On the Active Species of Aluminium(III) Bromide–Copper(II) Bromide Mixtures as Catalysts for the Isomerization of Pentane

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Mixtures of $AlBr_3$ and $CuSO_4$ have high catalytic activity and selectivity for the isomerization of pentane at room temperature. The isomerization obeys the first-order kinetics with respect to pentane and proceeds both in the liquid phase and on the surface of copper(II) sulphate. The complex formed from the two substances seems responsible for the catalytic activity.

ALUMINIUM CHLORIDE and metal chlorides such as NaCl form double salts of relatively low m.p.[1] and are known to catalyse some Friedel–Crafts reactions as homogeneous catalysts. However the co-catalytic role of metal chlorides is not well established [2] and their catalytic application for alkane activation has not been attempted. Ono *et al.*[3,4] have reported that mixtures of aluminium chloride and metal sulphate, or chloride, promote the isomerization of pentane at room temperature, though the components of the mixture, aluminium chloride or the metal salt, have no catalytic activity individually. In the case of $AlCl_3$–$CuSO_4$ mixtures, the interaction of $AlCl_3$ with the $CuSO_4$ surface leads to the formation of a strong acid of $-14.52 < H_0 < -13.75$.[5] In $AlCl_3$–$CuCl_2$ mixtures, the active species for isomerization was ascribed to a complex, $Cu(AlCl_4)_2$, since this compound could be isolated by heating the mixture in a glass ampoule and was found to have a high catalytic activity for pentane isomerization.[6]

The synergism is also found in aluminium bromide–metal sulphate mixtures, which have higher catalytic activity for pentane isomerization than the mixture of aluminium chloride and the corresponding metal sulphate.[7] The activity is comparable to those of some superacids, such as HF–$SbF_5(50:1)$ [8] and $HFSO_3$–$SbF_5(1:1)$.[9] The catalytic system is also characterized by the high selectivity to produce isopentane (99%). In this work, the isomerization of pentane with aluminium bromide–copper(II) sulphate mixtures was studied in order to obtain more detailed information on the cause of the synergism of the mixture.

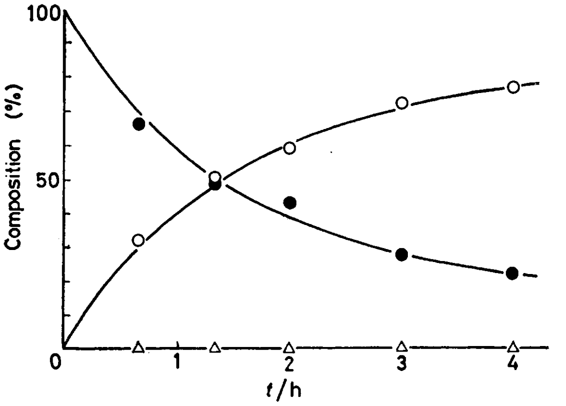


FIGURE 1 Change in liquid phase composition with time. Catalyst $AlBr_3$–$CuSO_4$ (3.75 mmol each). ●, n-Pentane; ○, isopentane; △, isobutane–hexanes. Reaction temperature 28 °C, volume of pentane 10 cm^3

RESULTS AND DISCUSSION

Time Course of Isomerization.—Figure 1 shows the change in liquid-phase composition with time in the isomerization of pentane with co-ground mixtures of aluminium bromide and copper(II) sulphate (3.75 mmol each) at 28 °C. After 4 h, the conversion reaches 78%. The main product is isopentane with a selectivity of 99%, and the remaining products are isobutane and hexanes. Aluminium bromide itself shows small activity. Thus, a pentane solution (10 cm^3) of aluminium bromide (3.75 mmol) gave a pentane conversion of 8% after 1 h, but the conversion remained the same thereafter, indicating deactivation of the catalyst. Since pure aluminium bromide has no activity for alkane isomerization,[10] the activity may be caused by the presence of impurities, probably water. Copper(II) sulphate alone has no activity.

