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SELECTIVE FORMATION OF BUTADIENE IN CHLORINATION OF BUTENES THROUGH MOLTEN SALTS

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The reaction of three butenes with chlorine through $ZnCl_2$-KCl-NaCl melts yielded selectively butadiene at 450°C while chlorination through CuCl-KCl-NaCl melts and thermal chlorination produced considerable amounts of C_4H_7Cl and $C_4H_8Cl_2$ along with expected butadiene.

In the course of our studies on the dehydrochlorination of a series of aliphatic chlorocompounds using molten salts as catalysts, it has been clarified that the chlorine atom at the allylic position of 2-butene is readily removed together with a far allylic hydrogen atom(via 1,4-elimination) to produce butadiene through molten salts such as $ZnCl_2$-KCl-NaCl melts$^{1)}$. From this point of view, the chlorination of three butenes through such molten salts was studied with the expectation that chlorination will take place at the allylic position of butenes and the subsequent dehydrochlorination assisted by molten salts will yield butadiene predominantly.

The reaction was carried out at 400°C and 450°C using an apparatus similar to that described in a previous paper$^{1)}$.

The results obtained in the chlorination of 1-butene, trans-2-butene and cis-2-butene through 60 % $ZnCl_2$-20 % KCl-20 % NaCl melts(abbreviated as $ZnCl_2$ melts) and 60 % CuCl-20 % KCl-20 % NaCl(abbreviated as CuCl melts) are shown in Table 1 together with those of the thermal chlorination.

Table 1 indicates that $ZnCl_2$ melts give predominantly expected butadiene starting from three isomers and this selectivity to butadiene increases with increase of the reaction temperature. On the other hand, considerable amounts of C_4H_7Cl and $C_4H_8Cl_2$ are produced along with butadiene through CuCl melts and in the thermal chlorination$^{2)}$.

In this chlorination, the reactivity of butenes is in the following order: trans-2-butene > cis-2-butene > 1-butene in any run and selectivities of butadiene from butenes: 1-butene > cis-2-butene > trans-2-butene. This high selectivity of 1-butene is attributed to the less isomerization of 1-butene to 2-butenes. Such isomerization among butene isomers may be considered to be catalyzed by appreciable amounts of HCl dissolved in the molten salts. Since by-products are almost the isomerized butenes it is clear that provided butene mixtures are used as starting materials and the unchanged butenes are recycled for the subsequent chlorination, butadiene may be obtained in a selectivity more than 93 %. This selective formation of butadiene can be said to be one of the characteristic reactions using molten salts-catalysts.

Table 1 Chlorination of butenes through molten salts a)

Feed	1-butene				trans-2-butene				cis-2-butene
Cl_2/Feed	0.98	1.0 b)	0.90	0.90	1.0	0.95 b)	0.90	1.0	0.90 b)
Melts	$ZnCl_2$		CuCl	- c)	$ZnCl_2$		CuCl	- c)	$ZnCl_2$
Temp.(°C)	400	450	450	450	400	450	450	450	450
Conv.(%)	65.2	67.2	48.5	36.6	81.8	80.4	69.7	60.0	73.9
Select.(%)	84.8	90.2	78.6	43.7	84.7	88.8	66.3	24.7	79.8
1-Butene	34.8	32.8	51.5	63.4	0.5	0.7	tr	tr	0.8
t-2-Butene	1.0	1.3	0.6	-	18.2	19.6	30.3	40.0	14.1
c-2-Butene	0.9	1.0	0.4	-	8.0	8.3	8.8	11.1	26.1
Butadiene	55.3	60.7	38.1	16.0	69.3	71.4	46.2	14.8	59.0
$\mathrm{C{=}\underset{Cl}{C}{-}C{-}C}$	0.3	0.1	0.3	0.5	-	tr	tr	-	tr
$\mathrm{t{-}C{-}\underset{Cl}{C}{=}C{-}C}$ d)	0.1	0.1	0.1	0.2	0.2	tr	0.4	0.5	tr
$\mathrm{C{=}C{-}\underset{Cl}{C}{-}C}$	0.1	0.1	0.2	3.7	0.2	tr	0.1	10.0	tr
$\mathrm{c{-}C{-}\underset{Cl}{C}{=}C{-}C}$ e)	0.5	0.4	0.3	-	0.4	tr	0.5	tr	tr
$\mathrm{C{=}C{-}C{-}\underset{Cl}{C}}$	5.0	2.7	6.1	6.5	0.7	tr	0.8	0.5	tr
$\mathrm{\underset{Cl}{C}{-}C{=}C{-}C}$	0.2	0.2	0.4	5.6	0.5	tr	0.4	16.6	tr
$\mathrm{C{-}\underset{Cl}{C}{-}\underset{Cl}{C}{-}C}$ f)	0.7	0.2	1.6	1.7	1.3	tr	11.6	6.5	tr
Others	1.1	0.4	0.4	2.4	0.7	tr	0.9	tr	tr

a) Duration of reaction: 30 min, Feed : Argon = 0.10 : 0.15 mole/hr.

b) In the absence of chlorine the passage of each butene through melts under these conditions did not yield any trace amount of butadiene.

c) Thermal chlorination.

d), e), f) With 1-butene as a reactant, these products are substituted for cis-$\mathrm{\underset{Cl}{C}{=}C{-}C{-}C}$, trans-$\mathrm{\underset{Cl}{C}{=}C{-}C{-}C}$, and $\mathrm{\underset{Cl}{C}{-}\underset{Cl}{C}{-}C{-}C}$, respectively.

References

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2) M. Ogawa and M. Kitabatake, J. Syn. Org. Chem. Japan, 23, 64 (1965).

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