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Catalytic Decomposition of Carbonate Esters of Diols on Copper

The literature contains no reports on the transformation of cyclic carbonates on metal catalysts. This is understandable, for the study of the metal-catalyzed reactions of organic compounds containing C–O bonds is not at the center of interest. A good illustration of this is the fact that a review of this field has not been published since the monograph by Bond (*1*). Research into the transformations of organic compounds on metals is concentrated mainly on the various types of hydrocarbons (*2*).

Copper was selected for our investigations for two reasons: it was demonstrated earlier that this metal catalyzes the transformations of certain compounds containing two C–O bonds (*3, 4*); and it catalyzes various reactions of compounds containing carbonyl functions (*1, 5*).

The three cyclic carbonates (**1A, 1B,** and **1C**) were chosen as model compounds for our studies. With the intent of investigating the reaction mechanism, experiments were also carried out under the same experimental conditions on the transformations of the corresponding diols (**9A, 9B,** and **9C**) on various copper catalysts (Cu/Al and other catalysts prepared by the reduction of different precursors (*4*), see Table 1). The reason for conducting studies on the different types of catalysts was to demonstrate clear-cut proof of the role of the copper. The Cu/Al catalyst always contains Al_2O_3 (Table 1 therefore also includes experimental information obtained on Al_2O_3). This Al_2O_3 contains electrophilic centers (*6*), whereas above 200°C the Cu/CS5 and Cu/KG do not contain acidic centers that can be titrated with NH_3.

Measurements were made in the vapor phase with a flow technique (catalyst volume, 7.5 ml; grain size, 0.63–1 mm; space velocity, 0.16 ml liquid/ml catalyst/h). The compounds formed, after isolation, were identified by GLC retention times of authentic compounds synthesized independently and by ir and NMR spectroscopy.

From the experimental results in Table 1 from Scheme 1, and from other observations, the following conclusions may be drawn:

(a) Three reaction types can be observed in the transformation of cyclic carbonates on copper: the formation of (**2**), (**7**) + (**8**), and (**3**) + (**4**) or (**5**) + (**6**).

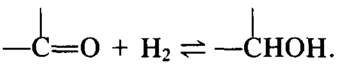
(b) The selectivity of the transformation is determined fundamentally by the structure of the cyclic carbonate; (**1A**) → (**2**); (**1B**) → (**3**) + (**5**); (**1C**) → (**7**).

(c) The carbonates containing five ring atoms are converted considerably more slowly than those containing six ring atoms.

(d) The experiment on γ-Al_2O_3 shows that the above reactions do not take place on the electrophilic centers of the catalysts, but that copper plays the determining role in these transformations.

(e) The cyclic carbonates (**1A, 1B,** and **1C**) and the corresponding diols (**9A, 9B,** and **9C**) exhibit a high degree of similarity in product composition.

To explain the above experimental results, we propose the reaction mechanism outlined in Scheme 2. In the construction of this, use was made not only of our own experimental results, but also the results of Boudart, Burwell, and their coworkers (*7, 8*) relating to the reaction mechanism of the process



$$-\overset{|}{C}{=}O + H_2 \rightleftharpoons -\overset{|}{C}HOH.$$

The first step in the process is the formation of the surface complex (**D**), in which

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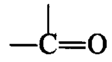
TABLE 1

Transformations of **1** and **9** on Various Copper Catalysts

Substrate	Catalyst (% Cu, precursor)	Temp. (°C)	Conversion (%)	Mole%							
				2	**3**	**4**	**5**	**6**	**7**	**8**	A[a]
1A	Cu/Al (70, Cu–Al alloy)	250	40	62	13	3	13	0	0	0	9 (1)
1B		200	100	0	29	6	54	3	2	2	4 (1)
1C		200	100	0	4	1	—	—	50	45	0
1C + H_2		200	100	0	0	0	—	—	30	70	0
9A		250	68	24	1	24	13	3	0	0	35 (3)
9B		200	100	0	14	16	61	3	1	2	3 (1)
9C		240	100	0	0	0	—	—	55	45	0
10		250	80	0	0	0	—	—	55	45	0
1A	Cu/CS5 (5, CuO/Cab-O-Sil)	290	28	50	16	5	19	1	1	0	8 (1)
1B		250	100	0	33	12	43	2	3	2	5 (1)
1C		220	90	0	0	0	—	—	40	60	0
1C		250	100	0	0	0	—	—	58	42	0
9A	Cu/KG (40, CuO/kieselguhr)	250	79	58	3	1	5	11	0	0	22 (4)
9B		200	100	0	10	18	44	3	4	14	7 (1)
9C		250	100	0	0	0	—	—	50	46	4 (1)
1C	γ-Al_2O_3	200	80	0	4	6	—	—	20	18	52 (5)

[a] Other identified and unidentified products; the numbers in parentheses are the numbers of compounds.

decarbonylation or dehydrogenation occurs in the cases of (**1**) and (**9**), respectively. The development of surface complexes of the copper alkoxide type is well known for alcohols. Formation of (**D**) from (**1**) is a reaction that can be followed easily by measurement of the CO. The determining nature of this reaction step, i.e., the fact that the presence of the



$$-\overset{|}{C}=O$$

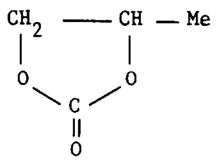
group in the molecule is indispensably necessary for the adsorption of (**1**), was proven experimentally: the 1,3-dioxanes (**11**) are not transformed on copper, even at 350°C. Otherwise, copper proved active in the decarbonylation of the formate (**10**) with a carbon skeleton similar to that of (**1C**) (see Table 1). The similar product compositions from (**1**) and (**9**) can be explained by the formation of common surface complexes (**D**) and (**E**).

