stant, thus producing a linear function of log solubility against $1/T$ °K. When the data for the various systems described in this paper are plotted in this way it is found that the majority of the slopes do remain constant and yield the approximate heats of solution given in Table VIII. In the case of the plots showing two slopes the values are for the portions of the curves corresponding to the higher temperature range except in the case of the solubility of Ag_2SO_4 in 1.35 m UO_2SO_4 where the converse is true. Solid phase transitions are clearly shown by discontinuities in the solubility curves.

TABLE VIII

THE ΔH_{soln} FOR SEVERAL METAL SULFATES IN UO_2SO_4 SOLUTION

	ΔH_{soln} (kcal./mole)		
Salt	In H_2O	In 0.1272 m UO_2SO_4	In 1.348 m UO_2SO_4
$Y_2(SO_4)_3$	−130	−80	−48
$La_2(SO_4)_3$	−120	−60	−43
$CdSO_4$	.....	−33	−13
Ag_2SO_4	3.8	6.6	11
Cs_2SO_4	1.6	1.6	4.9

The large decrease in the heat of solution of the solid phase as a function of increasing uranyl sulfate in the solution appears indicative of a large degree of interaction and/or complexing of the solute with either UO_2SO_4 or the ionic species in solution. Aqueous salt systems which do not complex the solute exhibit negligible change in the heat of solution as the aqueous salt concentration is increased. Perhaps some theoretical quantitative relationships can be derived to correlate the change in the heat of solution per unit change of concentration of the electrolyte species in solution with complexing constants of the reacting species.

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[CONTRIBUTION FROM TECHNICAL DEVELOPMENT LABORATORIES, COMMUNICABLE DISEASE CENTER, PUBLIC HEALTH SERVICE]

Chlorine Exchange between Aluminum Chloride and γ-1,2,3,4,5,6-Hexachlorocyclohexane

BY GEORGE W. PEARCE AND SONJA KRAUSE

RECEIVED JULY 23, 1956

Chlorine exchanges readily between aluminum chloride and γ-1,2,3,4,5,6-hexachlorocyclohexane (γ-HCC) at temperatures above 100° with some decomposition and isomerization, primarily to α-HCC and δ-HCC. Mechanisms for both exchange and isomerization are proposed.

Chlorinated hydrocarbon insecticides labeled with chlorine-36 would be very helpful in studies of the fate and toxicology of this class of compounds in resistant strains of arthropods as well as in higher animals. The use of exchange reactions appeared to offer a simpler way of preparing Cl-36 labeled compounds than their complete synthesis. In addition, study of exchange reactions can provide knowledge of the structural nature of compounds in relation to their properties in general. Using lindane, the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (γ-HCC), as a chlorinated hydrocarbon insecticide of importance chlorine exchange reactions between it and $AlCl_3$ labeled with Cl-36 have been attempted.

1,2,3,4,5,6-Hexachlorocyclohexane has previously been labeled by direct chlorination of benzene with chlorine-36.[1]

Experimental

Both the apparatus and the method of preparing labeled aluminum chloride were based on the work of Willard and colleagues[2,3] in which the reactions

$$HCl^* + AgNO_3 \longrightarrow AgCl^* + HNO_3$$

$$AgCl^* + Al \longrightarrow Ag + AlCl_3^*$$

are employed. The latter reaction is carried out under rigorously anhydrous conditions in an evacuated system. Two solutions of chlorine-36[4] one containing 41.6 mg. Cl/microcurie and the other 3.62 mg. Cl/microcurie, were available for this work. The silver nitrate was Mallinckrodt Reagent grade and the aluminum was Baker and Adamson, 16 to 60 mesh.

The AgCl was prepared in a tube protected from light and fused to a flask containing the γ-HCC[5] which was used without further purification. After the AgCl had been melted under vacuum to remove the last traces of water, Al was added, still under vacuum. When the mixture was heated to 460–500°, $AlCl_3$ was evolved as a gas and could be driven over into the flask containing the γ-HCC if this was cooled in liquid nitrogen. Heat had to be applied for one to two hours for complete conversion of the AgCl to $AlCl_3$. The flask containing $AlCl_3$ plus γ-HCC was then sealed off completely from the rest of the apparatus and could be treated as desired with the contents still under vacuum. A number of runs were made in which the heat treatment of the $AlCl_3$ and lindane and/or the shape of the reaction container were varied. Products from the reaction mixture were recovered by dissolving in ether and water and extracting each layer with small portions of the other solvent. Aliquots of the water phase and products obtained from the ether phase were assayed for Cl-36 activity after conversion to AgCl. A shielded end-window Geiger tube was used to count samples. The approximate disintegration rate was estimated by standardizing this count against a Q-gas flow counter which was assumed 50% efficient. Percentage exchange was calculated as percentage of total possible exchange at equilibrium.

