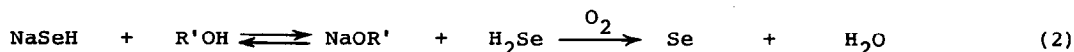
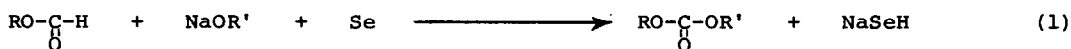


SELENIUM AS A NOVEL OXIDIZING AGENT. SELENIUM CATALYZED  
SYNTHESIS OF CARBONATES BY THE REACTION OF FORMATES WITH ALKOXIDES.

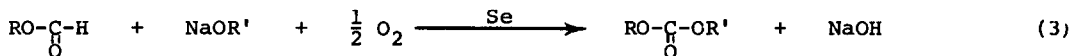
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In the previous communications we have described the synthesis of carbonates<sup>1</sup> from alkoxides and carbon monoxide and the synthesis of ureas<sup>2</sup> from amines and CO using selenium as a catalyst. We wish now to report that selenium acts as an unusual oxidizing agent of formates in the presence of alkoxides to give dialkylcarbonates in excellent yields at room temperature under N<sub>2</sub> [reaction (1)], and the facile oxidation of thus formed NaSeH to Se with molecular oxygen [reaction (2)] enables the reaction catalytic [reaction (3)]. Formation of the dialkylcarbonates was not observed, when formates were allowed to react with sodium alkoxide under the same condition in the absence of Se.



That is;



This reaction involves formal substitution of formyl hydrogen with alkoxy anion.

A typical reaction was carried out by adding metallic Se ( 1 mg atom ) and sodium methoxide ( 10 mmol ) to 20 ml tetrahydrofuran (THF) solution of methylformate ( 10 mmol ) at room temperature with vigorous stirring under N<sub>2</sub> for 1 hr. From g.l.c., the THF solution was revealed to contain dimethylcarbonate in the yield of 99.9 % based on Se used, and then the catalytic reaction was successfully

performed by adding oxygen gas into the THF solution at a rate of 1 mmol/hr at 24°C; by following gas-chromatography the quantitative formation of dimethylcarbonate based on O<sub>2</sub> added was observed. The catalytic reaction slowed down as sodium hydroxide was produced,<sup>3</sup> and the reaction could be stopped by addition of O<sub>2</sub> at a rate of 20 ml/min for 10 minutes. Filtration followed by distillation gave dimethylcarbonate ( 5.2 mmol, from g.l.c. ). Stoichiometric reaction ( catalytic reaction time; 0 hr ) of formates and Se with sodium alkoxides was examined to form corresponding carbonates, confirming the excellent oxidizing ability of Se, and catalytic synthetic reaction of a few carbonates was examined as shown in the Table.

Table. Oxidation Efficiency of Selenium in the Synthetic Reaction<sup>a</sup> of Carbonates.

RO-C-H O	NaOR'	Catalytic Reaction Time hr <sup>b</sup>	Oxidation Efficiency % <sup>c</sup>
R	R'		
Me	Me	0	99
Me	Me	3	370
Et	Et	0	99
Et	Et	1	250
Et	Et	4	490
Et	i-Pr	0	49 <sup>d</sup>
Et	n-Bu	0	85 <sup>e</sup>
i-Pr	i-Pr	0	77
n-Bu	n-Bu	0	99

a) Formate (10 mmol), metallic Se (1 mg atom), and sodium alkoxide (10 mmol) in THF at 24°C under N<sub>2</sub> with vigorous stirring. b) Catalytic reaction was carried out by addition of O<sub>2</sub> at a rate of 1 mmol/hr, and the reaction was stopped by addition of O<sub>2</sub> at a rate of 20 ml/min for several minutes.

c) (Oxidation Efficiency)% = (mmol of formed RO-CO-OR')/(mg atom of used Se)×100

d) (EtO)<sub>2</sub>CO (10%) and (i-PrO)<sub>2</sub>CO (trace) were also formed. e) (n-BuO)<sub>2</sub>CO ( 9% ) and (EtO)<sub>2</sub>CO ( 3% ) were also formed.

#### REFERENCES and FOOTNOTE

- (1) K. Kondo, N. Sonoda, and S. Tsutsumi, Tetrahedron Lett., 1971, 4885.
- (2) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, J. Amer. Chem. Soc., 93, 6344 (1971).
- (3) Dialkylcarbonate was found to decrease on prolonged contact with sodium hydroxide in alcoholic solution.