The Dehalogenation of Haloalkanes on SiO_2-supported Metals

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The dehalogenations of haloethanes and halopropanes over metals (Cu, Ag, Au, Fe, Co, Ni, Pd, and Pt) supported by silica gel were studied by means of the microcatalytic pulse technique in order to elucidate the mechanism of dehalogenation. The dechlorination reactivities of *cis-* and *trans*-1,2-dichloroethylenes and the dechlorination products from *dl-* and *meso*-2,3-dichlorobutanes were observed from the viewpoint of stereoselectivity. The order of catalytic activities among the metals for the dehalogenation of haloethanes was: $Pt > Cu \approx Ni > Ag \approx Co \approx Pd > Fe \approx Au$. Dehalogenation proceeded exclusively in the 1,2-dihaloethanes. However, dehydorhalogenation took place in the 1,2-dihalopropanes to an appreciable extent when the product distributions of dehydrohalogenation were similar to those on solid acids. Both 1,1,2-trichloroethane and 1,2-dichloropropane were more reactive than 1,2-dichloroethane. 1,2-dichloroethylenes from 1,1,2,2-tetrachloroethane and 2-butenes from *dl-* and *meso*-2,3-dichlorobutanes were nearly in an equilibrium ratio of *cis*/*trans* forms. From a comparison of these results with those of the dehydrohalogenation on solid acids, it is concluded that the dehalogenation of haloalkanes on metals proceeds through a radical-step-by-step mechanism.

It has been reported that the dechlorination of chloroethanes on chromia proceeds through an E2-concerted mechanism.[1] The dechlorination on metal sulfates has interest in connection with the stereoselectivity and activity which depend on the kind of metal ion.[2] It may be expected that the dehalogenation takes place selectivity on metals because of the nonpolar nature of their surfaces.

In the liquid phase, the reactions of *vic*-dibromoalkanes with metals such as Mg and Zn were studied, and an E2-concerted mechanism or a carbanion mechanism has been proposed on the basis of the product distribution.[3] It is interesting to compare the gas-phase dehalogenation on metals with the liquid-phase reaction.

In the present study, the dehalogenation of haloethanes and halopropanes on metals (Cu, Ag, Au, Fe, Co, Ni, Pd, and Pt) was investigated in order to elucidate the characteristics of metals compared with compound catalysts with regard to halogen-metal interaction. The activities of metals and the reactivities of several chloroalkanes were analyzed on the basis of the δ_C and δ_R LFER approaches.[1,2,4]

Additional information was obtained from the dechlorinations of 1,2-dichloroethylenes and 2,3-dichlorobutanes on several metals.

Experimental

Reagents. The reagents used in this work were obtained from the Tokyo Kasei Co. They were of an E.P. grade and were used without further purification. The *dl-* and *meso*-2,3-dichlorobutanes were obtained by the resolution of their mixture by using a DIDP (2 m, 20°C) column.

Catalysts. The metal catalysts supported by silica gel were obtained by impregnating silica gel (Wako) with an aqueous solution of metal salt (Cu, Ag, Co, Ni : nitrate, Au, Pd, Pt : chloride, Fe : hydroxide); then they were dried at 120°C in the atmosphere. Each catalyst contained 0.4 mg-atom/g-silica gel. Before use, all of them except Fe, Co, and Ni (Fe, Co : 450°C, Ni : 400°C) were reduced at 300°C by the hydrogen in the reactor.

Procedures. The reaction rates and selectivities were measured by the microcatalytic gas chromatographic technique in the temperature range from 200 to 450°C. TCP was used in an analytical column (60 or 120°C, 2 m). Silicon SF (4 m, room temperature) was also used for the separation of the butenes. Hydrogen gas was used as the carrier. Hydrogenolysis was very small, even on Pt, Ni, and Pd, in the reaction of 1,2-dihaloethane. However, decompositions other than dechlorination took place to a considerable extent in the reactions of 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane on Pd and Pt, so helium gas was used in these cases. The activities decreased from pulse to pulse (the second pulse conversion was *ca.* 50% of the first), so the reaction rates were obtained from the first pulse. This deactivation by reaction products means that the reaction observed in the present study is the halogenation of metals by haloalkanes. The reaction rates (m*l*/g·min) were measured below a 20% conversion. The details of the experiments have been described in previous papers.[1,2,5]

Results

Dehalogenation Activities of Metal Supported by Silica Gel. As for 1,2-dihaloethanes, dehalogenation took place exclusively on the metals supported by silica gel, except for 1,2-dibromoethane on Fe, where dehydrobromination took place to a considerable extent. The catalytic activities of metals for 1,2-dichloroethane are shown in Fig.1 as a function of the reaction temperature. The results for 1,2-dibromoethane are shown in Fig.2. The activities of the meatls at 300°C were in the order of $Pt > Cu \approx Ni > Co \approx Ag \approx Pd > Fe \approx Au$ in both dehalogenations. The reactivities of the two haloethanes are compared in Fig.3. The rates of debromination were larger than those of dechlorination. This difference was pronounced on Pt, Pd, and Fe. The apparent activation energies were smaller for debromination than for dechlorination, corresponding to the higher re-

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[1] I. Mochida and Y. Yoneda, *J. Org. Chem.*, **33**, 2163 (1968).

