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A Novel Synthesis of Alkyl Chloroformate in the Gas Phase by a Palladium-Catalyzed Reaction Using Cl_2, CO, and Alkyl Nitrite

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A novel synthesis of chloroformate was developed by a palladium-catalyzed reaction of Cl_2, CO, and alkyl nitrite in the gas phase. When $PdCl_2/\gamma\text{-}Al_2O_3$ or $PdCl_2/SiO_2$ was employed as a catalyst, chloroformate was formed in good yield and with high selectivity. It was confirmed that the reaction did not proceed via phosgene. Cl_2 is directly converted to methyl chloroformate. No HCl was formed. The reaction temperature greatly influenced the formation rate of chloroformate, and its selectivity depended on the nitrite/Cl molar ratio very drastically. The 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 being applied to many industrial processes. Especially, palladium-catalyzed reactions using alkyl nitrite, not only as substrate, but as re-oxidation reagent of palladium, have been widely explored, and a variety of organic compounds are now being produced by Ube Industries, such as dimethyl carbonate,[1—3] dibutyl oxalate,[4] and 3,3-dimethoxypropionitrile,[5] which is a key intermediate of vitamin B_1.[6]

Chloroformates are currently produced by the reaction of phosgene, which is formed by the reaction of Cl_2 with CO over an active charcoal catalyst, with alcohol according to

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

and

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

Because of the extremely high toxicity of phosgene, it is not a favorable method to produce chloroformate on the industrial scale. Furthermore, it is difficult to completely remove HCl from the product. It has been reported that the reaction of $PdCl_2$ and LiCl with CO in ethanol gives ethyl chloroformate and two by-products.[7] The synthesis of perfluoroalkyl chloroformates by direct carbonylation of perfluoroalkyl hypochlorites has also been reported.[8] Recently, Giannoccaro et al. have reported on chloroformate synthesis using the palladium bis(methoxycarbonyl) complex and $CuCl_2$.[9] However, these methods could not be applied to the catalytic synthesis of the usual alkyl chloroformates.

We report here a novel synthesis of alkyl chloroformate in the gas phase by a palladium-catalyzed reaction using Cl_2, CO, and alkyl nitrite. This method is safe, since it requires no highly toxic materials, such as phosgene. In this reaction chlorine is converted to methyl chloroformate, and no HCl is produced. Moreover, any NO produced can be used to reproduce methyl nitrite by the following reaction with methanol and oxygen:

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

Experimental

1. Materials. Methyl nitrite was prepared from controlled amounts of NO and O_2 by passing through methanol. Chlorine was purchased from Nippon Sanso Co., Ltd. as 1% or 10% standard gas (N_2 as the balance). The other gases were also purchased and used without any further purification. A 1% $PdCl_2/\gamma\text{-}Al_2O_3$ catalyst was purchased from N. E. Chemcat, and a 1% $PdCl_2/SiO_2$ catalyst was prepared using aqueous H_2PdCl_4 solution and silica gel purchased from Fuji Davision Co., Ltd.

2. Apparatus and Procedures. The apparatus for the experiment is shown in Fig. 1. A reaction tube (13 mmϕ) was filled with the required amount of catalyst and fixed vertically. Then, hot silicone oil was flowed in the jacket around the reaction tube in order to maintain the catalyst at the required temperature. From the top of reaction tube, the reactant gas, which had been passed through a cold trap kept under 5 °C, was introduced at the required flow rate. After being passed through the catalyst at atmospheric pressure, the 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%; Cl_2 concentration, 0.5—1 vol%; nitrite/Cl_2 molar ratio, 2—10; balance gas, N_2.

