tolyl-4-methylpyrrole were obtained after recrystallization of the resulting solid from ethanol-water,[6] mp 90–91°; ν_{N-H}, 3420 cm^{-1}. Test of this pyrrole with *p*-dimethylaminobenzaldehyde was positive.[7]

When the same reaction was carried out at −30°, 1.2 g of 1,2-di-*p*-toluylpropane was obtained; 2.2 g of pale yellow liquid (bp 130–140° (2.1 mm)) also was obtained after column chromatography on silica gel. This liquid showed the presence of a carbonyl group at 1770 cm^{-1} in the ir spectrum (characteristic of γ-lactones) and was assumed to be 2-methyl-4-*p*-tolyl-γ-butenyl lactone by analogy with another reaction described later and from ir and nmr spectra (crude yield, 17%).

The nmr spectrum showed peaks at τ 8.27 (d, 3 H), 7.76 (s, 3 H), 4.60 (d, H), 4.40 (m, H), 3.07 (s, 4 H).

1,2-Di-*p*-toluyl-1-phenylethane.—Phenylacetylene (5.1 g, 0.05 mol) was added into the ether solution of lithium *p*-toluyltricarbonylnickelate (0.05 mol) and stirring was continued for 5 hr at −70°. After the same treatment, white crystals (3.9 g, recrystallized from ethanol) were obtained, mp 129°, and were identified as 1,2-di-*p*-toluyl-1-phenylethane from results of nmr analysis (Table I), testing with $FeCl_3$ solution (negative), and analytical data.

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47; mol wt, 342.4. Found: C, 84.17; H, 6.30; mol wt, 344.

When the same reaction was carried out at −30°, 3.8 g of 1,2-di-*p*-toluyl-1-phenylethane and 2.0 g of white crystals (mp 110.5–111°, after recrystallization from petroleum ether) were obtained. The latter crystals were assumed to be 2-phenyl-4-*p*-tolyl-γ-butenyl lactone from results of ir spectroscopy and analytical data, $\nu_{C=O}$ 1750 cm^{-1} (15.7% yield).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64; mol wt, 250.3. Found: C, 81.76; H, 5.81; mol wt, 254.

Furthermore, an ether-insoluble solid was obtained and recrystallized from benzene to give white needles which were assummed to be the dimer of the γ-butenyllactone: mp 270–271° dec; $\nu_{C=O}$ 1750 cm^{-1}.

Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26; mol wt, 498. Found: C, 82.02; H, 5.41; mol wt, 493 (Rast method in camphor).

1,2-Di-*p*-toluylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium *p*-toluyltricarbonylnickelate solution at −70° and was stirred for 5 hr. After similar treatment, white crystals of 1,2-di-*p*-toluylethane were obtained, mp 159°. These crystals were too insoluble for nmr study.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; mol wt, 266.3. Found: C, 81.12; H, 6.75; mol wt, 266.

These crystals were treated with ammonia in acetic acid solution to give 2,5-di-*p*-tolylpyrrole: mp 198–199°; ν_{N-H} 3460 cm^{-1}. Furthermore, the reduction of these crystals with lithium aluminium hydride in ether solution gave white neeldes of 1,4-di-*p*-tolylbutane-1,4-diol: mp 139.5°; ν_{O-H} 3340 and 3390 cm^{-1}.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.23; H, 8.13.

1,2-Dibenzoyl-1-phenylethane.—Phenylacetylene (5.1 g, 0.05 mol) was added to the lithium benzoyltricarbonylnickelate solution at −70° and was stirred for 5 hr. After hydrolysis with 50 ml of 4 *N* HCl, the reaction mixture was treated as described above. A fraction of bp 220–225° (2.3 mm) gave white crystals after recrystallization from ethanol, mp 127°, and these crystals were identified as 1,2-dibenzoyl-1-phenylethane from results of nmr spectroscopy and analytical data.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.10; H, 5.85.

These crystals were treated with ammonia in acetic acid to give 2,4,5-triphenylpyrrole: mp 139–140° (recrystallized from ethanol); ν_{N-H} 3420 cm^{-1}.

Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.48; H, 5.83; N, 4.61.

1,2-Dibenzoylpropane.—Methylacetyene (2.0 g, 0.05 mol) was added into the lithium benzoyltricarbonylnickelate solution (0.05 mol) at −70° and stirring was continued for 5 hr. After treatment as described above, white crystals of 1,2-dibenzoylpropane were obtained, mp 105° (recrystallized from ethanol).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; mol wt, 252.3. Found: C, 81.19; H, 6.11; mol wt, 253.

The dioxime of these crystals had mp 163° dec.

Anal. Calcd for $C_{17}H_{18}O_2N_2$: C, 72.32; H, 6.43. Found: C, 72.49; H, 6.65.

1,2-Dibenzoylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium benzoyltricarbonylnickelate (0.05 mol) at −70° and was stirred for 5 hr. After the above treatment, white crystals of 1,2-dibenzoylethane were obtained, mp 146° (recrystallized from ethanol). These crystals were too insoluble for nmr study, but the melting point of these crystals was not depressed by admixture with authentic sample.[8]

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.92; H, 5.67.

1,2-Di-*p*-anisoylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium *p*-anisoyltricarbonylnickelate solution (0.05 mol) at −70° and stirring was continued for 5 hr. After similar treatment, white crystals of 1,2-di-*p*-anisoylethane were obtained, mp 154° (recrystallized from ethanol).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.35; H, 6.04.

***n*-Dodeca-5,8-dione.**—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium valeryltricarbonylnickelate solution (0.05 mol) at −70° and was stirred for 5 hr. After similar treatment, white leaflets of *n*-dodeca-5,8-dione were obtained, mp 53° (recrystallized from petroleum ether (40–60°).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; mol wt, 198.3. Found: C, 72.64; H, 11.26; mol wt, 202.

Registry No.—$C_{17}H_{14}O_2$, 15982-66-8; dimer of $C_{17}H_{14}O_2$, 16059-92-0; $C_{18}H_{22}O_2$, 15982-67-9; $C_{22}H_{17}N$, 3274-61-1; $C_{17}H_{18}O_2N_2$, 15982-69-1.

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[7] F. Feigl, "Spot Tests in Organic Analysis," 5th ed, Elsevier Publishing Co., Amsterdam, 1956, p 278.

[8] P. S. Bailey and R. E. Lutz, *J. Amer. Chem. Soc.*, **70**, 2412 (1948).

Elimination Reaction of Hydrogen Chloride from 1,1,2-Trichloroethane on Ion-Exchanged Molecular Sieves

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It has been reported in a previous paper[1] that the catalytic elimination reaction of hydrogen chloride from 1,1,2-trichloroethane proceeded with different selectivities on solid bases, solid acids, and alumina. The product distributions were 1,1-dichloroethylene > *trans*-1,2-dichloroethylene > *cis*-1,2-dichloroethylene on solid bases, and *cis* > *trans* > 1,1 on solid acids, and *cis* > 1,1 > *trans* on alumina. The reactivity order of five reactants in Table I on solid acids such as silica–alumina and alumina–boria was satisfactorily explained by the relative stability of a hypothetical E2

TABLE I

REAGENTS AND THEIR REACTION PRODUCTS

Reagent[a]		Reaction and products
1,1-Dichloroethane (75-34-3)	a	$CHCl{=}CH_2$
1,2-Dichloroethane (107-06-2)	b	$CHCl{=}CH_2$
1,1,1-Trichloroethane (71-55-6)	c	$CCl_2{=}CH_2$
1,1,2-Trichloroethane (79-00-5)	d	$CCl_2{=}CH_2$
	e	*trans*-$CHCl{=}CHCl$ and *cis*-$CHCl{=}CHCl$
1,1,2,2-Tetrachloroethane (79-34-5)	f	$CCl_2{=}CHCl$

[a] Registry numbers appear in parentheses.

