The thiophene used in this work was obtained through the courtesy of Drs. C. A. Hochwalt and O. J. Weinkauff of the Monsanto Chemical Co., St. Louis, Mo. The analyses were carried out by A. A. Sirotenko of this department.

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Interconversion of Hexachlorocyclohexane Isomers

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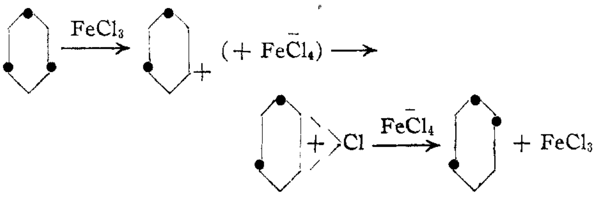
Because of the insecticidal properties of the γ-isomer, the 1,2,3,4,5,6-hexachlorocyclohexanes have received extensive investigation[1] but the interconversion of the isomers has apparently not been reported. A study of the pure α-, β-, γ- and δ-hexachlorocyclohexane isomers revealed that they are isomerized by heating with anhydrous ferric chloride in sealed tubes under nitrogen at temperatures of 140° or higher. Under these conditions the alpha was the most stable isomer and was isomerized slowly and in low conversion to a mixture of isomers from which delta was isolated and in which beta, gamma and epsilon were indicated by infrared spectrophotometric analysis. The β-isomer was converted readily and almost exclusively to alpha. Gamma was isomerized largely to the α- and δ-isomers; the change in composition of this product mixture with severity of heating suggested that delta was the primary product and was subsequently converted to alpha. Reaction of the pure delta was indeed found to give alpha with a lesser amount of gamma; however, only a small portion of the delta was isomerized. Other Friedel–Crafts type catalysts also promoted isomerization but were usually either less effective or like aluminum trichloride caused extensive degradation with formation of trichlorobenzene. Compositions of typical isomerization products are given in Table I.

The isomerization of the symmetrical β-isomer (135/246) configuration[2] to the α-isomer (124/356) requires the inversion of the positions of the chlorine atoms on any two adjacent carbon atoms. Such a change is highly suggestive of a displacement reaction with participation from a neighboring group as illustrated below.[3] In the formulas a dot represents a chlorine atom above the plane of the ring.



First, a ferric chloride molecule abstracts one of the three chlorine atoms on, for illustration, the top side of the cyclohexane ring. The electron deficient carbon atom then forms a cyclic ion with either of the two identical adjacent carbon atoms and the attached chlorine atom. This chlorine atom and hence the cyclic ion are necessarily on the under side of the cyclohexane ring. Approach to and return of a chlorine atom from the catalyst complex can then be only to the top side of the ring. Return of the chlorine atom to the original carbon atom reforms the β-isomer but return to the neighboring participating carbon atom results in the α-isomer.

Since all carbon atoms in the β-isomer are equivalent, isomerization by this mechanism can give only the α-isomer as a primary product. With the other known isomers in which all carbon atoms are not identical formation of two or more isomers would be expected. Since a carbon atom can participate with each of its two neighboring carbon atoms, four transformations are possible from each carbon atom or a total of 24 from all six. Many of these transformations will of course reform the starting isomer. In this mechanism the positions of both the abstraction and the return of the chlorine atom would be influenced by steric factors and selective formation of one or more isomers would be expected. The products predicted from each of the four isomers and the number of possible transformations giving rise to each product are shown in the table with the experimental results. In investigating the composition of the isomerization mixtures, no thorough attempt was made to isolate minor constituents. Since the spectra and indeed the

TABLE I

INTERCONVERSION OF HEXACHLOROCYCLOHEXANE ISOMERS

Isomer	Structure[2]	$FeCl_3$, % w. of isomer	Time, hr.	Temp.,[a] °C.	Composition, % w.[b] α	β	γ	δ	Total	Predicted products[e]
α	124/356	100	48	170	87	1.5	0.8	3.7[c]	93[d]	α(12),β(2),γ(4),δ(4),ε = 123/456(2)
β	135/246	8[f]	24	170	77.3	13.0	1.3	2.7	94.3	α(12),β(12)
		5	0.5	310	80.1[c]	10.3	1.0	1.3	92.7	
γ	1245/36	5	12	140	2.8	0.0	60.3	34.1	97.2	α(8),γ(8),δ(8)
		5	12	170	15	0	21	52[c]	88	
		20	122	170	50.0	2.3	4.6	44.0	100.9	
δ	1235/46	20	72	170	15.8	0.0	4.4	68.1	88.3	α(4),β(4),γ(4),δ(8),η = 1234/56(4)

[a] Heated in evacuated, sealed glass tube. [b] By infrared spectrophotometric analysis. [c] Presence confirmed by isolation. [d] Trace of ε-isomer indicated. [e] From displacement with participation from neighboring groups; figures in parentheses are the number of possible transformations out of the total of 24 which would give the indicated isomer. [f] $SbCl_3$, 61%, present as solvent.

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(1) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

(2) Following Cristol,[1] the numbers above the line indicate the positions of chlorine atoms which lie above a hypothetical planar cyclohexane ring and those below the line lie below the hypothetical planar cyclohexane ring.

(3) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

existence of the η- and θ-isomers[4] were not known at the time of these experiments, these and possibly other isomers may have been formed in small amounts. Also, secondary isomerization of primary products undoubtedly affected the final composition both qualitatively and quantitatively; the β-isomer in particular if formed should have largely isomerized to alpha. In view of these considerations the agreement of the observed results with those predicted appears sufficiently good to support the described mechanism. The ϵ-, η- and θ-isomers have not been available to us for isomerization so that we have not been able to use them to test the suggested mechanism.