3. Analysis. The analytical conditions of gas chromatography were 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.

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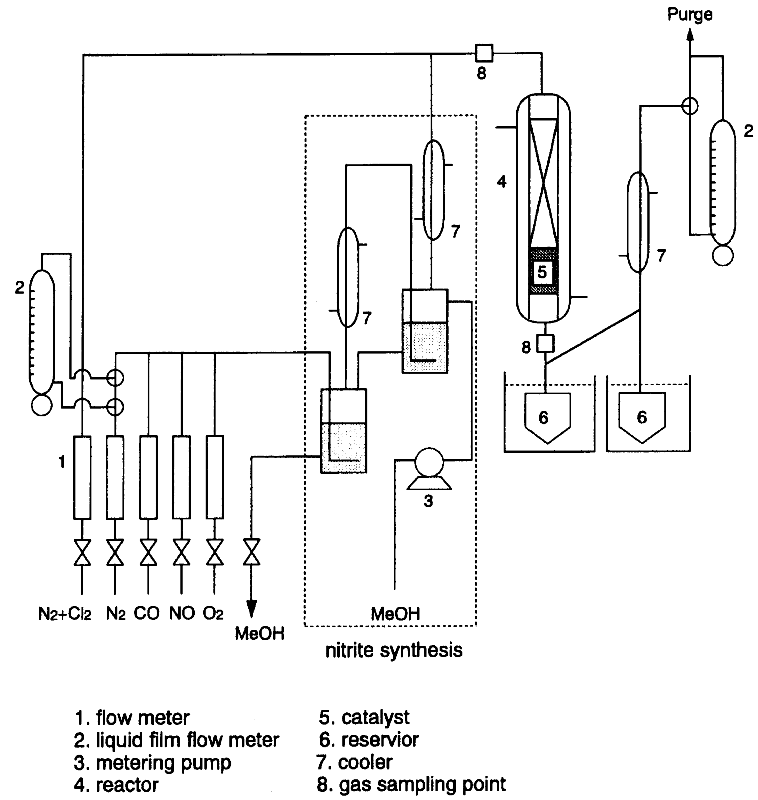


Fig. 1. Apparatus for the experiments.

Table 1. Reaction of Reactant Gas on γ-Al_2O_3[a)]

Run	Reactant gas concentration (in/out)					Products
	CO	MN	NO	MeOH	Cl_2	
			vol%			
1	7.1/7.1	0.0/0.0	0.0/0.0	0.0/0.0	1.0/—[b)]	No reaction
2	10.1/10.3	0.0/0.0	0.0/0.0	9.7/7.8	1.0/—[b)]	MF, ML, DCM,[c)] etc.
3	9.4/9.4	6.2/7.0[d)]	2.2/1.3[d)]	10.4/7.1	1.0/—[b)]	MF, ML, DCM,[c)] etc.

a) Reaction conditions γ-Al_2O_3 1 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$. b) Not determined. c) MN: Methyl nitrite, MF: Methyl formate, ML: Methylal (formaldehyde dimethyl acetal), DCM: Dichloromethane.

Results and Discussion

Conversion of Reactant Gases on γ-Al_2O_3. The conversion of reactant gases on γ-Al_2O_3 was examined. The results (listed in Table 1) show that the reaction between CO and Cl_2 did not proceed to form phosgene (Run 1). Cl_2 reacted with methanol to give dichloromethane, methylal (formaldehyde dimethyl acetal), methyl formate and a few unknown products. In all cases of Runs 1, 2, and 3, no chloroformate was detected.

Conversion of Reactant Gas on $PdCl_2$/γ-Al_2O_3. Similarly, the conversion of reactant gases on 1% $PdCl_2$/γ-Al_2O_3 was examined. Also, in this case, the reaction between CO and Cl_2 did not proceed. Cl_2 reacted with methanol to give almost the same results as on γ-Al_2O_3 alone (Table 2). However, quite a different result was obtained when Cl_2, CO, and methanol were reacted together: methyl chloroformate (MCF) was formed (Table 3). In this case, HCl and several kinds of by-products were also formed. Interestingly, when methyl nitrite was added to Cl_2 and CO, methyl chloroformate was obtained in high selectivity (99.7%) and in very good yield (1650 $mg\,h^{-1}$) (Run 3).

If methyl chloroformate was formed via phosgene, the theoretical maximum yield should be an equimolar amount of Cl_2 introduced (see Eqs. 1 and 2). Thus, under the reaction conditions of Cl_2 1 vol% and a gas flow rate 30000 $cm^3\,h^{-1}$, the yield of chloroformate should be 1153 $mg\,h^{-1}$ at most. However, when methyl nitrite was employed as a substrate, the yield (1650 $mg\,h^{-1}$) exceeded the theoretical value. Furthermore, methyl chloroformate was not formed by the reaction of HCl, CO, and methanol on 1% $PdCl_2$/γ-Al_2O_3. From these experimental facts, it can be concluded that chloroformate was not formed via phosgene.