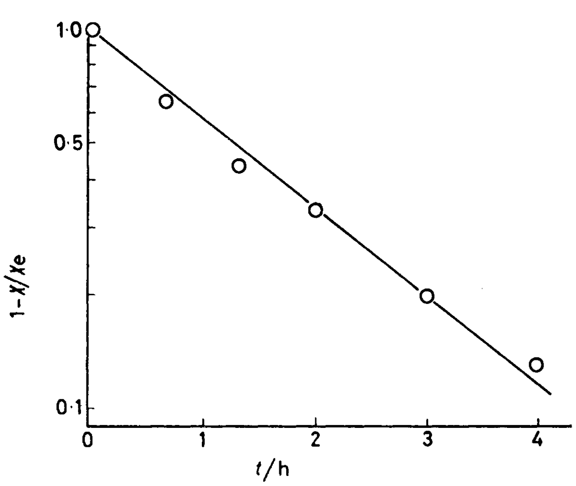


FIGURE 2 First-order plot for pentane isomerization. Catalyst $AlBr_3$–$CuSO_4$ (3.75 mmol each). Reaction temperature 28 °C

The rate of pentane isomerization was found to be the first order with respect to pentane as shown in Figure 2, where $\ln(1 - x/x_e)$ is plotted against time t. In equation (1) x and x_e are the conversion of pentane (or the molar fraction of isopentane) at time t and at equilibrium, respectively. Thus, the rate of pentane isomerization r is expressed by equation (2) where C_p and $C_{i\text{-}p}$ are the molar concentration of pentane and isopentane, V is the volume of the pentane phase, and k and k' are the rate

$$\ln(1 - x/x_e) = -\alpha t \qquad (1)$$

$$r = -V\mathrm{d}Cp/\mathrm{d}t = kC_p - k'C_{i\text{-}p} \qquad (2)$$

constants, which are functions of the amount and the composition of the $AlBr_3$–$CuSO_4$ mixture, as described later. Integration yields equation (1), by putting $\alpha = k_T/V$ and $k_T = k + k'$. The isomerization of pentane was also carried out with mixtures of aluminium bromide and copper(II) chloride. The change in liquid-phase composition with time is given in Figure 3. In this case, isopentane is not always the main product in contrast to the reaction with aluminium bromide–copper(II) sulphate mixtures. Isopentane was the main product for the first 1 h, but decreases gradually with time, while isobutane increases gradually with time and becomes the main product after 2 h. Hexanes are also formed in appreciable amounts. The large difference of the selectivity between reactions over $AlBr_3$–$CuSO_4$ and over $AlBr_3$–$CuCl_2$, suggests that the copper(II) salts play some essential role in determining the catalytic properties.

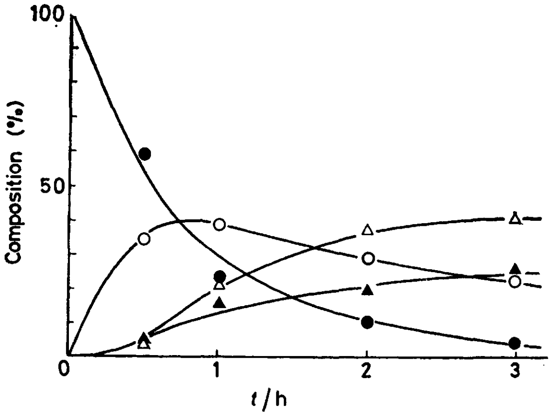


FIGURE 3 Change in liquid-phase composition with time. Catalyst $AlBr_3$–$CuCl_2$ (3.75 mmol each). ●, n-Pentane; ○, isopentane; △, isobutane; ▲, hexanes. Reaction temperature 28 °C, volume of pentane 10 cm^3

TABLE 1

Catalytic activities of $AlBr_3$ systems prepared in a vacuum system

Run no.	Catalyst	$AlBr_3$ (mmol)	$CuSO_4$ $CuCl_2$ H_2O (mmol)	$i\text{-}C_4H_{10}$ (%)	$n\text{-}C_4H_{10}$ (%)	$i\text{-}C_5H_{12}$ (%)	$n\text{-}C_5H_{12}$ (%)	C_6H_{14} (%)	Conversion (%)
1	$AlBr_3$	5.5		Trace	0	0.5	99.3	0.2	0.7
2	$AlBr_3$–H_2O	3.0	0.37	0.1	0	7.6	92.1	0.2	7.9
3	$AlBr_3$–H_2O	5.8	0.19	0.1	0	9.9	89.9	0.1	10.1
4	$AlBr_3$–$CuSO_4$	4.3	3.8	1.5	Trace	23.4	74.0	1.1	26.0
5	$AlBr_3$–$CuSO_4$	4.1	3.1	1.5	Trace	19.5	78.1	0.9	21.9
6	$AlBr_3$–$CuCl_2$	3.2	3.7	30.2	0.5	28.8	22.4	18.1	77.6

Reaction time 2 h, reaction temperature 28 °C, pentane 10 cm^3.

