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Catalytic Dehydrohalogenation of Haloethanes on Metal Sulfates

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The elimination reactions of hydrogen chloride and hydrogen bromide from chloroethanes and bromoethanes on metal sulfates were studied at 300° with the pulse technique. The small *trans*-1,2-dichloroethylene/*cis*-1,2-dichloroethylene ratio from 1,1,2-trichloroethane and the reactivity order among five chloroethanes on metal sulfates were common to those on solid acids, as expected from the metal sulfates belonging to the solid acid. However, it may be notable that characteristically small *trans*/*cis* ratio was observed on nickel sulfate, as much as 0.027, which was a fourth of that on silica–alumina, the smallest ratio reported previously. Small vinyl chloride/vinyl bromide ratios from 1-bromo-2-chloroethane on metal sulfates were also common to solid acids, and differed clearly from solid bases. The reaction mechanisms of concerted E2 (elimination bimolecular mechanism) in these eliminations on metal sulfates are discussed on the common base.

INTRODUCTION

It has been reported in previous papers (*1–3*), that the catalytic elimination reaction of hydrogen chloride from 1,1,2-trichloroethane proceeded with different selectivities on solid bases, solid acids, ion-exchanged molecular sieves and alumina. Some typical *trans*-1,2-dichloroethylene/*cis*-1,2-dichloroethylene (*trans*-1,-2/*cis*-1,2) selectivities are shown in Table 1. The reaction mechanism was estimated from the linear free energy relationships (LFER) approach as for five chloroethanes as well as *trans*-1,2/*cis*-1,2 selectivities, to be an ionic concerted elimination bimolecular mechanism (E2) on the solid acid, a stepwise E2 on the solid base, a homolytic E2 on alumina, and a transitional mechanism on the intermediate solid between acid and base (*1*).

Metal sulfates have been studied extensively as a typical group of solid acids since Walling (*4*) found solid acidity by the basic indicator test. They were used as the catalysts in various reactions (*5*). In the present work, the elimination reactions of hydrogen halide from haloethanes on metal sulfates were discussed with the LFER approach (*6*). Elimination reactions of hydrogen halide on metal sulfates have scarcely been attempted except for 1,1-dichloroethane on nickel sulfate (*7*).

EXPERIMENTAL METHODS

Several dichloro- and trichloroethanes were obtained from Tokyo Kasei. Metal sulfates were of Guaranteed Reagent from the Hayashi Co. The supported catalyst of nickel sulfate was obtained by impregnating silica gel (Wako) with 0.4 or 0.1 meq/g of nickel sulfate, and then dried at 120° in the atmosphere. The Y molecular sieve (Linde) was ion exchanged with a sufficient amount of nickel sulfate aqueous solution, dried at 120°, and calcined at 400° (Ni–Y) (*8*).

The reaction rates and selectivities were measured at 300° by the pulse technique as described in a previous paper (*1*). The metal sulfates were pretreated in the helium gas flow for 4 hr at a temperature range of 300–500°. The details of the experiments were described in previous papers (*1–3*).

RESULTS AND DISCUSSION

Elimination Reactions of 1,1,2-Trichloroethane on Metal Sulfates

Dechlorination, exchange of chlorine with hydrogen, and decomposition took place in addition to the elimination of hydrogen chloride, although they were minor except for dechlorination on cupric and ferric sulfates. Here dehydrochlorination was principally discussed. 1,1-Dichloroethylene was not detected by means of gas chromatography even at 80% conversion on all metal sulfates. The *trans*-1,2/*cis*-1,2 ratios on eight kinds of metal sulfates calcined at 300° are shown in Table 1, where some ratios on typical catalysts in previous papers and the equilibrium value are also shown for a comparison. Although small 1,1-dichloroethylene/1,2-dichloroethylene and *trans*-1,2/*cis*-1,2 ratios on metal sulfates are common to those on the solid acids as reported previously, the formation of *cis*-1,2-dichloroethylene was characteristically preferred to other dichloroethylene isomers, particularly on nickel and cobalt sulfates of which *trans*-1,2/*cis*-1,2 ratios were a fourth to a fifth of that on silica–alumina that was smallest in previous works (1–3).

TABLE 1

trans-1,2/*cis*-1,2 SELECTIVITIES FROM 1,1,2-TRICHLOROETHANE ON METAL SULFATES

Catalyst	Ratio[a]	Catalyst	Ratio
$NiSO_4$	0.027	$ZnSO_4$	0.074
$CoSO_4$	0.028	$Fe_2(SO_4)_3$	0.081
$MnSO_4$	0.034	SiO_2–Al_2O_3	0.11
$Cr_2(SO_4)_3$	0.057	Al_2O_3	0.17
$CuSO_4$	0.058	Cr_2O_3	0.14
$CdSO_4$	0.062	SrO	1.5

[a] Ratio: *trans*-1,2-dichloroethylene/*cis*-1,2-dichloroethylene; The equilibrium ratio at 300° is 0.645.