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

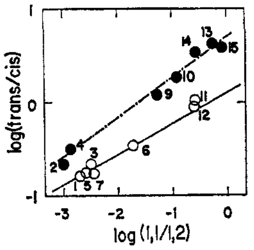

Figure 1.—Correlation between the *trans/cis* and 1,1/1,2 ratios in HCl elimination from 1,1,2-trichloroethane on molecular sieves. Numbers refer to Table II.

intermediate that was stabilized by α chlorine and unstabilized by β chlorine.[1] The reactivity orders on solid bases and alumina were well correlated with the corresponding values of delocalizabilities, quantum chemical reactivity indexes, *i.e.*, $D_r^N(H)$ and $D_r^R(Cl) + D_r^R(H)$, respectively.[1]

Recently, the ion-exchanged molecular sieves were reported to have high catalytic activities for the elimination reaction of hydrogen chloride from chloroethanes.[2]

In the present work, the elimination reaction of hydrogen chloride from the chloroethanes in Table I was investigated over several Molecular Sieves and the reactivities and selectivities were correlated with the acidities of catalysts.

Experimental Section

Chloroethanes used are listed in Table I with their reaction products. The molecular sieves used are listed in Table II. The 13X, 10X, 5A, and 4A sieves were obtained from the Linde Co. and the Y was donated by the Asahi Glass Co.; all were binder free. The modified ones were ion exchanged by a conventional chromatographic method using an aqueous solution of each chloride. The amount of the metal ion supplied was always nearly ten times the amount to be exchanged. H molecular sieves were obtained by the thermal decomposition of NH_4-exchanged sieves at 400° in the atmosphere. The reaction temperature was 300°, whereas the pretreatment was at 400° for 2 hr in the hydrogen flow for all catalysts. The rate constants and selectivities were measured by the microcatalytic gas chromatographic technique[1,3] with hydrogen as a carrier gas. The pulse size was 2 μl for all reactants. The pressure and flow rate of the carrier gas were 1.4 atm and 90 cc/min, respectively. The amount of 20–1000 mg of the catalysts in Table II was used in order to keep the conversion under 30%. Rate constants were calculated from the first pulse conversion, because the activity in the second pulse was nearly 80% of that in the first pulse when the most active catalyst was employed, hence the smallest amount of catalyst was used. Thus, the conversion of the first pulse may give a reasonable value of rate constant in spite of the variable catalyst size. The units of the rate constant (ml/g min^{-1}) in the elimination and dealkylation reactions are converted into the usual first-order units (mol/min atm^{-1} g^{-1} of catalyst) through multiplication by 4.16 × 10^{-5}. The isomerizations among 1,1-dichloroethylene, *trans*-1,2-dichloroethylene, and *cis*-1,2-dichloroethylene were found not to occur under the experimental conditions and any chloroethanes other than the reactant were not detected by gas chromatography. The material balance for carbon atoms was about 95% in the elimination reaction and those were nearly 90% in each pulse of dichloroethylene isomers under the experimental conditions. Details were described in a previous paper.[1]

TABLE II

ACID STRENGTH, RATE CONSTANTS OF ELIMINATION, AND CRACKING OF MOLECULAR SIEVES

No.	Catalyst	Cation	Acid strength[a]	Elimination rate constant[b]	Cracking rate constant[c]
1	H-Y	H^+	−8.2	7.0 × 10^3	9.1 × 10^3
2	Mg-10X	Mg^{2+}	−8.2	6.7 × 10^3	3.8 × 10^3
3	H-10X	H^+	−8.2	2.5 × 10^3	6.2 × 10^3
4	Li-10X	Li^+	−5.6	5.6 × 10^3	1.2 × 10^3
5	Ca-10X	Ca^{2+}	−5.6	4.9 × 10^3	1.2 × 10^3
6	10X	Ca^{2+}, Na^+	−3.0	3.9 × 10^3	1.1 × 10^3
7	Ca-5A	Ca^{2+}	−5.6	2.2 × 10^2	5.7 × 10
8	SA-1[d]		−8.2	3.8 × 10^2	6.0 × 10^3
9	Y	Na^+	+1.5	4.2 × 10^3	10
10	13X	Na^+	+3.3	5.7 × 10^3	10
11	4A	Na^+	+4.0	10^2	Not measurable
12	5A	Na^+, Ca^{2+}	+4.0	7.6 × 10	Not measurable
13	K-13X	K^+	+10	3.6 × 10^3	10
14	K-Y	K^+	+10	4.9 × 10^3	10
15	K-3A	K^+	+10	10^2	Not measurable

[a] See text. [b] The elimination rate constant of hydrogen chloride from 1,1,2-trichloroethane at 300° (ml/g min^{-1}). [c] The cracking rate constant of *t*-butylbenzene at 450° (ml/g min^{-1}) [d] Silica–alumina (13% Al_2O_3). see ref 1.

