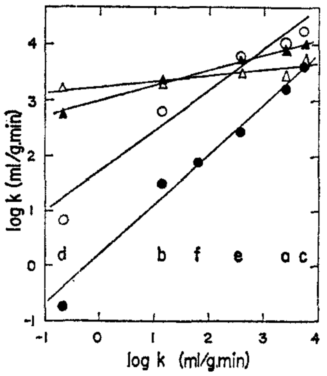

Figure 2.—Correlations among the reactivities of chloroethanes on SA-1, A-B-1, Mg-10X, 13X, and K-13X. The abscissa is the logarithm of the rate constants on SA-1. The alphabet designates the reactions in Table I: ●, A-B-1 (alumina-boria); ○, Mg-10X; ▲, 13X; △, K-13X.

TABLE III

PRODUCT DISTRIBUTION FROM 1,1,2-TRICHLOROETHANE

Catalyst	Product distribution	Conversion, %
13X	*trans* > *cis* > 1,1	
	58% 31% 11%	32
(200°)	66% 23% 11%	28
K-13X	*trabs* > 1,1 > *cis*	
	53% 34% 13%	30
Mg-10X	*cis* > *trans* > 1,1	
	84% 16% 0%	35
SA-1	*cis* > *trans* > 1,1	
	93% 7% 0%	14
SrO	1,1 > *trans* > *cis*	
	90% 6% 4%	9
Equilibrium[a]	*cis* > *trans* > 1,1	
	61% 39% 0%	

[a] P. Goldfinger and G. Martens, *Trans. Faraday Soc.*, **57**, 2220 (1957); K. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, **76**, 1493 (1954).

product distributions are different from those of any strong acids and bases. Among the catalysts investigated in the previous and present works, 13X gave the highest *trans* formation ratio, 58% at 300°. Over SA-1, 93% of the products was *cis*-1,2-dichloroethylene, and over SrO, 90% was 1,1-dichloroethylene. This means that any of these dichloroethylene isomers can be obtained in reasonably good yields from 1,1,2-trichloroethane by proper selection among these catalysts.

The activities of the molecular sieves for five chloroethanes are compared with those of SA-1 (silica-alumina) in Figure 2. They are all linearly correlated with each other, although the slopes of 13X and K-13X are distinctly smaller than those of alumina-boria(A-B-1)[1] and Mg-10X which are nearly unity. These linear correlations may imply that the activities of the molecular sieves are attributable to the acidic character common to these solids. If so, the reactivity order of the reactants can be explained by the same intermediate given in the case of solid acids.[1] On the other hand, the acid strength of these molecular sieves was measured with the Hammett's indicators[4] by the present authors as is given in Table II, which also shows their activities for cracking *t*-butylbenzene into benzene and isobutene. There is a trend that the more acidic molecular sieve generally has a high cracking activity as well as lower 1,1/1,2 and *trans*/*cis* ratios of the elimination reaction of hydrogen chloride from 1,1,2-trichloroethane. This trend is shown in Figure 3 as for *trans*/*cis* ratios. With the 4A, 5A, K-4A, and Ca-5A sieves, either 1,1,2-trichloroethane, *t*-butylbenzene, or the Hammett's indicators cannot enter into their small holes, so their reaction sites and sites of acid strength measurement are commonly restricted to those on the outer surface. With the Ca-5A, its low cracking activity in spite of its high acid strength and low *trans*/*cis* ratio may be attributable to its lack of the accessibility for *t*-butylbenzene at the inner surface.

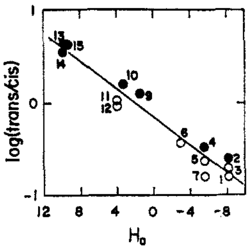

Figure 3.—Correlation between the *trans/cis* ratio and acid strength of molecular sieves in Table II. Numbers refer to Table II.

The correlation between the selectivity and acid strength coincides with the previous conclusion that the reaction mechanism changes gradually as the acid–base character of the catalyst varies.[1]

Registry No.—Hydrogen chloride, 7647-01-0.

Acknowledgments.—We owe thanks to Dr. Yasukazu Saito and Mr. Jun-ichiro Take for their helpful discussions. The authors are also grateful to the Asahi Glass Co. for the sample of the Y-type molecular sieve.

