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CO-PYROLYSIS OF 3,4-DICHLORO-1-BUTENE AND METHANOL ON ACTIVATED ALUMINA

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The co-pyrolysis of 3,4-dichloro-1-butene (3,4-DCB-1) and methanol on activated alumina was carried out at 230°C. The reaction products contained a significant amount of methoxy-compounds as well as the dehydrochlorinated and isomerized compounds.

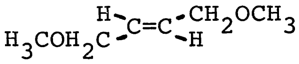
In the pyrolytic dehydrochlorination of 3,4-DCB-1, it has been found that 1-chloro-1,3-butadiene (CB) was formed instead of chloroprene (CP).[1] 3,4-DCB-1 isomerized to 1,4-dichloro-2-butenes (1,4-DCB-2) as well as dehydrochlorinated to CB over solid acid catalysts at 150 to 250°C.[2]

The co-pyrolysis of 3,4-DCB-1 and methanol on activated alumina was carried out at 230°C with the fixed bed flow reactor according to the previous work.[3] Activated alumina as catalyst (KHD-24) was supplied by Sumitomo Chemical Co. and the particle diameter was in the range of 2 to 4 mm. The mole ratio (CH_3OH/3,4-DCB-1) was varied, while the time factor was kept constant at 429.5 (g of catalyst/g-mol of 3,4-DCB-1/hr).

The reaction products were analyzed by gas chromatography (PEG 6000, 100°C). Then, the following methoxy-compounds were confirmed by IR and NMR techniques.

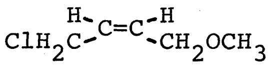
$CH_2{=}CH{-}CH(OCH_3){-}CH_2OCH_3$

(I)



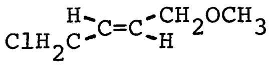
$H_3COH_2C{-}CH{=}CH{-}CH_2OCH_3$

(II)



$ClH_2C{-}CH{=}CH{-}CH_2OCH_3$

(III)



$ClH_2C{-}CH{=}CH{-}CH_2OCH_3$

(IV)

The product distributions in the pyrolyses with various mole ratios are shown in Table 1. As the mole ratio increased, the selectivity for CP formation [CP/(CP + CB)] was found to gradually decrease. On the other hand, the formation of methoxy-compounds rapidly increased with increasing the mole ratio.

Table 1. The effect of the mole ratio (CH_3OH/3,4-DCB-1) on the product composition

Mole ratio	Product composition (mol %)								
	CP	I	CB	3,4-DCB-2	II	III	IV	cis-1,4-DCB-2	trans-1,4-DCB-2
2.66	34.53	-	20.44	20.07	-	-	-	3.61	21.35
5.31	13.22	2.73	18.30	40.45	4.45	0.16	1.39	2.26	17.04
7.97	7.86	4.72	15.03	41.91	13.80	0.29	3.50	1.28	11.61
13.29	3.28	5.93	8.29	38.52	37.12	0.32	2.35	0.52	3.67
18.60	1.99	5.61	6.26	43.55	37.21	-	1.89	0.28	3.21

The elimination of hydrogen chloride took place only in the co-pyrolyses of chloroethanes with methanol on activated alumina and the methoxy-compounds were not found in the reaction products.$^{4)}$ On the contrary, it is well-known that the halogenated compounds were solvolyzed in alcohols into the alkoxy-compounds. II, III and IV were formed by treating 1,4-DCB-2 with 2.5 M methanolic sodium hydroxide at room temperature. The analogy between gas-phase catalytic reaction and solvolysis in alcohol was of interest in elucidating this heterogeneous reaction mechanism.

The adsorption of alcohol molecules on the basic sites of alumina by hydrogen bonding through the hydrogen of hydroxyl group generates incipient alkoxide anions.$^{5)}$ It was, therefore, suggested that the methoxide anion generated on the basic sites of alumina played an important role in the elimination of hydrogen chloride and the substitution of chlorine atom. The nucleophilic attack of the methoxide anion and the removal of chlorine occurred at the same time, CP and the methoxy-compounds being competitively formed. Both reactions might proceed according to E2 and S_N2 on the basic sites of activated alumina, respectively.

References

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