Isomerization using a Vacuum System.—The fact that aluminium bromide itself showed catalytic activity in isomerizations by method A (see Experimental section) suggested the possibility that impurities such as water or oxygen might be involved in the system and induce the catalytic activity. In the case of alkylation of benzene with alkanes by aluminium chloride and copper(II) chloride,[11] Olah *et al.*[12] suggested that protonic impurities acting as co-acids for aluminium chloride initiated the formation of a carbonium ion from the alkane. Here, in order to examine whether the synergetic effect is caused by impurities, the catalysts were prepared by using a vacuum system, in which the possibility of contamination could be minimized. The results are summarized in Table 1. With this method, aluminium bromide has only negligible activity (run 1), showing almost complete elimination of water from the system. Addition of some water gave rise to catalytic activity (runs 2 and 3) in accord with previously reported results.[10] The conversion of pentane is much greater in the presence of aluminium bromide and copper(II) sulphate than in the presence of aluminium bromide and water (runs 4 and 5). Similarly, the mixture of aluminium bromide and copper(II) chloride gave much higher conversions of pentane than aluminium bromide with water. These results suggest that the activity of aluminium bromide and copper(II) salt mixtures is not caused by the interaction of aluminium bromide and water, which might exist as an impurity.

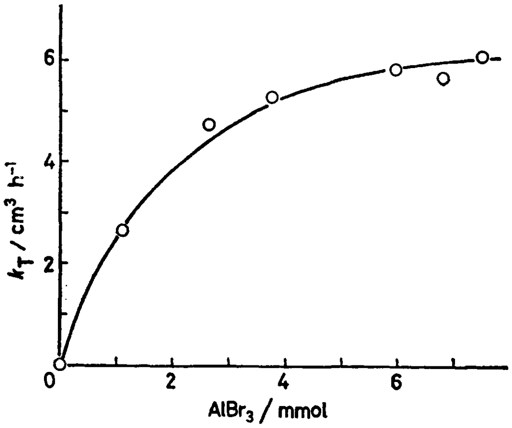


FIGURE 4 Dependence of k_T on the amount of $AlBr_3$. Amount of $CuSO_4$ 3.75 mmol, 28 °C

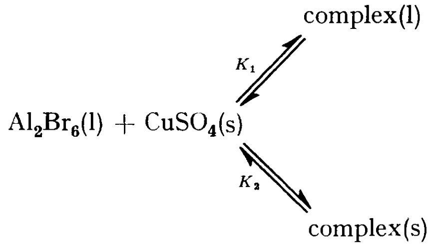
Effect of Catalyst Composition on Activity.—The effect of the catalyst composition on the isomerization activity was examined. Figure 4 shows the dependence of the rate constant k_T at 28 °C on the amount of aluminium bromide with a fixed amount of copper(II) sulphate (3.75 mmol). Without aluminium bromide, isomerization does not proceed at all. The rate increases gradually with the amount of aluminium bromide.

Figure 5 shows the dependence of the rate constant k_T at 23 and 28 °C on the amount of copper(II) sulphate when the amount of aluminium bromide is fixed. The rate constant k_T increases linearly with the amount of copper(II) sulphate as in equation (3) where k_1 and k_2

$$k_T = k_1 + k_2[CuSO_4] \tag{3}$$

are constants, and $[CuSO_4]$ denotes the amount of copper(II) sulphate in the system.

We presume here that aluminium bromide and copper(II) sulphate form a complex which is the active species in the isomerization. The complex exists in the pentane phase and also on the surface of copper(II) sulphate [reaction (4) where complex (l) and complex(s)



$$\begin{tikzcd} & \text{complex(l)} \\ Al_2Br_6(l) + CuSO_4(s) \arrow[ur, shift left, "K_1"] \arrow[dr, shift left] & \\ & \text{complex(s)} \arrow[ul, shift left, "K_2"] \end{tikzcd} \tag{4}$$

denotes the complex dissolved in pentane and that adsorbed on the surface of sulphate, respectively, and K_1 and K_2 are the equilibrium constants].

The concentration of the complex in pentane is proportional to the amount of aluminium bromide present, but does not depend on the amount of solid copper(II) sulphate in the presence of sufficient $CuSO_4$. The first term in equation (3) may be assigned to the rate induced by the complex dissolved in pentane.