Table 2. Reaction of Reactant Gas on $PdCl_2/\gamma\text{-}Al_2O_3$[a)]

Run	Reactant gas concentration (in/out)					Products
	CO	MN	NO	MeOH	Cl_2	
	vol%					
1	1.9/1.9	0.0/0.0	0.0/0.0	0.0/0.0	1.0/—[b)]	No reaction
2	9.7/10.0	0.0/0.0	0.0/0.0	0.0/0.0	1.0/—[b)]	No reaction
3	0.0/0.0	0.0/0.0	0.0/0.0	10.8/—[b)]	1.0/—[b)]	MF, ML, DCM,[c)] etc.

a) Reaction conditions 1% $PdCl_2/\gamma\text{-}Al_2O_3$ 1 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$. b) Not determined. c) MN: Methyl nitrite, MF: Methyl formate, ML: Methylal (formaldehyde dimethyl acetal), DCM: Dichloromethane.

Table 3. Formation Rate of Methyl Chloroformate[a)]

Run	Reactant gas concentration (in)					Formation rate	By-Products
	CO	MN	NO	MeOH	Cl_2	MCF	
	vol%					$mg\,h^{-1}$	
1	1.9	0.0	0.0	7.7	1.0	199	MF, ML, DCM,[b)] etc.
2	10.2	0.0	0.0	11.5	1.0	484	MF, ML, DCM,[b)] etc.
3	7.0	5.0	2.0	7.0	1.0	1650	DMC,[b)]

a) Reaction conditions 1% $PdCl_2/\gamma\text{-}Al_2O_3$ 1 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$. b) MN: Methyl nitrite, MCF: Methyl chloroformate, MF: Methyl formate, ML: Methylal (formaldehyde dimethyl acetal), DCM: Dichloromethane, DMC: Dimethyl carbonate.

Table 4. Mass Balance of Reactants and Product[a)]

Reactant gas flow rate (in/out(consumed amount))		Product flow rate (in/out(produced amount))	
CO	MN	NO	MCF
$mmol\,h^{-1}$		$mmol\,h^{-1}$	
51.6/34.2(17.4)	20.2/3.6(16.6)	22.4/38.4(16.0)	0.0/11.0(11.0)

a) Reaction conditions 1% $PdCl_2/\gamma\text{-}Al_2O_3$ 1 cm^3, 60 °C, gas flow rate 30000 $cm^3\,h^{-1}$, Cl_2: 0.5 vol% (6.2 $mmol\,h^{-1}$), MeOH: 4.24 vol% (51.7 $mmol\,h^{-1}$).

Verification of the Reaction Path. As described above, it was found that methyl chloroformate is formed in good yield from CO, Cl_2, and methyl nitrite. First, the chlorine balance was measured to verify the reaction path. When Cl_2 was introduced at a rate of 7.1 $mmol\,h^{-1}$ to 2 cm^3 of the catalyst (1% $PdCl_2/\gamma\text{-}Al_2O_3$) under the following reaction conditions: gas flow rate, 30000 $cm^3\,h^{-1}$; temperature, 65 °C; methyl nitrite, 6.02 vol%; CO, 6.00 vol%; methanol, 2.61 vol%; and NO, 1.22 vol%; methyl chloroformate was formed at a rate of 14.3 $mmol\,h^{-1}$. It can be concluded from this result that the molar ratio of chloroformate produced to introduced Cl_2 was 2. This means that no HCl was formed under the reaction conditions. Secondly, the mass balance of the reactants and the products was measured. The results are given in Table 4.

Based on these results, the following reaction path can be proposed:

$$Cl_2 + 2CO + 2CH_3ONO \rightarrow 2ClCOOCH_3 + 2NO. \qquad (4)$$

Effect of the Reaction Temperature. It was found that the reaction is very much influenced by the reaction temperature. The results are given in Fig. 2. The formation rate of chloroformate is the highest at around 60 °C, and decreases as the temperature becomes higher. Chloroformate decomposes to chloromethane and CO_2 at high temperatures on $\gamma\text{-}Al_2O_3$ (Eq. 5),[10)]