The different selectivities in the transformations of (**1A**), (**1B**), and (**1C**) on copper are determined by the strengths of the bonds in the surface species (**E**), which is essentially a triadsorbed hydroxylcarbonyl compound:

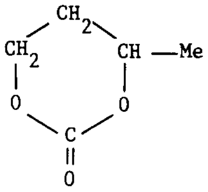
1. Since α-hydroxylcarbonyl compounds are considerably more stable than β-hydroxycarbonyl compounds, (**E**) is desorbed in the form of (**2**) in the cases of (**1A**) and (**9A**).

2. The triadsorbed β-hydroxylcarbonyl compound (**E**) is transformed further at high rate. If X is a quaternary carbon atom ((**1C**) and (**9C**)), then (**7**) + (**8**) are formed by further decarbonylation; if X is a secondary carbon atom ((**1B**) and (**9B**)), then deoxygenation occurs and (**5**) + (**6**) or (**3**) + (**4**) are formed.

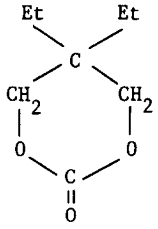
To summarize, on copper cyclic carbonates undergo structure-dependent fragmentation reactions which yield carbonyl compounds and alcohols; a reaction mechanism



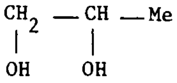
(1A)



(1B)

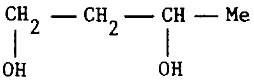


(1C)



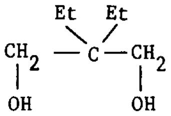
$\underset{OH}{CH_2}-\underset{OH}{CH}-Me$

(9A)



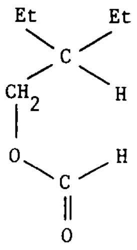
$\underset{OH}{CH_2}-CH_2-\underset{OH}{CH}-Me$

(9B)

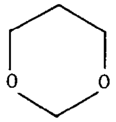


$\underset{OH}{CH_2}-\overset{Et\ Et}{C}-\underset{OH}{CH_2}$

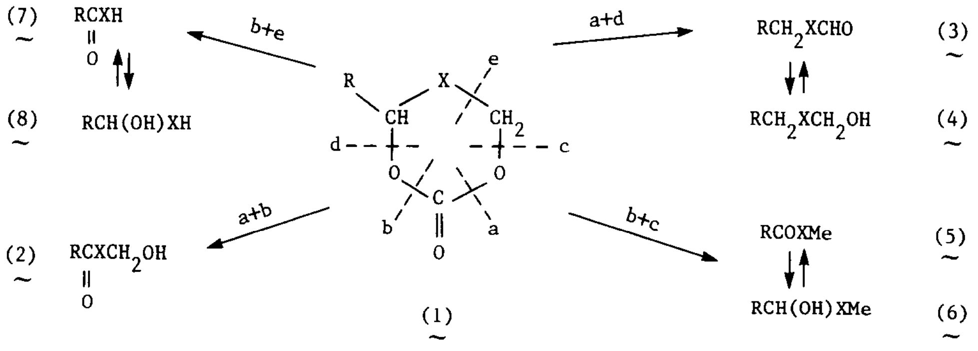
(9C)



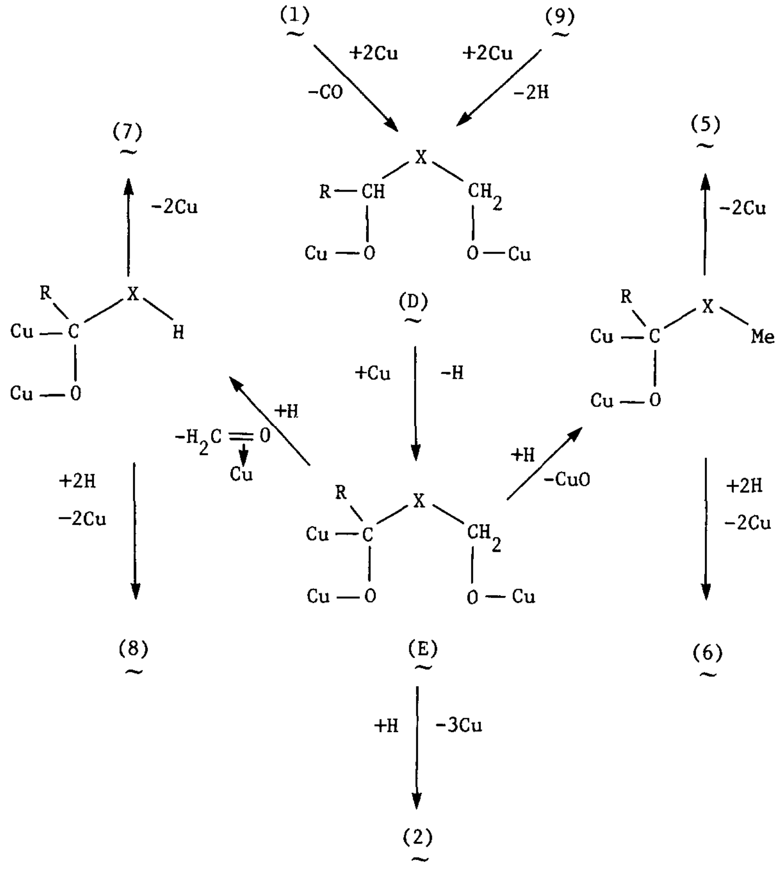
(10)



(11)



SCHEME 1. **A:** X = zero, R = Me; **B:** X = CH_2, R = Me; **C:** X = CEt_2, R = H.



SCHEME 2

is proposed to interpret this new metal-catalyzed transformation.

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