The relation between the conversion and the space velocity on nickel sulfate was shown in Fig. 1, where the space velocity was given by the weight of catalyst used (mg) under a constant carrier flow. The elimination of hydrogen chloride on nickel sulfate proceeded in a first order kinetics against the reactant.

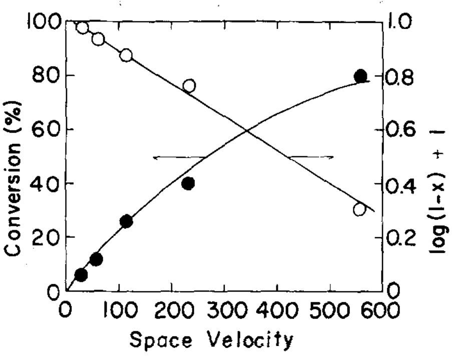

FIG. 1. The kinetics of the elimination reaction from 1,1,2-trichloroethane on nickel sulfate calcined at 300°. The space velocity was given by the weight of the catalyst (mg) under the constant carrier flow.

Reactivity Order of Chloroethanes on Nickel Sulfate

The reactivity order of five chloroethanes was 1,1,1-trichloroethane > 1,1-dichloroethane > 1,1,2-trichloroethane (into 1,2-dichloroethylene) > 1,1,2,2-tetrachloroethane > 1,2-dichloroethane. Such an order was similar to those on silica–alumina and other solid acids (1), as expected from that nickel sulfate belongs to the solid acid (5). In fact, pyridine poisoned this elimination reaction on nickel and cupric sulfates in such a manner as shown in Fig. 2.

On the same grounds as given in the previous papers (1, 2), the very small *trans*-1,2/*cis*-1,2 selectivity and the above reactivity order suggest that the reaction proceeds as an ionic concerted E2 reaction on nickel sulfate. The first order kinetics for the reactant is not contradictory to this mechanism.

In the previous paper, there was found a trend that the more acidic catalysts generally had the lower *trans*-1,2/*cis*-1,2 and 1,1/1,2 ratios of the elimination reaction of hydrogen chloride from 1,1,2-trichloroethane (1, 2). However nickel sulfate was deduced to be less acidic than silica–alumina from the reactivity in dealkylation and the Hamett indicator test (5, 9). So the small *trans*-1,2/*cis*-1,2 ratio of nickel

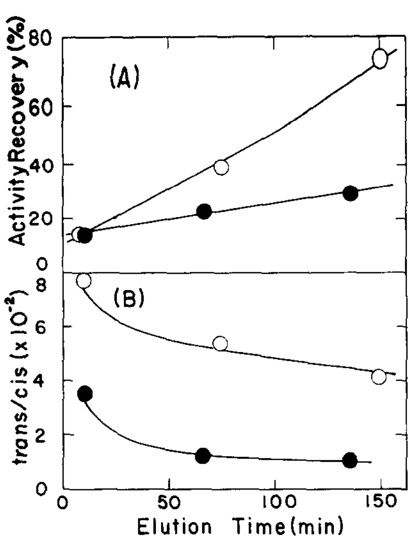

FIG. 2. Pyridine inhibition against the elimination reaction from 1,1,2-trichloroethane: (A) recovery of the catalytic activity; (B) recovery of *trans*-1,2/*cis*-1,2 selectivity. Two μl of pyridine were added to the catalyst of 200 mg; Elution and reaction temperatures were 300°; ●, $NiSO_4$; ○, $CuSO_4$.

sulfate cannot be understood on the same base as discussed in previous papers (*1*, *2*).

The Role of the Metal Ion in the Elimination Reaction

To examine the role of the metal ion in the very low *trans*-1,2/*cis*-1,2 selectivity of metal sulfate, *trans*-1,2/*cis*-1,2 ratios on various states of nickel sulfates are shown in Table 2. The calcination temperature had little effect on the *trans*-1,2/*cis*-1,2 ratio as well as total activity, although it has reportedly a distinct effect on selectivity and activity of nickel sulfate in some reactions (*5*, *9*).

TABLE 2
trans-1,2/*cis*-1,2 SELECTIVITIES FROM 1,1,2-TRICHLOROETHANE ON VARIOUS STATES OF NICKEL SULFATE

Catalyst	Temp. (°C)[a]	*trans*-1,2/*cis*-1,2
$NiSO_4$	550	0.028
$NiSO_4$	450	0.022
$NiSO_4$	400	0.025
$NiSO_4$	300	0.027
$NiSO_4$–SiO_2[b]	300	0.068
$NiSO_4$–SiO_2[c]	450	0.088
$NiSO_4$–SiO_2[c]	300	0.089
$Ni_3(PO_4)_2$	300	0.050
SiO_2	300	0.30

[a] Calcination temperature.

[b,c] $NiSO_4$, 0.4 and 0.1 meq/g, respectively.

Table 2 indicates that nickel ions other than nickel sulfate had not so small *trans*-1,2/*cis*-1,2 ratios.