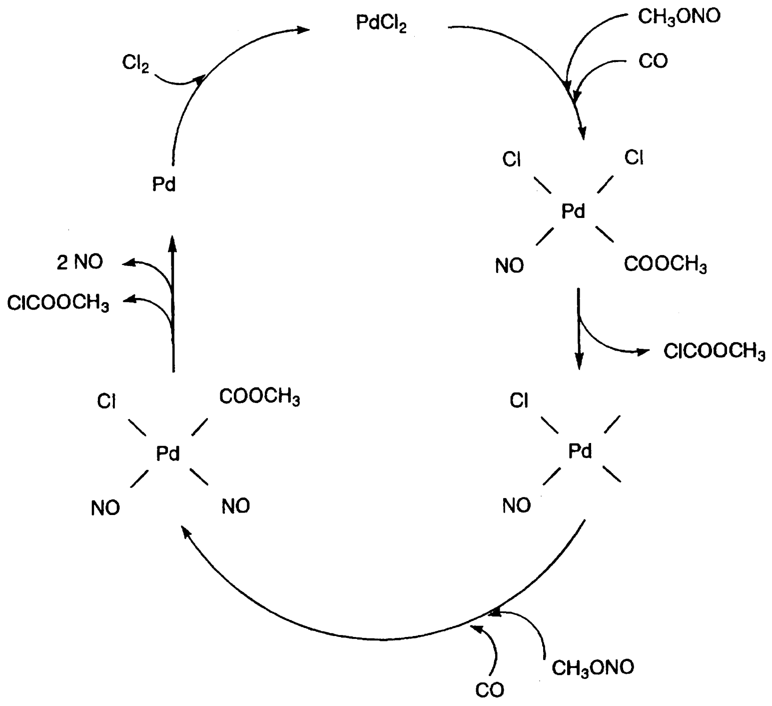
$$ClCOOCH_3 \rightarrow CH_3Cl + CO_2. \qquad (5)$$

At a temperature higher than 60 °C, dimethyl carbonate (DMC) begins to form.

Effect of the Reactant Concentration. The concentrations of CO and methyl nitrite also influence the formation rate of the products. The results are given in Figs. 3 and 4, respectively.

The formation rate of chloroformate is dependent on the concentration of CO, almost by first order. When the concentration of methyl nitrite is lower than twice the Cl_2 concentration, the rate is dependent on the concentration of methyl nitrite, also by first order.

Effect of the Nitrite/Cl Molar Ratio. It was



Scheme 1. Proposed catalytic mechanism for the formation of chloroformate in the presence of methyl nitrite.

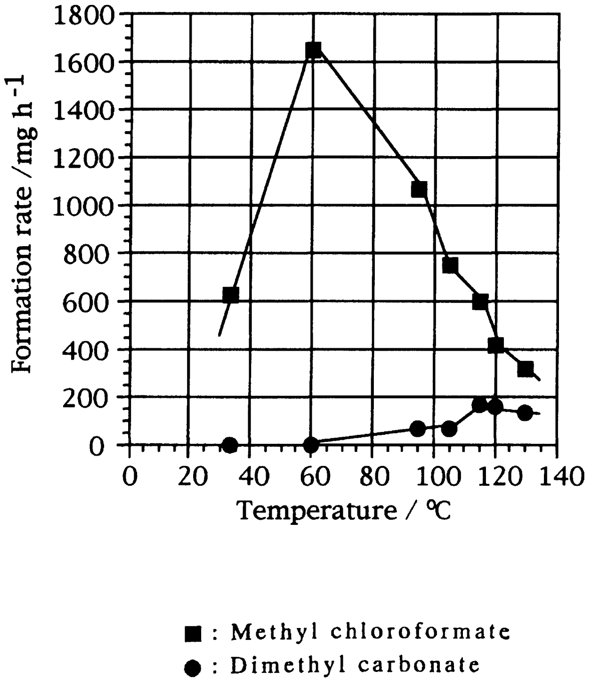


Fig. 2. Formation rate of products vs. reaction temperature. Reaction conditions: Pressure, 1 atm; Gas flow rate, 30000 $cm^3\,h^{-1}$; Catalyst, 1% $PdCl_2/\gamma\text{-}Al_2O_3$; Catalyst volume, 1 cm^3; CO, 7 vol%; Cl_2, 1 vol%; methyl nitrite, 5—6 vol%; NO, 1—2 vol%; methanol, 6—10 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