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[4] H. A. Benesi, *J. Amer. Chem. Soc.*, **78**, 5490 (1956); *J. Phys. Chem.*, **61**, 970 (1957).

Dehydrochlorination and Dechlorination of Chloroethanes on Chromia Catalyst

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In previous papers,[1,2] the dehydrochlorination of chloroethanes on solid acids and bases was studied by the LFER (linear free energy relationships) approach; the selectivities of the catalysts were reasonably well explained by an acid–base mechanism.

Chromia is a semiconductor catalyst usually used for dehydrogenation, but the products of an oxidation reaction, such as carbon dioxide, were scarcely found in the reaction under the hydrogen gas flow. The dehydrochlorination reaction has now been studied over chromia under conditions where oxidation need not be considered. Noller, *et al.*,[3] who briefly studied de-

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

[2] I. Mochida and Y. Yoneda, *ibid.*, **33**, 0000 (1968).

[3] H. Noller, W. Low, and P. Andreu, *Z. Elektrochem.*, **68**, 663 (1964).

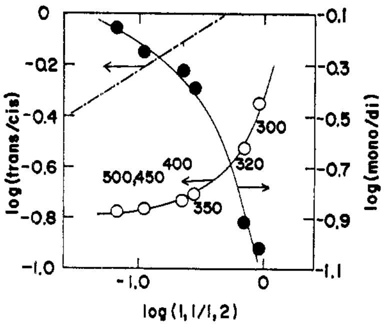

Figure 1.—Correlations of 1,1/1,2 selectivity with *trans/cis* and dechlorination/dehydrochlorination selectivities from 1,1,2-trichloroethane on the chromia catalysts reduced at various temperatures. The figures represent the reducing temperatures. The broken line is the selectivities of the typical solid acids and bases:[1] ○, *trans/cis*; ●, mono/di.

hydrochlorination of chlorobutane on a chromia catalyst, reported that its product distribution was similar to that observed with alumina.

In the present work, the LFER approach as for reactants and catalysts was applied to the results obtained during the dehydrochlorination and dechlorination of chloroethanes over chromia in order to get information about the behavior of a transition metal oxide in these reactions.

Experimental Section

Reactants are listed in Table I with their reaction products. The chromia catalyst (Cr-2) was made from chromic anhydride of G. R. grade. The calcination temperature was gradually raised to 450° and kept there for 3 hr. In the course of raising the temperature, the chromia gel underwent the glow phenomenon at about 200°, but the calcination was continued and the stable chromia gel, whose surface area was 27 m^2/g, was obtained.

Table I

Reagents and their Reaction Products

Reagent[a]	Reacn product	Dehydrochlorination no.
1,1-Dichloroethane[b] (75-34-3)	$CHCl{=}CH_2$[c]	1
1,2-Dichloroethane (107-06-2)	CH_2CH_2[d] $CHCl{=}CH_2$[c]	 2
1,1,1-Trichloroethane[b] (71-55-6)	$CCl_2{=}CH_2$[c]	3
1,1,2-Trichloroethane (79-00-5)	$CHCl{=}CH_2$[d] $CCl_2{=}CH_2$[c] *trans*-$CHCl{=}CHCl$[c] *cis*-$CHCl{=}CHCl$[c]	 4 5
1,1,2,2-Tetrachloroethane (79-34-5)	*trans*-$CHCl{=}CHCl$[d] *cis*-$CHCl{=}CHCl$[d] $CHCl_2{=}CHCl$[c]	 6

[a] Registry numbers appear in parentheses. [b] The dechlorination reactions were negligible for these reagents. [c] From a dehydrochlorination reaction. [d] From a dechlorination reaction.

The reaction rates and selectivities were measured at 300° by the pulse technique as described in a previous paper.[1] The catalyst was pretreated in the hydrogen gas flow for 4 hr at a temperature range of 300–500°. During the pretreatment at up to 500° in the hydrogen, violent phenomena such as glow were not observed. However, the over-all activity fell gradually owing to the decrease of the surface area. The over-all catalytic activity for 1,1,2,2-tetrachloroethane of the chromia reduced at 500° was about one-fourth of that of the chromia at 300°. Catalysts reduced at the same temperature gave constant product distributions independent of conversions. The reaction rate was calculated from the first pulse conversion because the activity as well as the selectivity of the catalyst changed gradually from pulse to pulse. The reproducibility of the first pulse was sufficiently good. The details of the experiments were described in previous papers.[1,2]