The amount of complex on the surface should be proportional to the surface area and thus to the amount of copper(II) sulphate. The second term in equation (3) may be assigned to the rate induced by the complex adsorbed on the surface of copper(II) sulphate.

The dependence of the rate constant k_2 on the concentration of aluminium bromide is determined by the adsorption isotherm of the complex on copper(II) sulphate, while the rate constant k_1 is proportional to aluminium bromide concentration.

Location of Active Species.—In order to confirm the existence of the active species in liquid phase, the following experiment was carried out. The mixture of aluminium bromide and copper(II) sulphate was suspended in pentane (10 cm^3) for 5 min. Most of the liquid was then transferred into an ampoule under nitrogen and kept for 2 h at 28 °C, and the liquid composition was analysed. Pentane (10 cm^3) was added to the remaining solid and shaken for 3 min, and then most of the liquid was removed. The same procedure was repeated four times. The catalytic activity of the remaining solid was examined by adding pentane (10 cm^3) and keeping the system at 28 °C for 2 h. The results are given in Table 2. Isomerization proceeds in the liquid phase. The conversion of pentane in the absence of solid is about half that in its presence. Thus, the substance formed by the interaction of aluminium bromide and copper(II) sulphate exists in the liquid phase and promotes the isomerization. Thus, the remaining half of the activity must be caused by the active species on the surface of copper(II) sulphate. However, as shown in Table 2, the solid thoroughly washed by pentane shows only trace activity. This shows that the active species on copper(II) sulphate is washed out by the repeated washing treatment as expected from equilibrium (4).

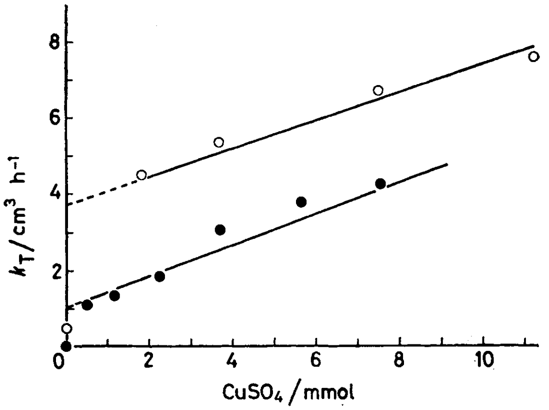


FIGURE 5 Dependence of k_T on the amount of $CuSO_4$. ○, At 28 °C; ●, at 23 °C. Amount of $AlBr_3$ 3.75 mmol

TABLE 2

Catalytic activity of the dissolved complex and washed solid

Catalyst $AlBr_3$–$CuSO_4$			$i\text{-}C_4H_{10}$ (%)	$i\text{-}C_5H_{12}$ (%)	$n\text{-}C_5H_{12}$ (%)	C_6H_{14} (%)	Conversion (%)
(mmol)	(mmol)						
3.75	2.00	With solid	1.0	52.6	45.4	1.0	54.6
		Without solid	0.5	31.2	67.5	0.8	32.5
		Washed solid	0.2	1.6	97.8	0.4	2.2
3.75	1.00	With solid	0.8	36.9	61.1	1.2	38.9
		Without solid	1.3	15.7	81.6	1.4	18.4
		Washed solid	0.1	0.8	98.7	0.4	1.3

Reaction temperature 28 °C, reaction time 2 h, pentane 10 cm^3.

Appearance of Copper Species in Pentane.—If the suggestion that the complex between aluminium bromide and copper(II) sulphate is correct, a copper species should appear in pentane. To confirm this, the solution properties of copper in pentane were examined. Pentane was added to a pre-kneaded mixture of aluminium bromide and copper(II) sulphate and shaken for 5 min; part of the liquid was then removed by a syringe. The copper content of the liquid was determined by atomic absorption spectroscopy. The dependence of copper concentration on the amount of aluminium bromide was examined by fixing the amount of copper(II) sulphate (3.75 mmol). The results are shown in Figure 6. Without aluminium bromide, copper(II) sulphate does not appear in pentane and the amount dissolved is seemingly proportional to the concentration of aluminium bromide, in agreement with expectation from equation (4).