[2] a) I. Mochida, A. Kato, and T. Seiyama, *J. Catal.*, **18**, 33 (1970). b) I. Mochida, Y. Anju, H. Yamamoto, A. Kato, and T. Seiyama, This Bulletin, **44**, 3305 (1971).

[3] L. Crombie and S. Harper, *J. Amer. Chem. Soc.*, **72**, 1707 (1950), H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958).

[4] I. Mochida and Y. Yoneda, *J. Catal.* **8**, 223 (1967).

[5] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, This Bulletin, **45**, 1635 (1972).

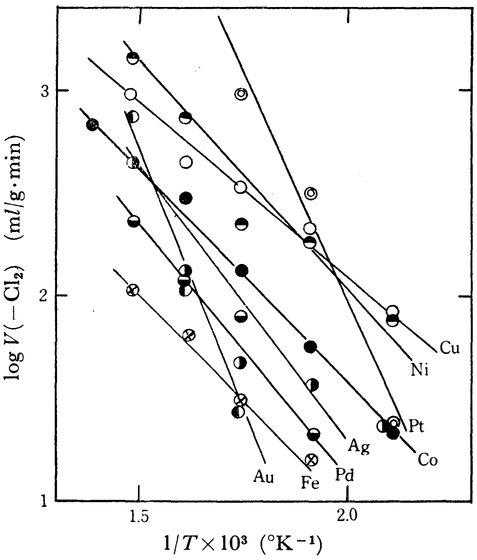

Fig. 1. Arrhenius plots of dechlorination of 1,2-dichloroethane on metals supported by silica gel.

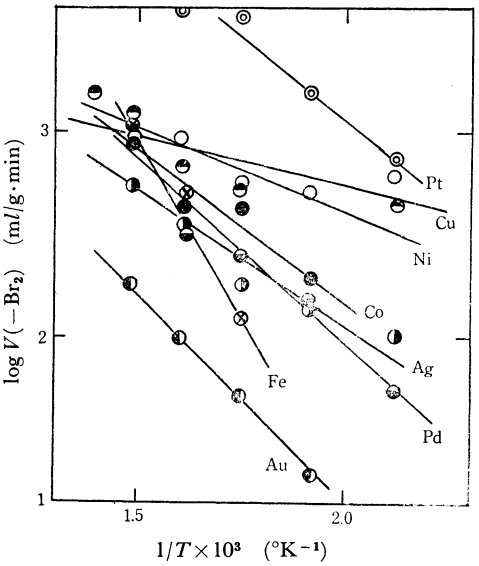

Fig. 2. Arrhenius plots of debromination of 1,2-dibromoethane on metals supported by silica gel.

activity of the bromoethane. One can observe a correlation between the values of the apparent activation energies for the two dehalogenations. This correlation, together with the correlation of reactivities shown in Fig.3, indicates a similarity in the mechanisms between the two reactions.

On the other hand, the reactivity order among the three dihaloethanes, 1,2-dichloroethane, 1,2-dibromoethane and 1-bromo-2-chloroethane, varied according to the kind of metal as may be seen in Fig.3. The debromochlorination-reactivity of 1-bromo-2-chloroethane was near the debromination-reactivity of 1,2-dibromoethane on Cu, Ni, Co, and Ag, but was rather close to the dechlorination-reactivity on Pt, Pd, Au, and Fe. The first metal group shows a small activation energy, as may be seen in Fig.4. These results may reflect the difference between the two groups in the affinity of the metal to chlorine and bromine.