Results and Discussion

For 1,1,2-trichloroethane, the selectivities of chromia catalysts reduced at various temperatures are shown in Figure 1; the *trans/cis* and 1,1/1,2 ratios represent the selectivities in the dehydrochlorination, whereas the mono/di ratio shows the dechlorination/dehydrochlorination selectivity. Monotonic correlations were found between both *trans/cis* and 1,1/1,2 and mono/di and 1,1/1,2. The chromia reduced at a higher temperature has a lower 1,1/1,2, a lower *trans/cis*, and a higher mono/di ratio. The correlation between the former two was similar to that found on solid acids and bases,[1] which is shown as a broken line in Figure 1. However, the relation between *trans/cis* and acidity of the catalyst was just opposite of that observed on the typical solid acids and bases, in which the more acidic catalyst had a lower *trans/cis*[2] ratio, reduced chromia was reportedly less acidic than the oxidized chromia.[4]

The dehydrochlorination reactivity order of five reactants on the chromia reduced at 450° was 3 > 1 > 6 > 5 > 2 > 4 (the numbers designate the dehydrochlorinations listed in Table I.). This reactivity order was the same as on alumina,[1] and was correlated monotonically with $D_r^R(Cl) + D_r^R(H)$[5] after consideration for the symmetry number (the combination number of hydrogen and chlorine atoms) as in the previous paper.[1] Based on the same grounds as given in a previous paper,[1] the *trans/cis* ratio from 1,1,2-trichloroethane and the above reactivity order suggest that the reaction proceeds typically as a radical concerted E2 reaction when the chromia is reduced at high temperatures.

Dechlorination of 1,1,2,2-tetrachloroethane was also examined over the chromia, and the *trans/cis* selectivities after pretreatment at various temperatures are shown in Table II. As with 1,1,2-trichloroethane, the catalysts reduced at higher temperatures had higher dechlorination/dehydrochlorination ratios which are represented by the di/tri ratios in Table II. This de-

Table II

The Product Distribution from 1,1,2,2-Tetrachloroethane on Chromia Reduced at Different Temperatures

Reducing temperature, °C	Di/tri[a]	*trans/cis*[b]
300	0.03	0.56[c]
450	0.30	0.52
500	0.53	0.53

[a] The ratio of dichloroethylene/trichloroethylene shows the dechlorination/dehydrochlorination selectivity. [b] The ratio of *trans*-$CHCl{=}CHCl$/*cis*-$CHCl{=}CHCl$, the dechlorination products. [c] 1,1-Dichloroethylene was about 1% of dichloroethylenes in the case of the 300° reduction and was not detected in the cases of higher reduction temperatures.

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[4] S. E. Voltz, A. E. Hirshler, and A. Smith, *J. Phys. Chem.*, **64**, 1594 (1960).

[5] D_r^R is the delocalizability, one of the reactivity indexes by the molecular orbital theory, proposed by Fukui, *et al.*, for radical abstractions: K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **34**, 1111 (1961); I. Mochida and Y. Yoneda, *J. Catal.*, **9**, 57 (1967).

chlorination reaction was found to form *trans-* and *cis-*1,2-dichloroethylene nearly in equilibrium[2] which was independent of the reducing temperature. Very little dechlorination was observed for 1,1,1-trichloroethane and 1,1-dichloroethane (chlorine attached to the same carbon atom), but considerable dechlorination occurred with 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. These facts suggest that this elimination reaction may proceed through an $\alpha\beta$ concerted E2 mechanism similar with the debromination of 1,1,2,2-tetrabromoethane by iodide, which was postulated from an isotopic effect study.[6]

The dechlorination reactivity order after consideration for symmetry number (the combination number of chlorine atoms) was 1,1,2-trichloroethane (7.8 ml/g min^{-1}) > 1,2-dichloroethane (4.9) ≈ 1,1,2,2-tetrachloroethane (4.5) on the catalyst reduced at 450°. This reactivity order is not correlated with the sum of D_r^R(Cl).[5] The hypothetical intermediates are assumed to be stable in the following order by the contribution of the chlorine atom.