Experimental Results

Run 1: 500 mg. lindane in 100-ml. reaction flask, 42.6 mg. Cl containing 1 microcurie. Lindane and $AlCl_3^{36}$ heated about 7 minutes at 115–130°; no discoloration m.p. 111.5–112.5° (recrystallized product); exchange, 16%.

Run 2: 500 mg. lindane in Y-shaped tube, 41.84 mg. Cl containing 11.5 microcuries. Lindane and $AlCl_3^{36}$ driven back and forth several times by heating alternate arms of

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[1] J. T. Craig, P. F. Tryon and W. G. Brown, *Anal. Chem.*, **25**, 1661 (1953).

[2] C. H. Wallace and J. E. Willard, THIS JOURNAL, **72**, 5275 (1950).

[3] M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951).

[4] Cl-36-P Processed, Oak Ridge National Laboratory, AEC, Isotope Catalogue, July, 1952.

[5] Pure samples of α-, β-, γ-, δ- and ε-isomers were obtained from the Ethyl Corporation.

the reaction tube. Slight discoloration, m.p. 110–112° (recrystallized product); exchange, 5%.

Run 3: 500 mg. lindane in 100-ml. flask, 83.68 mg. Cl containing 23 microcuries. After melting the lindane several times by alternate flaming and cooling of the reaction flask, the reaction mixture was held in a melted condition at 112–115° for about 15 minutes by placing the apparatus in an oven. Extensive discoloration, m.p. 113–159° (recrystallized product). Melting point data indicated isomerization occurred.

Run 4: Same as run 3, except reaction mixture was subjected to less heat treatment and only a moderate amount of discoloration occurred. Melting point observations of the product again indicated some isomerization took place although not as extensively as in run 3.

Since isomerization appeared evident in runs 3 and 4, the products were chromatographed by the method of Harris[6]; the delta isomer was recovered by extracting the column with acetone.[7] Estimates of the activity and the percentage of the isomers isolated and their m.p.'s when possible are presented in Table I.

TABLE I

	Run 3			Run 4		
Isomer	%	M.p.[a] (recrys. product)	d./m./μg.[b]	%	M.p., °C.[a]	d./m./μg.[b]
α	65	153–155	43	10	103–108 (unrecryst. and before chromatographing)	35
γ	2	.....	50	90		2.2
δ and other products (column residue)	33	130–137	30	Trace		11

[a] Published m.p. of isomers involved: α 158°; γ 112.5°; δ 138°. [b] Disintegrations/minute/microgram.

Since isomerization occurred with the more severe heating a run was made in which the reactants (same as in runs 3 and 4) were held for 4 days at 70° in a 250-ml. flask. No discoloration occurred and the unrecrystallized product melted at 108.5–112.5° indicating no significant change in the lindane. A small but definite exchange amounting to 1 to 2% occurred.

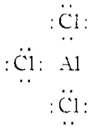
For the purpose of later discussion data for the d./m./μg. have been calculated for 100% exchange at the molar ratio of $AlCl_3$ and γ-HCC used in the experiments assuming all the chlorines of solid $AlCl_3$ exchange at the same rate. Under these conditions the d./m./μg. varies only with the number of HCC chlorines that may exchange. The calculated values are applicable to runs 3 and 4 since the same amount of $AlCl_3$ and γ-HCC was employed in these runs. If one chlorine exchanges from each molecule of HCC, the product should have 42 d./m./μg. Exchange of 2Cl yields 60 d./m./μg.; exchange of 3Cl yields 69 d./m./μg.; and exchange of all 6Cl yields 82 d./m./μg.

Discussion

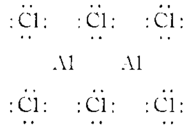
The experimental data show that $AlCl_3$ exchanges chlorine readily with γ-HCC at temperatures at or above the melting point of γ-HCC, *i.e.*, 112.5°. Prolonged heating results in the isomerization of the γ-HCC mainly to α-HCC, with some formation of δ-HCC. It is the purpose of this discussion to propose a simple mechanism for both exchange and isomerization.

Willard and colleagues[2,3] have shown that $AlCl_3$ will exchange chlorine with organic compounds only while it is in the solid state. Exchange will not occur when the $AlCl_3$ is gaseous or dissolved.