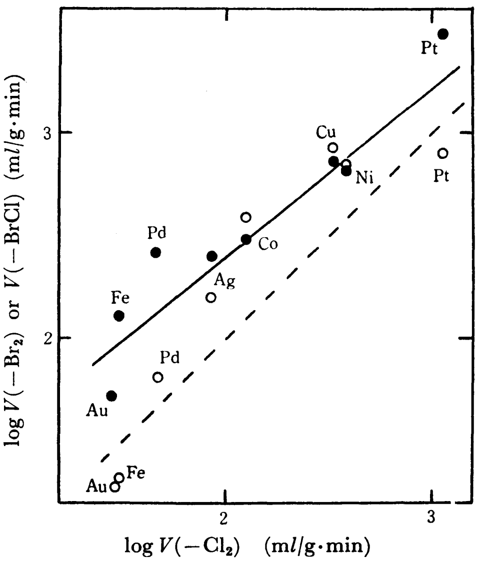

Fig. 3. Dehalogenation-reactivities of 1,2-dihaloethane at 300°C, abscissa; dechlorination of 1,2-dichloroethane, ordiate; debromination of 1,2-dibromoethane(●), and dechlorobromination of 1-bromo-2-chloroethane(○). Dotted line indicates the rate equal to dechlorination of 1,2-dichloroethane.

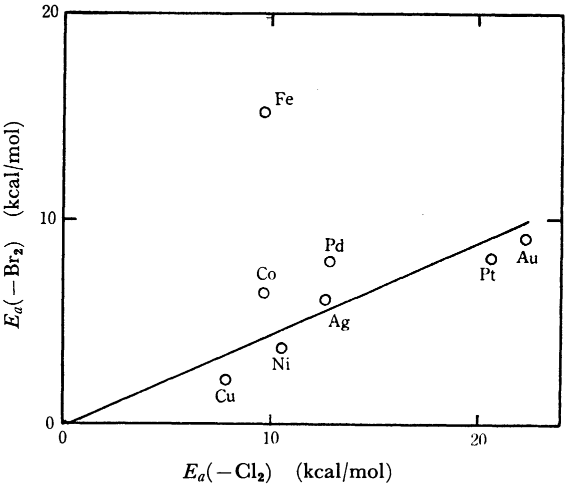

Fig. 4. Apparent activation energies of dehalogenation, abscissa; dechlorination of 1,2-dichloroethane, ordiate; debromination of 1,2-dibromoethane.

Substituent Effects on the Dechlorination Reactivity. The reactivities of three chloroethanes and 1,2-dichloropropane on some metals at 300°C are shown in Table1. The order of the reactivity was 1,1,2,2-tetrachloroethane > 1,1,2-trichloroethane > 1,2-dichloropropane > 1,2-dichloroethane. This order is different from that in dehydrohalogenation on solid acids, where 1,1,2-trichloroethane is much more reactive than 1,1,2,2-tetrachloroethane.[6] The above order is rather similar to that of dehydrochlorination on solid bases, but the reactivity differences among these reactants are not so large as in the dehydrochlorination on solid bases.[6]

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[6] I. Mochida, J. Take, Y. Saito, and Y. Yoneda, *J. Org. Chem.*, **32**, 3894 (1967).

TABLE 1. THE RATES OF DECHLORINATION OF SOME CHLOROETHANES AND 1,2-DICHLOROPROPANE ON METALS AT 300°C

Metal	Reactant			
	1,2-dichloropropane	1,2-dichloroethane	1,1,2-trichloroethane	1,1,2,2-tetrachloroethane
Cu	580	340	630	950
Ag	89	87	141	185
Au	98	89	109	140
Fe	18a)	30	46	110
Co	186a)	130	250	310
Ni	550	380	970	990
Pdb)	19	6.7	20	19
Ptb)	68	43	49	153

a) The rate of dehydrochlorination was very large as shown in Table 2.
b) Helium was used as a carrier gas.

TABLE 2. ELIMINATION OF 1,2-DIHALOPROPANE ON METALS SUPPORTED BY SILICA GEL AT 300°Ca)
THE RESULTS WITH REGARD TO SOLID ACIDS WERE SHOWN FOR COMPARISON

Cat.	Reactant									
	1,2-dichloropropane					1,2-dibromopropane				
	$-Cl_2$(A)	$-HCl$(B)b)	B/A	all./1d)	t/ce)	$-Br_2$(C)	$-HBr$(D)c)	D/C	all./1d')	t/ce')
SAf)	16.8	948	56.2	0.608	0.140	91	1575	17.3	3.86	0.390
Ag)	16.3	247	15.1	0.184	0.024	212	391	1.84	0.634	0.134
Fe	18.5	420	22.7	0.499	0.132	459	1248	2.75	0.805	0.377
Co	186	215	1.15	0.107	0.084	438	539	0.965	0.809	0.162
Ni	554	101	0.182	0	0.233	740	197	0.266	0.989	0
Cu	583	178	0.305	0.022	0.317	818	236	0.289	0.243	0
Ag	88.9	29	0.326	0.544	0.027	395	176	0.446	1.07	0.162
Au	98.2	6.2	0.070	0	0	67	30.7	0.458	—	—
Pdh)	19.4	0	0			185	0	0		
Pth)	68.4	0	0			990	0	0		