$$\underset{+\ \ -}{\mathrm{ClCHCH_2}} > \underset{+\ \ -}{\mathrm{CH_2CH_2}} \approx \underset{+\ \ -}{\mathrm{ClCHCHCl}}$$

The above stability is considered in the same manner as was the reactivity orders on solid acids in a previous paper.[1]

The chromia reduced at higher temperatures may have more surface chromium ions which have a stronger affinity to chlorine than to hydrogen. The chromia reduced at lower temperatures may have more surface oxygen ions which can attack hydrogen atoms preferably. Thus, the surface change which resulted from reduction of the catalyst may have been responsible for the differences of the 1,1/1,2 and *trans/cis* ratios from 1,1,2-trichloroethane and of dechlorination/dehydrochlorination selectivity as the catalyst was treated at different temperatures.

Acknowledgments.—We are grateful to Dr. Yasukazu Saito and Mr. Jun-ichiro Take for their helpful discussions.

[6] W. G. Lee and S. I. Miller, *J. Phys. Chem.*, **66**, 655 (1962).

The Addition of Nitrosyl Chloride to 3-Methylbutadiene-1,2

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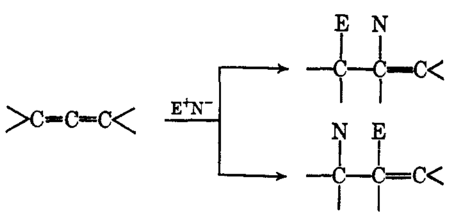
Electrophilic addition to allenes may lead to attachment of the electrophile either to a terminal carbon atom or to the central carbon atom of the allenic system.



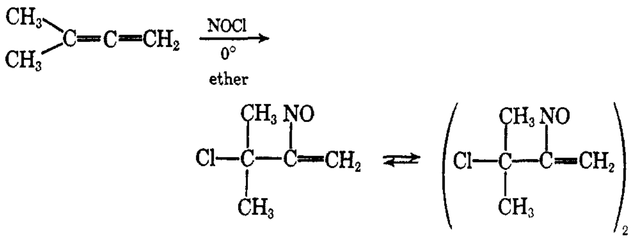
In the report describing the first preparation of allene, Gustavson and Demjanoff[2] noted that hydration in the presence of sulfuric acid afforded acetone. It was subsequently found[3,4] that hydration of monosubstituted allenes gave methyl ketones. Other examples of electrophilic additions to allenes apparently proceeding *via* protonation of an sp^2 hybridized carbon atom are the addition of hydrogen fluoride to allene to give 2,2-difluoropropane,[5] and the addition of methyl alcohol to 1,2-hexadiene in the presence of boron trifluoride and mercuric oxide affording the dimethyl ketal of 2-hexanone.[5]

The formation of a mixture of 2-chloro-2-hexene and 2,2-dichlorohexane upon treatment of 1,2-hexadiene with dry hydrogen chloride established that the terminal double bond can be the first attacked.[5]

In contrast to these cases, Kondakov[6] found that the addition of hydrogen chloride to 3-methylbutadiene-1,2 gave 3-chloro-3-methylbutene by proton attachment at the sp hybridized carbon atom. Jacobs and Johnson[7] observed that while the addition of dry hydrogen chloride to 1,2-butadiene proceeded by proton attachment at a terminal allenic carbon forming 2-chlorobutene, hydrogen chloride addition to 3-methylbutadiene-1,2 resulted in central attachment of electrophile forming a mixture of allylic chlorides.

Griesbaum[8-10] and coworkers observed the formation of cyclobutane derivatives upon heterolytic hydrobromination of allene, showing that this addition is not concerted. Sharma, Shoulders, and Gardner[11] found that attachment of the electrophile during oxymercuration of 1,2-cyclononadiene occurs at the central carbon of the allenic system.

We wish now to report that heterolytic addition of nitrosyl chloride to 3-methylbutadiene-1,2 at 0° in ether results in attachment of the electrophile at the sp hybridized carbon atom giving 2-nitroso-3-chloro-3-methylbutene (1).



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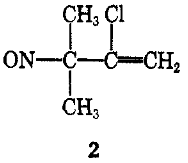

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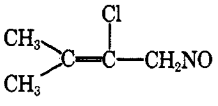

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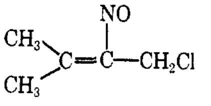

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