Results and Discussion

The activities for HCl elimination on the molecular sieves are shown in Table II. They were very large except for the A types. Venuto, *et al.*,[2] reported the highest activity of the 5A sieve for the elimination of ethyl chloride, whereas in the present experiment it was less active for the reaction of 1,1,2-trichloroethane. This may be due to the smaller effective surface accessible for 1,1,2-trichloroethane, a comparatively larger molecule, than that for ethyl chloride. The activity of Mg-10X, one of the most active among the ion-exchanged molecular sieves in Table II, was ten times higher than that of the amorphous silica–alumina.

The activities of Mg-10X and K-Y were nearly equal, although their acid strengths were much different. This insensitivity of the over-all activity to the acid strength might be due to the high activity per unit of surface area of basic catalysts,[1] however, the discussion about the comparison among the absolute rates of various catalysts is somewhat complicated because of the difficulty of estimating the size of the true accessible sites. Thus, the reactivity order and selectivity are mainly dealt with in the present paper.

The selectivities of the elimination from 1,1,2-trichloroethane on these molecular sieves are shown in Figure 1. In general, the molecular sieve with a higher 1,1-dichloroethylene to 1,2-dichloroethylene ratio (1,1/1,2) had a higher *trans/cis* ratio. This accords with the general trend observed on the solid base and acid. However, some molecular sieves composed a group different from the typical solid acids and bases. This group gave an unusually high *trans/cis* ratio, for which we have no explanation. The product distributions on some representative molecular sieves are shown in Table III, together with those of silica–alumina, strontium oxide, and the equilibrium at 300° [1] for reference. The catalysts, Mg-10X, H-10X, and H-Y, which had low 1,1/1,2 ratios gave the same trend of *cis* > *trans* > 1,1 as did silica–alumina.[1] This is in marked contrast with the orders of *trans* > *cis* > 1,1 on 13X and *trans* > 1,1 > *cis* on K-13X. These

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[2] P. B. Venuto, E. N. Givens, L. A. Hamilton, and P. S. Landis, *J. Catal.*, **6**, 253 (1966).

[3] R. J. Kokes, H. Tobin, and P. H. Emmett, *J. Amer. Chem. Soc.*, **77**, 5860 (1955); D. W. Bassett and H. W. Habgood, *J. Phys. Chem.*, **64**, 769 (1960).

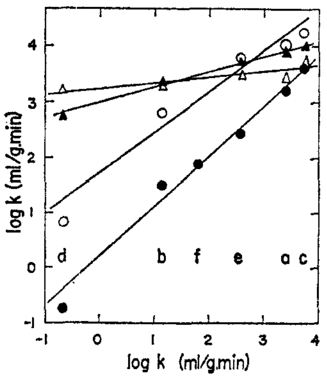

Figure 2.—Correlations among the reactivities of chloroethanes on SA-1, A-B-1, Mg-10X, 13X, and K-13X. The abscissa is the logarithm of the rate constants on SA-1. The alphabet designates the reactions in Table I: ●, A-B-1 (alumina-boria); ○, Mg-10X; ▲, 13X; △, K-13X.

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

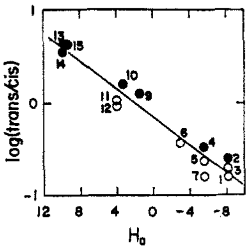

Figure 3.—Correlation between the *trans/cis* ratio and acid strength of molecular sieves in Table II. Numbers refer to Table II.

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.

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.

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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-

(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).