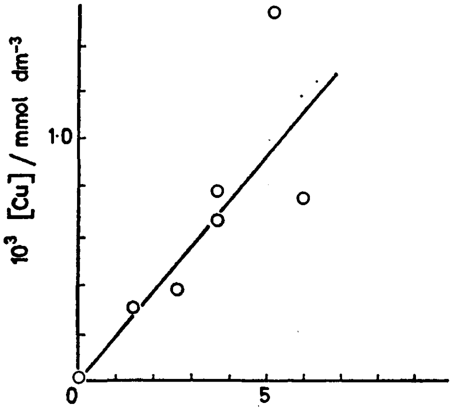


FIGURE 6 Dependence of copper concentration in pentane on the amount of AlBr$_3$. Amounts of CuSO$_4$ 3.75 mmol, volume of pentane 10 cm^3

Interaction of AlBr$_3$ *and* CuSO$_4$.—Aluminium bromide is known to react with several metal bromides to form complexes, *e.g.* CoAl$_2$Br$_8$,[13,14] FeAl$_2$Br$_8$,[15] PdAlBr$_8$.[16] In the case of AlCl$_3$–CuCl$_2$, Cu(AlCl$_4$)$_2$ formed by co-grinding the mixture has been found to be the active species for pentane isomerization. The results described above suggests the formation of a complex between aluminium bromide and copper(II) sulphate, which may be the active species for isomerization. When aluminium bromide and copper(II) sulphate are co-ground, a pronounced red-brown colour develops, indicating a chemical interaction between the two substances. This is confirmed by the reflection spectrum of the mixture. As shown in Figure 7, copper(II) sulphate has an absorption band due to a *d–d* transition at 860 nm and a charge-transfer band below 300 nm, while the mixture of aluminium bromide and copper(II) sulphate has absorption bands at 470, 825, 1 060, and 1 260 nm. Though the assignment of the latter bands is not yet clear, the formation of a new substance by reaction of the two components seems obvious.

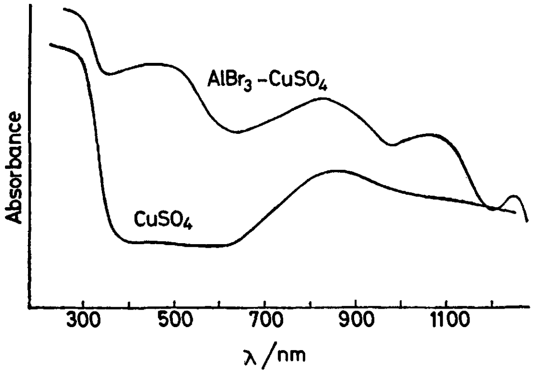


FIGURE 7 Electronic spectra of AlBr$_3$–CuSO$_4$ kneaded mixture and CuSO$_4$

EXPERIMENTAL

The isomerization was carried out by two different methods, A and B.

Method A.—Pentane (Kanto Chemical Co.) was distilled and dried with sodium wire. Aluminium bromide was purified by sublimation from a eutectic mixture of commercial aluminium bromide and sodium bromide with a small amount of aluminium powder at 110 °C. Anhydrous copper(II) sulphate was prepared by heating CuSO$_4$,5H$_2$O in air at 350 °C for 3 h and then under vacuum at 250 °C for 2 h. Anhydrous copper(II) chloride was prepared by heating CuCl$_2$,2H$_2$O in air at 150 °C for 3 h and then under vacuum at 250 °C for 2 h. The catalysts were prepared by grinding a mixture of aluminium bromide and anhydrous copper(II) sulphate (or chloride) in a porcelain mortar for 5 min under nitrogen. The mixture was then sealed in a glass tube with pentane (10 cm^3) and shaken in a temperature-controlled bath for 2 h at 28 °C.

Method B.—To minimize the influence of impurities, the catalysts were prepared in a vacuum system. Copper(II) sulphate prepared as in method A was placed in a glass tube and heated at 350 °C in the vacuum system. Aluminium bromide, purified by two sublimations, was then sublimed onto it.

Analysis and Spectra.—The products were analysed by g.l.c. with a hydrogen flame detector using a 6 m column packed with VZ-7 operating at 55 °C. The concentration of copper dissolved in pentane was determined by atomic absorption spectroscopy with a JEOL atomic absorption analysing spectrometer (JAA 7000S). Electronic and e.s.r. spectra were measured with a Shimazu MPS-5000 spectrophotometer and a JEOL X-band spectrometer (PE-1X), respectively.

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