Dehydrohalogenation from 1-Bromo-2-chloroethane on Metal Sulfates

1-Bromo-2-chloroethane was converted into vinyl chloride and vinyl bromide on metal sulfates. Although dehalogenation and disproportionation into 1,2-dichloroethane and 1,2-dibromoethane were also found on metal sulfates, here the discussion was limited on dehydrohalogenation.

Dehydrohalogenation selectivities on metal sulfates, as well as on typical acids and bases, are shown in Table 3 as vinyl chloride/vinyl bromide (chloride/bromide) ratios. Vinyl bromide should be produced preferably on every catalyst, if the reaction were in the equilibrium.*

TABLE 3
CHLORIDE/BROMIDE SELECTIVITIES FROM 1-BROMO-2-CHLOROETHANE ON METAL SULFATES[a]

Catalyst	Ratio	Catalyst	Ratio
$NiSO_4$	0.126	$Fe_2(SO_4)_3$	0.020
$CoSO_4$	0.144	$Ni_3(PO_4)_2$	0.086
$MnSO_4$	0.104	Al_2O_3	0.65
$CuSO_4$	0.083	KOH–SiO_2	5.3
$ZnSO_4$	0.077	SiO_2–Al_2O_3	0.10

[a] Ratio: $CHCl{=}CH_2/CHBr{=}CH_2$.

However, the selectivity varied markedly from catalyst to catalyst. From these chloride/bromide ratios, catalysts were qualitatively classified into three groups: the solid acids including metal sulfates have a small chloride/bromide ratio that means the preferential elimination of hy-

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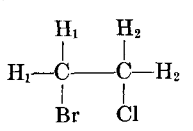
* The free energies of formation for reaction products are as following: $CHBr{=}CH_2$, 23.42 kcal/mole; HCl, −23.41; $CHCl{=}CH_2$, 16.84; and HBr, −13.76 at 300°. (Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," p. 641. Wiley, New York, 1968.)

drogen chloride; and on the other hand, the solid base, potassium hydroxide on silica gel, has a large chloride/bromide ratio; and alumina has an intermediate value. This variable selectivity according to the acid–base nature of the catalyst seems to be in the same situation as was found in the *trans*-1,2/*cis*-1,2 selectivity from 1,1,2-trichloroethane (*1*). So the same qualitative explanation may be applicable to these eliminations. On solid bases, the elimination may proceed through an $\alpha\beta$ stepwise E2, so that the hydrogen with less electron density is eliminated more readily. In order to estimate the electron densities of the hydrogen atoms of 1-bromo-2-chloroethane, a comparison between chemical shifts of ethyl bromide and ethyl chloride in NMR (*10*), was made (Table 4). These data show that a chlorine atom is more electrophilic against α hydrogen, but less against β hydrogen than a bromide atom (*11*). The tendency observed in the effect for α hydrogen was consistent with the electron negativity order (*12*). In the case of 1-bromo–2-chloroethane, it may be deduced from the above consideration that the hydrogen atom at 2 position must be of less electron density than that at 1 position due to α chlorine and β bromine, so that the elimination of hydrogen bromide should be preferred to that of hydrogen chloride, resulting in a preferential formation of vinyl chloride. This selectivity might be different from that expected through the E1 carbanion mechanism as reported by Hine *et al.* (*13*), but similar to the elimination reactivity ratio of chlorohexyl halide (*14*).

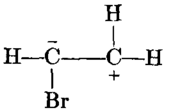
TABLE 4
Chemical Shifts of Ethyl Bromide and Ethyl Chloride

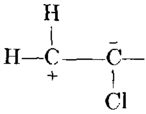
Halogen	α Hydrogen^{a} ppm	β Hydrogen^{a} ppm
Bromide	3.43	1.67
Chloride	3.57	1.48

^{a} $\underset{\beta}{CH_3}$-$\underset{\alpha}{CH_2}$-X.


$$H_1-\underset{Br}{\overset{H_1}{C}}-\underset{Cl}{\overset{H_2}{C}}-H_2$$
(I)

On the solid acid, following hypothetical concerted E2 reaction intermediates were assumed against formations of vinyl chloride and vinyl bromide, respectively, in the same manner as described in a previous paper (*1*). The intermediate II may be more stable than III from the viewpoint of the ionic structure, because a bromine may contribute more to the stabilization of the ionic intermediate by the more ability of the *d* orbital resonance with the negative charge (*13*, *15*) than a chlorine in the same position. Thus, vinyl bromide formation may be preferable to vinyl chloride formation. The reaction mechanism may vary gradually from the concerted E2 on the solid acids to the stepwise E2 on the solid bases according to the acid–base character of the catalysts, and the gradual change gives the variable selectivity.


$$H-\underset{Br}{\overset{-}{C}}-\underset{+}{\overset{H}{C}}-H$$
(II)


$$H-\underset{+}{\overset{H}{C}}-\underset{Cl}{\overset{-}{C}}-H$$
(III)

A more general and fine explanation for selectivities including all solid acids is yet in question; however, a balance of affinities of the catalyst against halogen and hydrogen atoms of the substrate seems an important factor for these elimination reactions.

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