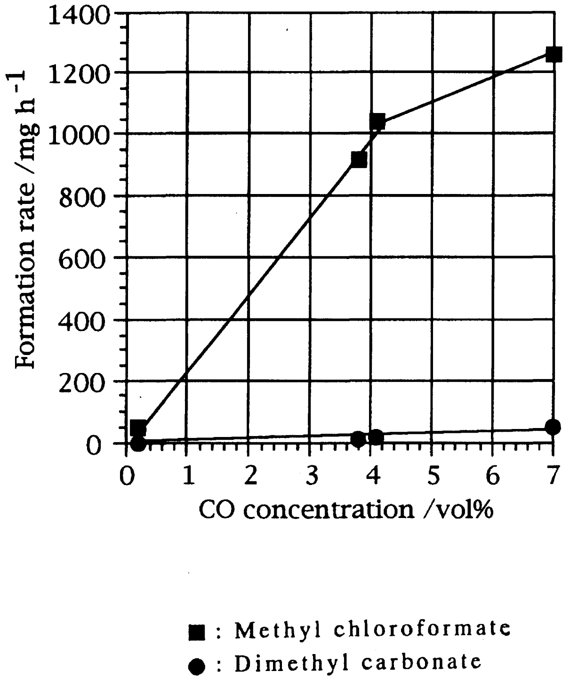


Fig. 3. Formation rate of products vs. CO concentration. Reaction conditions: Pressure, 1 atm; Temperature, 60 °C; Gas flow rate, 30000 $cm^3\,h^{-1}$; Catalyst, 1% $PdCl_2/\gamma\text{-}Al_2O_3$; Catalyst volume, 2 cm^3; Cl_2, 0.5 vol%; methyl nitrite, 1.5—2.5 vol%; NO, 0.6—0.9 vol%; methanol, 3—4 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

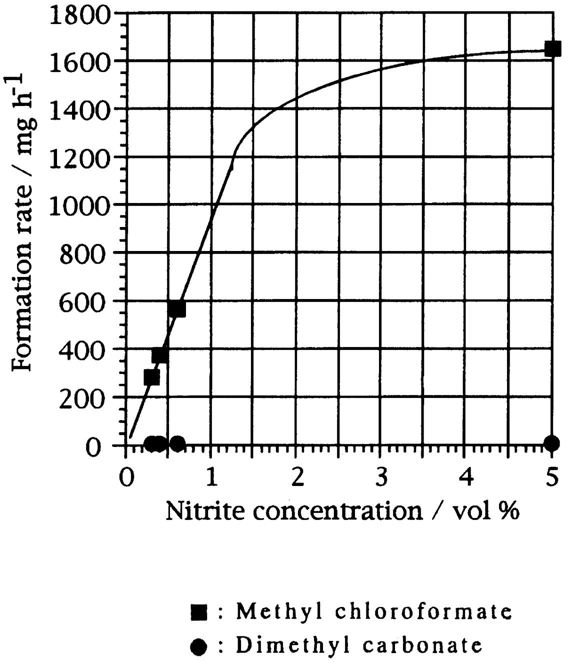


Fig. 4. Formation rate of products vs. methyl nitrite concentration. Reaction conditions: Pressure, 1 atm; Temperature, 60 °C; Gas flow rate, 30000 cm^3 h^{-1}; Catalyst, 1% $PdCl_2/\gamma$-Al_2O_3; Catalyst volume, 1 cm^3; Cl_2, 1 vol%; CO, 7 vol%; NO, 0—1 vol%; methanol, 7—11 vol%. Closed squares and circles in the figure correspond to methyl chloroformate and dimethyl carbonate, respectively.

also found that the nitrite/Cl molar ratio influences the selectivity of methyl chloroformate very drastically. The results are given in Fig. 5. The selectivity is defined as follows:

$$\text{MCF selectivity (\%)} = \frac{\text{MCF(mmol h}^{-1}) \times 100}{\text{MCF(mmol h}^{-1}) + \text{DMC(mmol h}^{-1})}. \qquad (6)$$

Interestingly, when the nitrite/Cl molar ratio is less than 2, the selectivity is almost 100%. As the concentration of methyl nitrite increases relative to the Cl_2 concentration, the selectivity decreases due to the formation of carbonate.

Mechanism. A mechanism which accounts for the formation of chloroformate is proposed in Scheme 1. $PdCl_2$ reacts with CO and methyl nitrite to form a methoxycarbonyl complex $[PdCl_2(COOCH_3)(NO)]$. A similar type of complex has been isolated by Bréchot et al. as a phosphine adduct $[PdCl_2(COOBu)(NO)(PPh_3)]$ as an active intermediate of the catalytic oxidative carbonylation of olefin.[11] From the complex, methyl chloroformate is produced through a reductive elimination to form an unsaturated complex [Pd(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, which is reoxidized by Cl_2 to reproduce $PdCl_2$.