a) Dehydrohalogenation did not proceed on Pd and Pt at all.
b) 2-chloropropylene was not detected at all except on Ni.
c) 2-bromopropane was detected on Fe, Co, Ni, but the mount was very small except Ni.
d, d') The ratio of allylchloride/1-chloropropylene and that of allylbromide/1-bromopropylene, respectively.
e, e') The ratio of *trans*-1-chloropropylene/*cis*-1-chloropropylene and that of *trans*-1-bromopropylene/*cis*-1-bromopropylene, respectively.
f) Silica alumina (13% Al_2O_3)
g) Alumina (calcined at 550°C)
h) Helium was used as a carrier gas.

The dehydrohalogenation of 1,2-dihalopropanes took place simultaneously with the dehalogenation to various extents, according to the kind of metal. The ratios of dehydrohalogenation/dehalogenation are shown in Table 2. The ratio is high on Fe and Co. The dehydrohalogenation-activities of metals were in the following order: Fe>Co>Cu, Ag, Ni, Au≫Pt, Pd. Allyl chloride, and 1-chloropropylenes, mainly *cis*-1-chloropropylene, were formed by the dehydrochlorinaiton of 1,2-dichloropropane. These product distributions are similar to those on solid acids.7)

Stereoselectivity in Dechlorination. The products of dechlorination of 1,1,2,2-tetrachloroethane were *trans*- and *cis*-1,2-dichloroethylenes. 1,1-dichloroethylene was not detected. The ratios of *trans*-1,2/*cis*-1,2 obtained were near to the equilibrium value (0.654 at 300°8)) on most metals except for Cu and Au, where the ratios were nearly unity. These selectivities were considered to be those for the primary product, since the rates of the isomerization of 1,2-dichloroethlyene were small compared with those of the dechlorination. It is interesting that the ferric and cupric sulfates on silica gel also gave, respectively, the equilibrium value and unity for this selectivity.

The *meso*- and *dl*-forms of 2,3-dichlorobutane have been used to investigate the stereospecificity in the eliminations: the dechlorination on zinc and magnesium metals in the liquid phase3) and the dehydrochlorination on alkali- and alkali earth-metal salts.9) In the present dechlorination on metals in the vapor

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7) H. Tominaga, T. Nakamura, H. Arai, and T. Kunugi, *Kogyo Kagaku Zasshi*, **74**, 199 (1971).

8) A. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, **67**, 1493 (1954).

9) H. Noller, P. Andreu, and M. Hunger, *Angew. Chem. Int. Ed.*, (*Engl.*), **10**, 172 (1971).

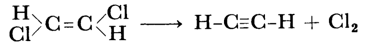
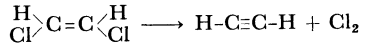
Table 3. The ratio of 2-butenes, that is the ratio of dechlorination products from *dl*- and *meso*-2,3-dichlorobutanes

Metal	Reaction temperature	*trans*/*cis*[a)]	*trans*/*cis*[b)]
Cu[c)]	100°C	1.9	2.0
Pt[d)]	300°C	1.4	1.6

a) The ratio of 2-butenes, from *dl* form.
b) The ratio of 2-butenes, from *meso* form.
c) Hydrogen was used as a carrier gas.
d) Helium was used as a carrier gas. *i*-Butene was the main dechlorination product.

Table 4. The rates of *trans*- and *cis*-elimination ($-Cl_2$) of 1,2-dichloroethylenes at 300°C

Metal	Rate of *trans*-elim.[a)] (m*l*/g·min)	Rate of *cis*-elim.[b)] (m*l*/g·min)	Ratio $\left(\frac{trans\text{-elim.}}{cis\text{-elim.}}\right)$
Cu[c)]	91	78	1.2
Pt[d)]	15	52	0.3

a) 
$$\underset{Cl}{\overset{H}{}}\!\!>C{=}C<\!\!\underset{H}{\overset{Cl}{}} \longrightarrow H\text{-}C{\equiv}C\text{-}H + Cl_2$$
b) 
$$\underset{Cl}{\overset{H}{}}\!\!>C{=}C<\!\!\underset{Cl}{\overset{H}{}} \longrightarrow H\text{-}C{\equiv}C\text{-}H + Cl_2$$
c) Hydrogen was used as a carrier gas.
d) Helium was used as a carrier gas.

phase, both *meso*- and *dl*-2,3-dichlorobutanes produced *trans*- and *cis*-2-butenes to the same degree, as is shown in Table 3; this is in contrast to the dechlorination on zinc and magnesium metals in the liquid phase, where *meso*- and *dl*-forms gave *trans*- and *cis*-2-butenes respectively.[3)] The rates of the isomerization of the 2-butenes were negligibly small on these metals under the same conditions. The lack of stereospecificity in the dechlorination of 2,3-dichlorobutanes indicated that the dechlorination took place through an intermediate in which the rotation of the C–C bonds was free. Therefore, a similar situation might occur in the dechlorination of 1,1,2,2-tetrachloroethane to 1,2-dichloroethylene.