If a molecule with empirical formula $AlCl_3$ existed, it would be a Lewis acid, an electron acceptor. However, it has been shown that both gaseous[8,9] and liquid[10] $AlCl_3$ exists as Al_2Cl_6 dimers, which have lost the electron-accepting properties of the hypothetical $AlCl_3$. Solid aluminum chloride, however, is in ionic form[11] and should retain some of the acidic properties of the hypothetical monomer, *i.e.*, some of the aluminum atoms at the surface will be electron acceptors.



$AlCl_3$



Al_2Cl_6

When a molecule of γ-HCC approaches one of these electron acceptors, the unshared pair of electrons on one of the γ-HCC chlorines is probably attracted to that spot and may be held tightly enough to remove that chlorine from the molecule. As the rest of the molecule tumbles about the aluminum chloride surface, it soon picks up another chlorine ion to complete the exchange. Before considering the isomerization, it will be helpful to study Fig. 1 showing linear models of the HCC isomers.[12] The true configurations of these isomers correspond primarily to the "chair" form of cyclohexane. (The vertical lines represent the relative position of the chlorines.)

After a chlorine has been removed from a carbon of the γ-HCC molecule, it is probable that the three remaining bonds on that carbon should tend to become planar, thus giving the hydrogen a chance to "flip" over into the position formerly occupied by the chlorine. The "exchange" chlorine would then appear in the position formerly held by the hydrogen. It can be seen from Fig. 1 that the reversal of the chlorine at positions 2, 3, 5 or 6 will give one of the α-HCC mirror images. Positions 1 and 4 are considered later.

The data show that continued heating of the reactants causes more and more of the γ-HCC to convert to α-HCC; the α-HCC does not isomerize back to γ-HCC. Models of both isomers, constructed from Fisher–Hirschfelder models, illustrates a possible reason for this. Two of the chlorines in γ-HCC, in the 2,6-biaxial position, are situated so close to each other that their mutual repulsion is probably considerable. If either of these chlorines "flips over," α-HCC is formed. In order for the isomerization to reverse, the chlorine would have to return to the axial (higher energy) position.

The preceding mechanism requires that no α-HCC be formed without the exchange of at least one chlorine with the aluminum chloride. Appropriate evidence for this is shown in data for runs 3 and 4. In run 3, the α-HCC could be recovered pure, with activity 43 d./m./μg.; when one HCC chlorine has exchanged completely the activity should be 42 d./m./μg. (experimental error is probably about 10% or more). In this run the γ-HCC had 50 d./m./μg., while in run 4 it had only 2.2 d./m./μg. The impure α-HCC recovered in run 4, however, still had more than 35 d./m./μg. Thus, the minimum activity of the α-HCC is independent of the amount of γ-HCC that has had a chance to exchange.

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(6) T. H. Harris, *J. Assoc. Official Agr. Chemists*, **32**, 684 (1949).

(7) L. L. Ramsey and W. I. Patterson, *ibid.*, **29**, 337 (1946).

(8) H. Deville and L. Troast, *Compt. rend.*, **45**, 821 (1857).

(9) K. J. Palmer and N. Elliott, THIS JOURNAL, **60**, 1852 (1938).

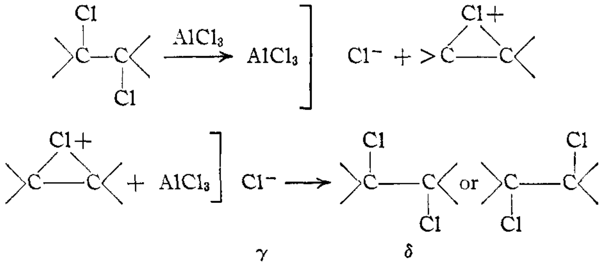
(10) R. L. Harris, R. E. Wood and H. L. Ritter, *ibid.*, **73**, 3151 (1951).

(11) J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

(12) I. Hornstein, *Science*, **121**, 206 (1955).

Although no pure δ-HCC was recovered, the evidence for the presence of this isomer is fairly conclusive. The absence of all other HCC isomers has not been established.

It is impossible to give a simple mechanism for the formation of the δ-HCC at this time; however, two possibilities can be discussed. First, it is possible that δ-HCC is formed from the α-HCC previously produced from the γ-HCC by the "flipping over" of chlorine 4. It is also possible that the delta isomer is formed from the gamma directly. When one of the 2,6-biaxial chlorines is removed, chlorine 1 is in the proper *trans* position to form a bridge between carbons 1 and either 2 or 6.[13] A chlorine ion may then be picked up in either of two positions as illustrated



Thus, either gamma or delta or mixtures of the two may result. It is, of course, possible that both mechanisms suggested occur.

