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REACTIONS OF CARBON DIOXIDE WITH TRANSITION METAL ALKOXIDES

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Alkoxides of transition metals, such as Fe, Ti, Nb,and Zr, were found to react with atmospheric carbon dioxide in benzene solution at 30°C. The measurement of CO_2 volume absorbed and IR data suggest that transition metal alkoxides are partially carbonated.

Insertion reactions of carbon dioxide with metal alkoxides to give the corresponding carbonates have not been studied, except for magnesium methoxide[1], tributyltin methoxide[2], and copper methoxide[3]. In this paper, we report that carbon dioxide reacts smoothly also with various transition metal alkoxides. When benzene solutions (5-20 wt%) of $Ti(O\text{-}\underline{n}Bu)_4$, $Zr(O\text{-}\underline{n}Bu)_4$, $Fe(OEt)_3$, $Nb(OEt)_5$, and $Zr(OEt)_4$ in a thermostated flask (30°C) were brought into cantact with an atmosphere of dry carbon dioxide (1 atm), CO_2 absorption of the solution quickly occurred at a rather high rate and ceased in 2-20 minutes. The volume of carbon dioxide absorbed was measured with a gas burette attached to the reaction system. The volume of CO_2 reacted with the alkoxides was obtained by deducting a part absorbed to benzene from the total volume absorbed.

Table 1. Molar ratio of CO_2 absorbed to $M(OR)_n$ (1 atm, 30°C)

$M(OR)_n$	$M(OR)_n$ ($\times 10^{-4}$ mol)	CO_2 absorbed (ml)	Molar ratio of absorbed CO_2 to $M(OR)_n$
$Ti(OBu)_4$	7.17	7.9	0.49
$Zr(OBu)_4$	6.42	13.8	0.96
$Fe(OEt)_3$	5.92	7.8	0.59
$Nb(OEt)_5$	6.03	8.3	0.61
$Zr(OEt)_4$	6.53	4.5	0.31

The results are listed in Table 1. The absorbed volume of carbon dioxide is below one mole based on one mole of transition metal alkoxides. IR spectra of alkoxides in benzene showed strong additional peaks at about 1600, 1420, and 1330 cm^{-1}, after the reaction with CO_2. And the intensities of these peaks decreased when N_2 gas was bubbled through the above benzene solutions. These additional peaks are coincident to the IR data reported previously for $Bu_3Sn(O\overset{\overset{O}{\|}}{C}OMe)$[2] and $Cu(O\overset{\overset{O}{\|}}{C}OMe)_2$[3] (see Table 2.). And the reaction of $M(OEt)_n$-CO_2 mixture (M=Fe, Nb, and Zr) with ethyl iodide at 150°C yielded diethyl carbonate. From these results, it is considered that the reactions of transition metal alkoxides with CO_2 are expressed by the following equation,

$$M(OR)_n + CO_2 \rightleftharpoons M(OR)_{n-1}(O\overset{\overset{O}{\|}}{C}OR),$$

(M=Fe, Ti, Nb, or Zr; R=Et or n-Bu)

and that, in the present case except for $Zr(OBu)_4$, the equilibrium lies not so far to the right at 30°C and under 1 atm of CO_2.

Table 2. Newly appeared IR peaks* of $M(OR)_n$ after the reaction with CO_2

$Fe(OEt)_3$-CO_2	1570^{s} (cm^{-1})	1412^{s}	1325^{s}	1106^{sh}	
$Nb(OEt)_5$-CO_2	1602^{s}	1414^{s}	1330^{s}		807^{w}
$Zr(OEt)_4$-CO_2	1600^{s}	1424^{s}	1338^{s}		810^{w}
$Bu_3Sn(O\overset{\overset{O}{\|}}{C}OMe)$**	1600^{vs}			1095^{s}	820^{m}
$Cu(O\overset{\overset{O}{\|}}{C}OMe)_2$ **	1665		1305		

* Measured in benzene (5 wt%) using a 0.1 mm NaCl cell.

** For comparison, IR data of these carbonates are listed.[2,3]

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