We gratefully acknowledge the aid of Messrs. W. R. Harp, Jr., and F. S. Mortimer in making the spectroscopic analyses, and the suggestions of Dr. A. G. Kridl on the mechanism of isomerization.

[4] A. J. Kolka, H. D. Orloff and M. E. Griffing, Abstracts of Papers, 121st Meeting of American Chemical Society, Buffalo, N. Y., March 24-27, 1952.

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Tracer-diffusion in Liquids. IV. Self-diffusion of Calcium Ion and Chloride Ion in Aqueous Calcium Chloride Solutions[1]

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The salt diffusion of calcium chloride in its aqueous solutions has been the subject of experimental study of many workers in the past fifteen years. The results obtained by Harned and Levy[2] indicate that the measured salt diffusion coefficients of calcium chloride are lower than the values computed from the Onsager–Fuoss theory in solutions of concentration between 0.001 and 0.005 formula weight per liter. The salt diffusion coefficients of calcium chloride in concentrated aqueous solutions have been determined by Hollingshead and Gordon[3] and by Robinson and Chia[4] by means of the diaphragm cell method, and independently by Stokes and coworkers[5] and by Lyons and Riley[6] by means of the optical method. Their results show that in calcium chloride solutions of concentration above 0.2 formular weight per liter the salt diffusion coefficient increases with increasing salt concentration up to about 2.2 formular weight per liter. This phenomenon has generally been attributed to the continual decrease of the activity coefficient of the salt along the diffusion path. In self-diffusion, however, the chemical composition and hence the activity coefficient of the diffusing ions is constant along the diffusion path, the theoretical relationship between the diffusion coefficient and salt concentration becomes simpler and we may expect the shape of the D *vs.* $\sqrt{c}$ curves for self diffusion to be quite different from that for salt diffusion. Furthermore, it should be of interest to see how the self diffusion coefficients for different ions in the same solution vary as the salt concentration of the solution increases continually up to saturation. In the present work the self-diffusion coefficients of calcium ion and chloride ion in aqueous calcium chloride solutions at 25° have been measured by means of the improved capillary method.

Experimental

Radioactive Tracers.—Ca^{45} and Cl^{36} were used as tracers in the self-diffusion measurements. These were obtained from the Isotopes Division of the U. S. Atomic Energy Commission at Oak Ridge, Tennessee.

Diffusion Measurement.—The experimental techniques involved were already discussed in paper I of this series. The radioactivity of the diffusion samples was measured with a windowless, continuous flow counter. Since dry calcium chloride is hygroscopic in air, the calculated amount of sodium fluoride solution was added to each sample before evaporation to dryness under an infrared lamp. The samples so prepared contained approximately equal amounts of dry residue (solid sodium chloride and calcium fluoride) and were kept in a desiccator overnight before counting. Since in the calculations to obtain the diffusion coefficients only the ratio of the concentrations of radioactive tracers is involved, possible errors due to self-absorption of β-radiation are automatically eliminated.

Results.—The measured self-diffusion coefficients of Ca^{++} and Cl^- in aqueous calcium chloride solutions at 25° are listed in Table I. Each value listed in Table I is the average result of at least four measurements.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF Ca^{++} AND Cl^- IN $CaCl_2$ (aq.) AT 25°

Concentration formular wt./liter	$D_{Ca^{++}} \times 10^5$, cm.²/sec.	$D_{Cl^-} \times 10^5$, cm.²/sec.
0.0100	0.778 ± 0.028	
.0705	.782 ± .015	1.89 ± 0.02
.282	.767 ± .008	1.72 ± .04
.803	.646 ± .025	1.60 ± .04
1.41	.560 ± .020	1.42 ± .03
2.68	.405 ± .015	0.907 ± .020
4.02	.225 ± .002	0.447 ± .015
5.36	.100 ± .009	0.159 ± .010

Discussion.—Using apropriate units the Onsager equation may be written as[7]

$$D_j = \frac{RT\lambda_j^0}{|Z_j|\mathfrak{F}^2}\,\frac{\lambda_j^0|Z_j|\mathfrak{F}}{3N\mathfrak{D}} \times 2.694 \times 10^{16} \times \sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \mathrm{d}(\omega_j)]\,\sqrt{\sum_i c_i Z_i^2} \quad (1)$$

where D_j is the tracer-diffusion coefficient of ions of the jth kind in a salt solution, Z_i is the charge in electronic units and c_i the concentration in moles per liter of ion i, λ_j^0 the limiting equivalent conductance of ion j, $\mathfrak{D}$ the dielectric constant of the solvent k the Boltzmann constant, $\mathfrak{F}$ the Faraday constant, T the absolute temperature, and $\mathrm{d}(\omega_j)$ a function given by

$$\mathrm{d}(\omega_j) = \frac{1}{\sum_i c_i Z_i^2}\,\Sigma\,\frac{c_i|Z_i|\lambda_i^0}{(\lambda_i^0/|Z_i|) + (\lambda_j^0/|Z_j|)} \quad (2)$$

For the diffusion of tracer amount of ions of species 1 in salt solution containing ions of species 2 and 3, we have

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[1] Contribution No. 1134 from the Department of Chemistry of Yale University: Paper I, THIS JOURNAL, **74**, 1182, 6317 (1952); paper II, **74**, 1611 (1952); paper III, **74**, 1612 (1952).

[2] H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949).

[3] E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9**, 152 (1941).

[4] R. A. Robinson and C. L. Chia, THIS JOURNAL, **74**, 2776 (1952).

[5] Hall, Wishaw and Stokes, private communication.

[6] P. A. Lyons and J. F. Riley, private communication.

[7] See paper I or II of this series.