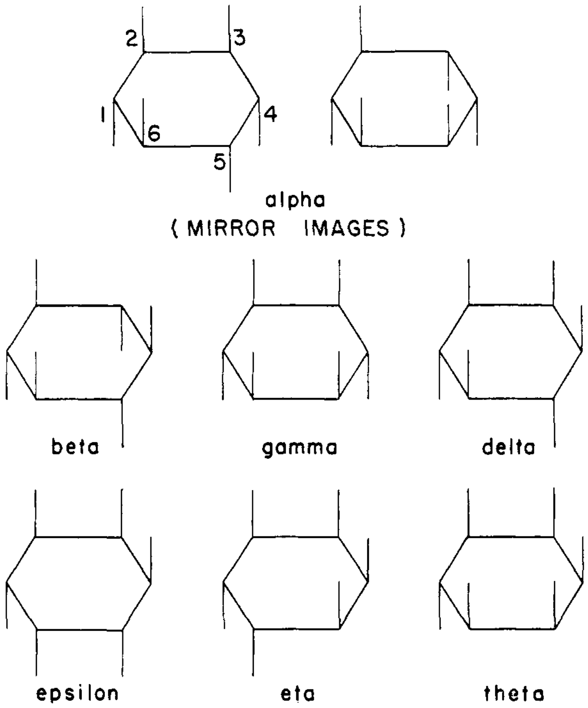


Fig. 1.—Linear models of 1,2,3,4,5,6-hexachlorocyclohexane.

In spite of the tendency for isomerization to occur in the chlorine exchange reaction between lindane and $AlCl_3$ sufficient quantities of labeled gamma isomer were obtained for use in tracer studies. The reaction is being studied further in an effort to arrive at conditions where isomerization can be kept to a minimum. Reagents other than $AlCl_3$ are also being considered as exchange media.

Acknowledgment.—The authors wish to thank Dr. D. S. Noyce, University of California, who helped with nomenclature and clarified some of the ideas on mechanism presented.

SAVANNAH, GEORGIA

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[13] S. Winstein, *Colloq. intern. Montpellier*, **18**, 55 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

On the Use of Iodine as a Radical Detector in Hydrocarbon Radiolysis[1]

BY RICHARD W. FESSENDEN[2a] AND ROBERT H. SCHULER[2b]

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The effects of radiation on solutions of iodine in cyclohexane have been studied over the iodine concentration range of 5×10^{-6} *M* to 5×10^{-2} *M*. The yield for the formation of alkyl iodide in deaerated solution is independent of iodine concentration from 10^{-5} *M* to 5×10^{-3} *M* but is somewhat higher at higher concentrations. In the lower concentration region the radiation yield, *G*(RI), is found for both Co^{60} γ radiation and 2 Mev. Van de Graaff electrons to be 5.6 molecules of alkyl iodide produced per 100 e.v. absorbed by the system. Aerated solutions of iodine in cyclohexane have lower yields than the corresponding deaerated solutions. For aerated solutions *G*(RI) is proportional to the iodine concentration at low concentrations and the kinetics indicate a simple competition between iodine and dissolved oxygen. The yield of uptake of radio-iodine to form stable alkyl iodides has been found to be equal to the yield of iodine disappearance, showing that the production of hydrogen iodide and hydrolyzable iodides is negligible.

The kinetics of the radiation-induced reaction between iodine and various hydrocarbons have previously been investigated[3-5] and it has been shown that the radiation yield is independent of temperature from 25 to 75° and of iodine concentration in the range 0.5×10^{-3} *M* to 5×10^{-3} *M*. These observed kinetics indicate that the formation of organic iodides can be taken as a measure of radical production in the substrate. Further work over a wider range of concentration is however clearly desirable and is the subject of the present investigation.

In the above-mentioned studies the extent of reaction of iodine was determined by spectrophotometric measurement of the decrease in iodine con-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956.

[2] (a) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts. (b) Department of Radiation Research, Mellon Institute, Pittsburgh, Pa.

[3] R. H. Schuler and W. H. Hamill, THIS JOURNAL, **74**, 6171 (1952).

[4] P. F. Forsyth, E. N. Weber and R. H. Schuler, *J. Chem. Phys.*, **22**, 66 (1954).

[5] E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 68 (1955).