos-

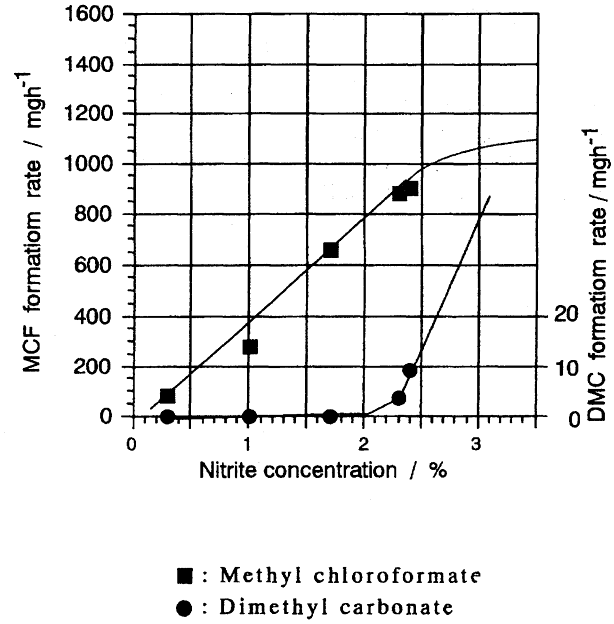


Fig. 4. Formation rate of products vs. methyl nitrite concentration. Reaction conditions: Pressure: 1 atm; Temperature: 60 °C; Gas flow rate: 30000 cm^3 h^{-1}, Catalyst: 1% $PdCl_2/Al_2O_3$; Catalyst volume: 2 cm^3; HCl: 1 vol%; CO: 1.8—3 vol%; NO: 2—4 vol%; MeOH: 6—9 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

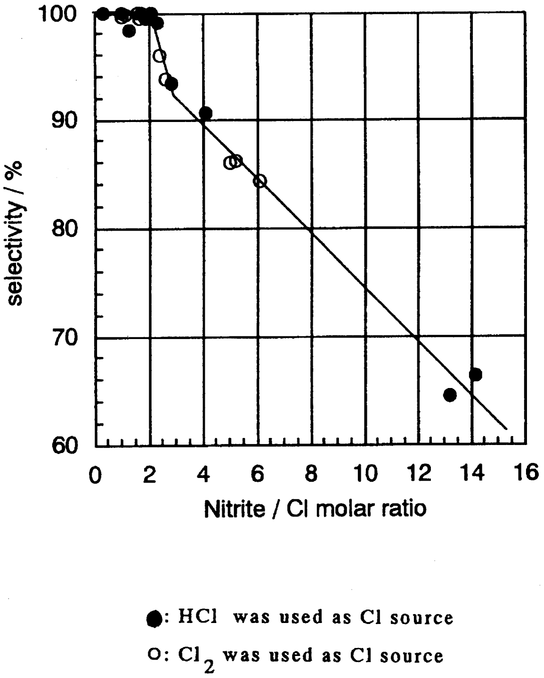
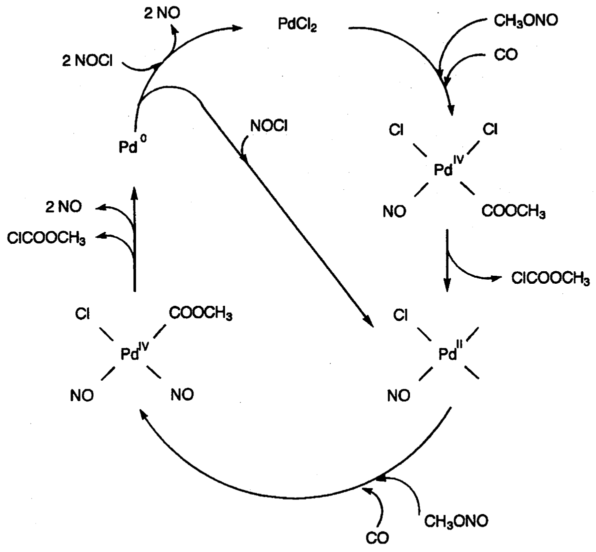


Fig. 5. Selectivity of methyl chloroformate vs. nitrite/Cl molar ratio. The results when HCl was used are indicated as closed circles. Open circles correspond to the results when Cl_2 was used.



Scheme 1. Proposed catalytic mechanism for the formation of chloroformate.

phine adduct [$Pd^{IV}Cl_2(COOBu)(NO)(PPh_3)$] as an active intermediate of catalytic oxidative carbonylation of olefins.$^{13)}$ From the complex, methyl chloroformate is produced through reductive elimination to form an unsaturated complex [$Pd^{II}(NO)Cl$], which reacts with CO and methyl nitrite to form another methoxycarbonyl complex. Then additional chloroformate is produced together with NO to form Pd. Pd^0 is reoxidized by NOCl to reproduce $PdCl_2$ or unsaturated complex [$Pd^{II}(NO)Cl$]. This mechanism is consistent with the fact that high nitrite concentrations cause the formation of carbonate. It can be explained that an excess amount of nitrite reacts with methoxycarbonyl complex [$Pd^{IV}ClX(COOCH_3)(NO)$] (X=Cl or NO) to produce carbonate. When the nitrite/chloride molar ratio is less than 2, all of the nitrite can be converted to a methoxycarbonyl group on Pd and to chloroformate by successive reductive elimination with Cl.

Another Support. Finally, when 2 cm^3 of 1% $PdCl_2/SiO_2$ was used as the catalyst, methyl chloroformate was formed at a rate of 935 mg h^{-1} under the reaction conditions of gas flow rate 30000 cm^3 h^{-1}, temperature 90 °C, HCl 1 vol%, methyl nitrite 2.5 vol%, CO 4.5 vol%, methanol 7.7 vol% and NO 1.5 vol%.

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References

1) Japan Patent (kokoku) 62-8113 (1987).
2) Japan Patent (kokai) 3-141243 (1991).
3) Japan Patent (syutugan) 4-296971 (1992).
4) Japan Patent (kokoku) 56-12624 (1981).
5) Japan Patent (kokoku) 61-45975 (1986).

6) K. Nishihira, M. Nakai, Y. Chiba, S. Yamamoto, and M. Yamashita, *Kagakukogaku*, **55**, 433 (1991).

7) "12093 No Kagaku-Syohin," Kagakukogyo Nippo-sha, Tokyo (1993), p. 393.

8) M. Graziani, P. Uguagliati, and G. Carturan, *J. Organomet. Chem.*, **27**, 275 (1971).

9) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, **9**, 723 (1969).

10) P. Giannoccaro, N. Ravasio, and M. Aresta, *J. Organomet. Chem.*, **451**, 243 (1993).

11) M. Murakami and N. Manada, *Bull. Chem. Soc. Jpn.*, accepted.

12) J. A. Leermakers and H. C. Ramsperger, *J. Am. Chem. Soc.*, **54**, 1837 (1932).

13) P. Bréchot, Y. Chauvin, D. Commereuc, and L. Saussine, *Organometallics*, **9**, 26 (1990).