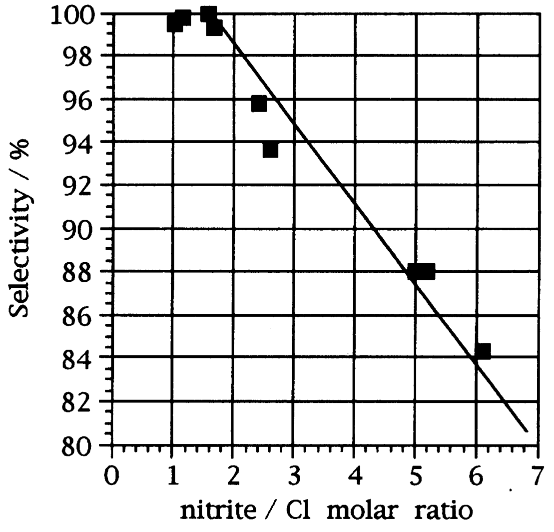
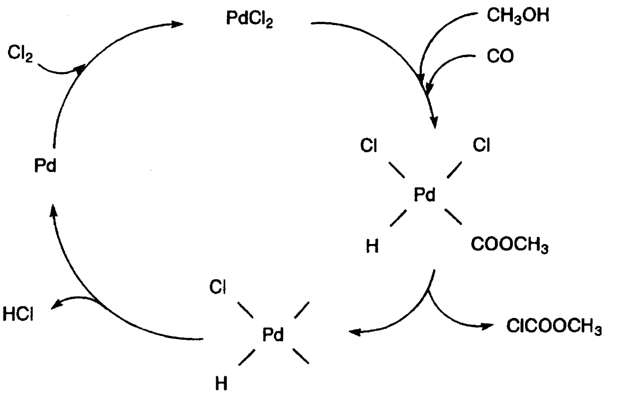


Fig. 5. Selectivity of methyl chloroformate vs. nitrite/Cl molar ratio.

This mechanism is consistent with the fact that a high nitrite concentration causes the formation of carbonate. It can be explained that an excess amount of nitrite reacts with the methoxycarbonyl complex $[PdClX(COOCH_3)(NO)]$ (X=Cl or NO) to produce carbonate before elimination of the chloroformate. When the nitrite/Cl molar ratio is less than 2, all of the nitrite can be converted to a methoxycarbonyl group on Pd, and to chloroformate by a successive reductive elimination with Cl. Similarly, the formation of chloroformate in the absence of nitrite can be explained by Scheme 2. In this case, half of the Cl_2 reacted on Pd is converted to HCl.

Another Supports. Finally, when 2 cm^3 of 1% $PdCl_2/SiO_2$ was employed as a catalyst, methyl chloroformate was formed at a rate of 607 mg h^{-1} under the following reaction conditions: gas flow rate, 30000 cm^3 h^{-1}; temperature, 90 °C; Cl_2, 0.4 vol%; methyl nitrite, 3.1 vol%; CO, 5.1 vol%; methanol, 4.3 vol%; and NO, 0.0 vol%. However, 1% $PdCl_2/\alpha$-Al_2O_3 showed



Scheme 2. Proposed catalytic mechanism for the formation of chloroformate in the absence of methyl nitrite.

very low catalytic activity, possibly due to the small surface area of the support.

Conclusion

A novel synthesis of alkyl chloroformates in the gas phase by a palladium-catalyzed reaction using Cl_2, CO, and alkyl nitrite was developed. By this method, methyl chloroformate can be produced in good yield and in high selectivity. The reaction proceeds according to Eq. 4.

This reaction is very clean and suitable for the production of chloroformate in industrial process.

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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) M. Graziani, P. Uguagliati, and G. Carturan, *J. Organomet. Chem.*, **27**, 275 (1971).
8) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, **1969**, 723.
9) P. Giannoccaro, N. Ravasio, and M. Aresta, *J. Organomet. Chem.*, **451**, 243 (1993).
10) Japan Patent (Syutugan) 5-119871 (1993).
11) P. Bréchot, Y. Chauvin, D. Commereuc, and L. Saussine, *Organometallics*, **9**, 26 (1990).