Discussion

Mechanism of the Dehalogenation of Haloalkanes on Metal. In contrast to the selective occurence of dehydrohalogenation on solid acids and bases, the dehalogenation of haloethanes took place predominantly on the metals examined in the present study. Solid acids and bases have polar sites on their surface, whereas there are no such polar sites on matel surfaces. This difference between metals and solid acids or bases in the nature of the surface may be responsible for the variation in the elimination products. An ionic-step-by-step mechanism has been proposed for the dehydrohalogenation on solid acids,[2b)] in this mechanism, the first step is the abstraction of a halogen atom as a halide ion. Judging from the nonstereospecific dechlorination of 2,3-dichlorobutanes, the dehalogenation of haloalkanes on metal may also occur by a step-by-step mechanism. The difference in elimination products, however, shows that the manner in the halogen abstraction is different between metals and solid acids. From the nonpolar nature of the metal surface, a non-ionic mechanism may be considered likely for the dehalogenation on matels. The small substituent effect on the dehalogenation reactivity on metals, compared with the dehydrohalogenation-reactivity on solid acids and bases, indicates a non-ionic intermediate in the dehalogenation on metals.[10)]

A similar difference between metals and solid acids or bases was observed in the elimination reaction of 1,2-dichloroethylenes. On solid acids and bases, *cis*- and *trans*-1,2-dichloroethylenes underwent dehydrochlorination when the *cis*-form showed a much higher reactivity than the *trans*-form.[11)] On the other hand, the dichloroethylenes underwent dechlorination on metals, as was observed on haloalkanes, and the reactivity difference of both isomers was not very large, as is shown in Table 4. The higher reactivity of *cis*-1,2-dichloroethylene is characteristic of an ionic medium, such as solid acids or bases and basic solutions. The comparable reactivity of the two isomers on metals, accordingly, shows that the dechlorination occurs through a non-ionic mechanism on metals.

From these comparisons between metals and solid acids or bases, it can be concluded that the dehalogenation of haloalkanes on metals proceeds though a radical-step-by-step mechanism.

The interaction between the halogen atom and a metal surface may result from the coordination of a lone pair of the halogen atom to the unoccupied orbitals. In the above mechanism, the first step of the dehalogenation of haloalkanes on metals is the abstraction of the halogen atoms by a metal surface. The fact that 1-bromo-2-chloroethane shows a close reactivity to 1,2-dibromoethane on Cu, Ni, Co, and Ag can be easily understood by the above radical-step-by-step mechanism, provided that the weaker C–Br bond is broken in the first step on both reactants. 1-bromo-2-chloroethane showed, on the other hand, a lower reactivity than 1,2-dibromoethane on Pt, Pd, and Au. This may be related to the large back-donating powers of these metals in M-Br coordination.[12)]

The dehydrohalogenation which was observed with regard to 1,2-dihalopropane may proceed *via* an El carbonium ion mechanism, as is indicated by the product distribution being similar to that on the solid acids.[7)] This mechanism can explain the high dehydrohalogenation reactivity of 1,2-dihalopropane from the electron-donating effect of the methyl group, as has been described previously.[2)] High ratios of $-HX/-X_2$ were observed on Fe and Co, showing that these metals have a considerable ability to abstract the halogen atom as a halide ion besides a radical. The metals with a high value of dehydrohalogenation/

[10)] J. E. Leffler and E. Grunwald, "Rates and Equilibrium of Organic Reactions," Wiley, New York (1963), p. 226.

[11)] Y. Anju, H. Yamamoto, I. Mochida, A. Kato, and T. Seiyama, unpublished observations.

[12)] R. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967), H. Matsumoto, Y. Saito, and Y. Yoneda, *J. Catal.* **19**, 101 (1970).

dehalogenation selectivity (Fe and Co) and the metals with a low ratio (Pt and Pd) also showed a high activity for acetaldehyde formation and ethylene formation respectively from ethylene chlorohydrin.[5) The former was considered to proceed through a carbonium-ion mechanism, and the latter, through a radical mechanism.[5)